

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236132887>

# Miyittah, M.K., S. Gadekar, P. Pullammanappillil, C.D. Stanley, J.C. Bonzongo, and J.E. Rechcigl (2012): Application of Polymath Chemical Equilibrium Model for Struvite Precipitatio...

Article in *Water Air and Soil Pollution* · January 2012

CITATIONS

0

READS

114

6 authors, including:



**Michael Miyittah**

University of Cape Coast

16 PUBLICATIONS 139 CITATIONS

[SEE PROFILE](#)



**Craig D Stanley**

University of Florida

66 PUBLICATIONS 826 CITATIONS

[SEE PROFILE](#)



**Jean-Claude J Bonzongo**

University of Florida

87 PUBLICATIONS 3,094 CITATIONS

[SEE PROFILE](#)



**J.E. Rechcigl**

University of Florida

72 PUBLICATIONS 1,101 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



N Requirements of Landscape Plants [View project](#)



US-EPA Funded project [View project](#)

# Application of Polymath Chemical Equilibrium Simulation Model for Struvite Precipitation in Soils

Michael K. Miyittah · Sachin Gadekar ·  
Pratap Pullammanappallil · Craig D. Stanley ·  
Jean-Claude Bonzongo · Jack E. Rechcigl

Received: 23 February 2011 / Accepted: 12 October 2011 / Published online: 29 October 2011  
© Springer Science+Business Media B.V. 2011

**Abstract** A new speciation model developed and implemented in Polymath was found to be successful in predicting struvite precipitation in soils. Struvite ( $\text{NH}_4\text{MgPO}_4$ ) has been identified as a mineral for the recovery of nitrogen (N) and phosphorus (P). Predicting struvite precipitation potential in soil is important for optimal quantification of nutrient species. Polymath and Visual Minteq models were used for prediction of several solid phases in the soil. One approach to immobilize P for solid-phase formation is by co-blending. Immobilization was achieved through the blending of an Al-based water treatment residual (Al-WTR) and with Ca–Mg-based materials [slag and magnesium oxide (MgO)]. The

results suggest that Polymath model revealed solid Phases of dicalcium phosphate pentahydrate (DCPP), magnesium hydroxide (MHO), magnesium orthophosphate (v) docosahydrate (MP22), magnesium orthophosphate (v) octahydrate (MP8), and struvite, which were lacking in the modeling from Visual Minteq. Residual leachate from the co-blended amendments; Soil+WTR+Slag, Soil+WTR+MgO, Soil+MgO, Soil+Slag, Soil+WTR, and the control (without amendment) had struvite of 353, 199, 119, 90, 37, and 12  $\text{mg l}^{-1}$ , respectively. This implies that struvite, a phosphate mineral can be precipitated in the soil and could be released as nutrients for plant uptake. Struvite precipitation in soil and for reuse may reduce cost and may be a safe practice for sustainable environmental nutrient management.

---

M. K. Miyittah · C. D. Stanley · J. E. Rechcigl  
Soil and Water Science Department, University of Florida,  
IFAS, Gulf Coast Research and Education Center,  
Wimauma, FL 33598, USA

S. Gadekar · P. Pullammanappallil  
Department of Agricultural and Biological Engineering,  
University of Florida,  
Gainesville, FL 32611, USA

J.-C. Bonzongo  
Department of Environmental Engineering Sciences,  
University of Florida,  
Black Hall, P.O. Box, 116450, Gainesville, FL 32611, USA

M. K. Miyittah (✉)  
Center for Environmental and Human Toxicology,  
University of Florida,  
P.O. Box 110885, Gainesville, FL 32611, USA  
e-mail: miyittah@ufl.edu

**Keywords** Struvite · Manure-impacted soil ·  
Phosphorus · Chemical equilibrium modeling

## 1 Introduction

Phosphorus (P) pollution from agriculture sources is primary a contributor to more than 40% of impaired lakes in the United States (USEPA 2000). Phosphorus from dairy manure-laden soils has also been identified as non-point source leading to eutrophication and water quality degradation (Nair et al. 1995). Significant research has been carried out in recent times to understand P dynamics in animal manure and the

interactions of the manure P components with soils (Güngör et al. 2007).

Soil P has been found to be strongly associated with iron (Fe)–aluminum (Al) and calcium (Ca)–magnesium (Mg) metal hydr(oxides) depending on the prevailing pH. In acid soils, Fe–Al hydr(oxides) and other metals react with P to form solid phases. On the other hand, under alkaline condition, Ca and Mg activities tended to control the solubility of P in soils (Lindsay 2001; Güngör et al. 2007).

In Florida, spodosols are usually characterized by low contents of Fe–Al and Ca–Mg due to coarse texture sandy soils. In addition, the prevailing high rainfall also leads to leaching of basic cations and significant loss of applied P through runoff (Silveira et al. 2006). Various management practices have been suggested to reduce potential P losses and subsequent impact on water bodies. One approach is the use of amendments to increase the soil sorption capacity for P retention. Successful soil amendments include industrial by-products and municipal wastes that contain metals (e.g., Fe, Ca, Al) for P retention. Metal salts [e.g.,  $Al_2(SO_4)_3$ ,  $FeCl_3$ ] have also been used to mitigate P solubility and mobility in poultry manure and poultry manure-amended soils (Moore and Miller 1994; Moore et al. 1999; Malecki-Brown & White 2009).

The reaction of these metal cations of Fe–Al and Ca–Mg in soils containing high P has been a subject of recent investigations. The importance of the metal cation is to form a solid phase of P in order to prevent future release. However, phosphate solid phases vary greatly in soils depending on the metal cations available. It is therefore of great advantage to understand solubility of P if different metal cations are co-blended in various ratios. By co-blending, we refer to the mixing or blending of two or more by-products containing aluminum water treatment residual (Al-WTR) with Ca–Mg-based materials [slag and low-activity magnesium oxide (MgO)] (Miyittah et al. 2011).

Geochemical model (MINTEQA2) has been used as a predictive tool for solid-phase speciation of P in manure-impacted soils using Al-WTR as sorbent (Silveira et al. 2006; Agyin-Birikorang et al. 2009). However, the model used failed to identify struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) as one of the phosphate minerals in the soils. The availability of struvite, a sparingly soluble mineral if present, suggests slow release of P for plant uptake. Consequently, the slow release of nutrients from struvite may prevent the likelihood of

adverse risk of excess P into water bodies. In addition, the available struvite in the soils, if quantified, could provide insight on how much P, N, and Mg could be released.

In animal manure study (pig, cattle, sheep, and poultry litter), struvite has been identified using qualitative scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), X-ray powder diffraction (XRD), and solid-state  $^{31}P$  NMR techniques (Güngör and Karthikeyan 2005; Toor et al. 2006). In addition, sophisticated equipment like XANES has been used to evaluate the Mg phosphates (struvite) in animal manure (Güngör et al. 2007). However, the use of these methods in investigating the presence of struvite is labor-intensive and expensive, and quantitative assessment becomes difficult. To our knowledge, to predict struvite in soil is a daunting task. However, Polymath simulation model has been used to predict struvite in wastewater (Gadekar and Pullammanappallil 2009).

The Polymath simulation model was developed essentially for predicting magnesium- and calcium-related minerals. It is a mathematical simulation model for precipitation, which uses physicochemical equilibrium expressions, mass balance equation for N, P, Mg, and charge balance. The equations derived from the expressions are solved using Polymath education version 6.1 (Gadekar and Pullammanappallil, 2009).

The objective of this study is to compare the results of the prediction of struvite in soil with Polymath and that of Visual Minteq model due to co-blending of aluminum residual and Ca–Mg-based materials.

## 2 Materials and methods

### 2.1 Soil and amendments characterizations

A manure-impacted sample of Immokalee fine sand (sandy, siliceous, hyperthermic Arenic Haplaquod) was obtained from a field site on a dairy cattle ranch located in the Lake Okeechobee County watershed. This soil was selected for its high total P due to long-term manure application and/or fecal deposition, as well as the soil's geographic extent in South Florida. Random samples were collected from A horizons (0–15 cm) and were thoroughly mixed to yield a composite sample. The soil was air-dried and sieved through a 2-mm stainless steel screen.

The Al-WTR was collected from a drinking water treatment plant in Bradenton Florida. In characterizing the amendments, pH was measured in a 1:2 (w:v) aqueous suspension as reported elsewhere (Silveira et al. 2006). Redox potential (Eh as mV) was also measured using two electrodes connected to the pH meter (Accument XL60, Fisher Scientific, USA). The reference electrode and temperature sensor were connected to an interface multichannel (pH meter/redox meter), which enabled simultaneous readings of pH and Eh. After every ten samples, Eh monitoring was constantly evaluated to avoid drifts in voltage through quality assurance/control (QA/QC) maintenance (Rabenhorst 2009).

The Al-WTR samples were air-dried and sieved through <math>850\ \mu\text{m}</math> screen to minimize slaking and increase reactivity (Dayton and Basta 2005). Two Ca and/or Mg products, low-activity MgO, and slag were characterized in a similar manner as the Al-WTR. Total recoverable Fe, P, Al, Ca, and Mg were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Plasma 2100DV, Perkin-Elmer, Waltham, MA, USA), following digestion according to EPA Method 3050B (USEPA 1996).

## 2.2 Soil extractions, co-blending, and leaching

The soil was sequentially extracted for P according to Chang et al. (1983) using 1:20 soil/solution ratio, with modification as in Silveira et al. (2006). The sequential extraction procedure is an operational defined scheme of fractionating the soil P. The extraction procedure utilized (1) 1 M KCl to determine the soluble or exchangeable P (This P fraction is easily leachable and most responsible for algal growth); (2) 0.1 M NaOH to determine the chemisorbed P onto oxides and hydroxides of Fe, Al, and Mn; (3) 0.5 M HCl to determine P associated with Ca and Mg complexes (Hieltjes and Lijklema 1980; Ruttenberg 1992; Stumm and Morgan 1996). However, at the end of the analysis, the recalcitrant P was not analyzed.

Amendments containing Ca-, Mg-, and Al-based were co-blended as described elsewhere (Miyittah et al. 2011). In brief, amendments were applied at 0%, 1%, and 2% by mass to dry weight (d.w.) of the soil. For example, amendments used at 2% application (Al-WTR, slag, and MgO) is equivalent to  $20\ \text{gkg}^{-1}$ , respectively. The samples obtained from the co-blending

process were Al-WTR+MgO and Al-WTR+Slag at ( $10+10\ \text{gkg}^{-1}$  or 1%+1%) or ( $10+10\ \text{gkg}^{-1}$  or 1%+1%), respectively. In all, the co-blended resulted in soils receiving a total of  $20\ \text{gkg}^{-1}$  amendments. A soil without amendment was used as a control (0%). All treatments were replicated three times in a completely randomized design.

Soil column setup was similar as previously reported in Silveira et al (2006). DDI water (100 ml, adjusted to pH 5 to mimic the pH of rainfall in South Florida) were added to each column weekly. Each leaching event corresponded to approximately 1 pore volume. Leachate of the column studies were collected and major anions ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ ) and cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{NH}_4^+$ ), pH plus EC were analyzed. Cations with the exception of ammonium were analyzed using ICP-OES. Ammonium was measured with ion-selective electrode (Fisher Scientific, USA). Phosphate,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  were analyzed using ion chromatograph (Metrohm USA), alkalinity and  $\text{NO}_2^-$  with discrete analyzer (AQ2, Seal Analytical, Wisconsin, USA), dissolve organic carbon (DOC) with TOC-5050A (Shimadzu, Kyoto, Japan) by the difference between total and inorganic carbon concentrations.

QA/QC protocols were followed including the use of 5% repeats and 5% spikes and blanks for each procedure (Kennedy et al. 1994). Standard calibration curves, as well as quality check standards, were prepared for each procedure. Repeats were within 10% relative standard deviation. In situation where sample standard deviation falls outside the 10% range, repeats were conducted to cross-check any anomaly. Spike recovery varied with procedure, but all fell within acceptable levels (95–110%). External QC checks achieved recoveries within 98–110%. Statistical tests were performed to validate the model fitness. A root-mean-square error (RMSE), coefficient of determination ( $R^2$ ), and  $d$ -statistics or index of agreement was used in the model evaluation.

## 2.3 Chemical equilibrium speciation modeling

Phosphorus chemical speciation was calculated for the leachates from the control (without amendment) and for 2% application rate of Al-WTR, slag, and MgO, respectively, to the manure-impacted soil. In addition, speciations were calculated for manure-impacted soils co-blended with (1%+1%) each of

Al-WTR+MgO and Al-WTR+Slag, respectively. Previous work from Silveira et al. (2006) using several weeks of leachates suggested that the number of weeks of selected leachate used did not have any significant difference in chemical speciation. Based on that, the 1st week of data was selected for the chemical speciation equilibrium modeling. In addition, after the 2nd to 4th weeks, due to P immobilizations by the amendments application, the measured  $\text{PO}_4^{3-}$  was almost zero. The low observed  $\text{PO}_4^{3-}$  limits the prediction of possible phosphate minerals in the leachates. Leachate anions analyzed were  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , ammonium, and  $\text{PO}_4^{3-}$ . Cations analyzed were  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . The pH, electrical conductivity (EC), and alkalinity data were also analyzed as inputs for the chemical speciation. Ionic strength (I), as  $\text{mol l}^{-1}$  of the extracts was calculated from the EC, i.e.,  $I = \text{EC} \times 0.013$  (Celen et al. 2007).

The use of Visual Minteq (version 2.61) (Visual Minteq 2009) has a wide application in water quality assessments. The model has borrowed and incorporated wide thermodynamic databases from MINTEQA2. Visual Minteq utilizes the activities of dissolved chemical species in calculating saturation index (SI) of different mineral phases. The SI of each solid is defined as:

$$\text{SI} = \log \frac{\text{IAP}}{K_{\text{sp}}} \quad (1)$$

where IAP is the ion activity product of the respective chemical species, and  $K_{\text{sp}}$  is the solubility product of the estimated solid phase. For any particular mineral solid, if the calculated  $\text{SI} > 0$ , it implies that solution/leachate is supersaturated with respect to that mineral. Similarly, if calculated  $\text{SI} < 0$ , it means that the leachate is undersaturated with the mineral phase. On the other hand, if  $\text{SI} = 0$ , it suggests that the solid has reached equilibrium (Zhu and Anderson 2002).

## 2.4 Chemical equilibrium modeling with polymath

A chemical equilibrium model was developed recently with the aid of Polymath Education version 6.1. The simulation model was validated and reported in details for predicting magnesium-related minerals such as struvite (Gadekar and Pullammanappallil 2009). The mathematical model uses physicochemical equilibrium expressions, charge

balance, solubility equilibrium expressions, and mass balance equations for N, P, and Mg. Values of equilibrium constants and solubility products used in the model were reported in Gadekar and Pullammanappallil (2009). The model is comprehensive for magnesium-related minerals in terms of the number of solid species considered, wide range of flexibility, and applications. The model can be applied to reactors as in soil systems to explicitly determine the concentrations of all species (dissolved, ionic, and solid) for quantification of purity and yield of struvite under various conditions of pH and initial concentrations of  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ , and  $\text{PO}_4^{3-}$ . Initial conditions, which include pH, total concentrations of nitrogen, magnesium, phosphorus, inorganic carbon, and calcium, are inputs along with equilibrium constants. Initial guesses for  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2+}$ , and  $\text{Ca}^{2+}$  were provided. The Polymath Educational version 6.1 program solved the expressions and gave concentrations of dissolved, ionic species, and concentrations of solid components. These expressions included as mass balance equations for total magnesium ( $\text{Mg}_t$ ), calcium ( $\text{Ca}_t$ ), ammonia-N ( $\text{N}_t$ ), inorganic carbon (TIC), and phosphorus ( $\text{P}_t$ ). The expressions were written as functions of corresponding ionic species concentrations in molar quantities. In all, the model predicted the formation of 15 different solid phases when solutions containing ammonium, calcium, phosphate, and carbonates species are mixed. Struvite is one of the solids predicted. Using the charge balance equation, the appropriate [Exion] concentration was determined. This gives the acid or base requirement to maintain the pH. The following charge balance equation applies to the system:

$$\begin{aligned} &[\text{NH}_4^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{Na}^+] + [\text{H}^+] \quad (2) \\ &+ [\text{MgH}_2\text{PO}_4^+] + [\text{MgOH}^+] = 3[\text{PO}_4^{3-}] \\ &+ 2[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + 2[\text{CO}_3^{2-}] \\ &+ [\text{HCO}_3^-] + [\text{H}_2\text{PO}_4^-] + [\text{MgPO}_4^-] \\ &+ [\text{Cl}^-] + [\text{OH}^-] + [\text{Exions}] \end{aligned}$$

$$[\text{Exions}] = \sum [\text{other cations}] - \sum [\text{other anions}]$$

[Exion] was calculated from the charge balance, a positive value indicated addition of alkali, and a negative value indicated addition of an acid for pH balance. The resulting outcome from the Polymath

computation suggests all possible Mg, Ca, K, N, P, and carbonates based on mineral availability. However, it should also be noted that, in high matrix complex, such as soils, containing significant high sulfate concentrations, Polymath modeling appears to be limiting.

### 3 Results and discussion

#### 3.1 Amendments, soil, and leachate composition

The physicochemical properties of Al-WTR taken from Bradenton, FL showed 86 gkg<sup>-1</sup> Al content and 2.3 gkg<sup>-1</sup> Fe content (Table 1). The relative high Al content in Al-WTR suggests that the material might reasonably achieve high P sorption (Grubb et al. 2000; Arias et al. 2006). The slag contained Ca, Mg, and Al (598, 106, and 156 gkg<sup>-1</sup>), respectively. In comparison, MgO had a greater Mg content (897 gkg<sup>-1</sup>) than slag. The pH of Al-WTR was 6.3, which was consistent with values reported elsewhere (6.0–8.4; Makris and O'Connor 2007). The Al-WTR had P concentration of 0.02 g P kg<sup>-1</sup>, which was slightly below the range reported for Al-WTRs (0.3–4.0 g P kg<sup>-1</sup>; Makris and O'Connor 2007; Dayton et al. 2003). The MgO and slag amendments had alkaline pH values of 10.9 and 11.5, respectively, consistent with values reported by Cucarella and Renman (2009). The soil pH was 7.1. Oxalate-extractable Fe and Al are usually associated with amorphous phases of oxides and suggest that P will be attached to the sesquioxides and other forms of hydr(oxides) present in the soil (Table 1). Total P in the Okeechobee test soil was approximately 2,800 mg kg<sup>-1</sup> indicating a high P load (Nair et al. 1995). In the soil, most of the reactive P was associated with Ca–Mg representing, 62% of total reactive P, whereas P associated with Al–Fe was 23% and easily leachable P~15% (Table 1). The above fractionation data are consistent with results from Nair et al. (1995) and Sharpley et al. (2004), showing that Ca–Mg-bound P dominated the forms of phosphorus in a manure-impacted soil. The total P concentration of MgO was below the instrument's detection limits, and slag P content was approximately 0.03 g P kg<sup>-1</sup>.

The results of the measured chemical parameters in the leachate are presented in (Table 2). The control soil without amendment and soil amended with Al-WTR (Soil+Al-WTR) had a pH of 7.7. Soil amended with MgO and slag had pH ranging from 8.2 to 9.5,

**Table 1** General properties of amendments and soil

Properties <sup>a</sup>	Total Elemental (g kg <sup>-1</sup> )						
	P	Ca	Mg	Al	Fe	Al	pH
Amendments							
Al-WTR	0.02	4.6	0.5	86	2.3	86	6.3
Slag	0.03	598	106	156	14	156	11.5
MgO	BDL <sup>c</sup>	9.0	897	2.0	2.0	2.0	10.9
Soil <sup>b</sup>	pH	Sequential extracted P oxalate extractable (mg kg <sup>-1</sup> )					
A-horizon	7.1	NaOH <sup>e</sup>	HCl <sup>f</sup>	Total P	Al	Fe	Al
		640	1720	2800	210	348	210
		400					

<sup>a</sup> Values are means of triplicate

<sup>b</sup> Okeechobee soil

<sup>c</sup> BDL (below detection limits of  $1 \times 10^{-3}$  mg l<sup>-1</sup>)

<sup>d,e,f</sup> Soil fractionations [KCl–P (soluble or exchangeable P), NaOH–P (extractable P bound to Al–Fe) and HCl–P (extractable P bound to Ca–Mg)] determined using the method of Chang et al. (1983)



indicating the alkaline nature of Ca–Mg amendments. The EC of the control soil and soil with amendment ranged from 5.58 to 8.8 mS cm<sup>-1</sup>. The relative high values of EC indicate the presence of dissolve inorganic constituents in the samples. The dissolve inorganic constituents analyzed were NH<sub>4</sub>, PO<sub>4</sub>, SO<sub>4</sub>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and alkalinity (Table 2). The chemical values obtained were a reflection of manure deposition, although these values differ from one place to another depending on the extent of the deposition (Josan et al. 2005). The DOCs of the control soil and Soil+Al-WTR were 3,000 and 2,000 mg l<sup>-1</sup>, respectively. On the other hand, soil amended with MgO and slag had DOC concentrations ranging from 30 to 60 mg l<sup>-1</sup>. The reduction in DOC values of soil amended with Ca–Mg materials, compared to the control and Soil+Al-WTR, may be attributed to the neutralizing effects of Ca–Mg amendments on dissolve soluble organics. Similar reduction effects were observed for PO<sub>4</sub> in solution when Ca–Mg materials were amended. Phosphate concentration reduced from 90 mg l<sup>-1</sup> for control soil to 12 mg l<sup>-1</sup> when amended with MgO. The reduction in PO<sub>4</sub> may be attributed to sorption of PO<sub>4</sub> released in solution onto Al, Ca/Mg hydr(oxide) surfaces (Miyittah et al. 2011). The chemical values presented were used as inputs for the geochemical models of Visual Minteq and Polymath, respectively.

### 3.2 Simulation vs. experimental data using Polymath model and Visual Minteq

#### 3.2.1 Solid-phase equilibria from the literature

Experimental, synthetic, and actual waste water data taken from the literature were simulated using Visual Minteq and Polymath simulation models (Gadekar and Pullammanappallil 2009). The input data for simulations utilized the concentrations of total NH<sub>4</sub>-N, Mg, PO<sub>4</sub>-P, Ca, total inorganic carbon, and pH. The current version of Visual Minteq used did not include struvite in its database. Thermodynamic parameters for struvite were added before running the computer model in Visual Minteq for the prediction of solid phases. The results are presented in Tables 3 and 4. A graphical representation of the amount of struvite predicted versus that of the experimental values is plotted (data not shown). The results showed clearly, the relative strength of Polymath model ( $R^2=0.57$ )

**Table 2** Leachate chemical composition from soil matrix for geochemical modeling

Treatments <sup>#</sup>	pH	EC (mS cm <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (mg l <sup>-1</sup> )	Cl <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>2</sub> <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	PO <sub>4</sub> <sup>3-</sup> (mg l <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	Na <sup>+</sup> (mg l <sup>-1</sup> )	Ca <sup>2+</sup> (mg l <sup>-1</sup> )	Mg <sup>2+</sup> (mg l <sup>-1</sup> )	DOC (mg l <sup>-1</sup> )	Alkalinity (CaCO <sub>3</sub> ) (mg l <sup>-1</sup> )
Soil (control)	7.7	5.6	28.7	199	287	233	90	222	538	676	883	3,000	2,000
Soil+MgO (2%)	9.5	8.3	61.3	537	613	313	40	279	273	605	1,087	30	2,500
Soil+Slag (2%)	8.4	6.4	23.8	235	291	277	12	255	302	469	737	35	2,400
Soil+Al-WTR (2%)	7.7	8.9	35.0	384	350	430	48	343	285	589	571	2,000	1,380
Soil+WTR+MgO (1+1%)	9.2	8.5	41.0	445	350	430	45	315	274	141	1,160	60	2,400
Soil+WTR+Slag (1+1%)	8.2	8.8	31.5	340	315	471	14	324	295	574	682	50	2,440

<sup>#</sup> Values are means triplicate of the soil (Table 1). Standard errors of the means (leachate chemical composition) are significantly low (vary between±0.01 to 0.05)

**Table 3** Data<sup>a</sup> taken from literature to simulate model predictions of polymath and Visual Minteq

Type of wastewater	pH	Initial concentrations (mM)			Exptd struvite (mg l <sup>-1</sup> )	Model predictions struvite (mg l <sup>-1</sup> )	
		Mg <sub>T</sub>	P <sub>T</sub>	N <sub>T</sub>		Visual Minteq	Polymath
Solutions prepared by adding NH <sub>4</sub> Cl, KHPO <sub>4</sub> , MgCl, carbonate, and acetate	6.8	8.3	12.9	21.43	601	0	223.6
Synthetic urine containing PO <sub>4</sub> , NH <sub>4</sub> , Na, Mg, K, Ca, Cl, citrate, and carbonate	8.0	20.0	13.45	20.18	1,685	0	1,253.3
Synthetic urine containing PO <sub>4</sub> , NH <sub>4</sub> , Na, Mg, K, Ca, Cl, citrate, and carbonate	9.4	7.42	14.83	18.70	1,045	1,006	987.07
Synthetic urine containing PO <sub>4</sub> , NH <sub>4</sub> , Na, Mg, K, Ca, Cl, citrate, and carbonate	9.4	14.8	14.83	18.70	2,011	1,087	1,845.0
Liquid manure	8.5	2.39	5.51	80.00	338	319	322.2
Supernatant from anaerobically digested sludge dewatering centrifuge	8.5	1.51	1.97	43.88	195	171.05	200.9
Anaerobic digester effluent supernatant	8.5	7.03	6.38	24.5	805	825	818.2
Synthetic samples prepared by using MgCl <sub>2</sub> , NaH <sub>2</sub> PO <sub>4</sub> , and NH <sub>4</sub> Cl	9.0	14.3	14.26	14.26	1,714	1,581	452.4
Domestic wastewater+ 2% landfill leachate	9.2	7.79	7.79	7.79	1,036.9	681.7	207.4
Supernatant from sludge centrifuges in a biological nutrient removal plant	8.1	1.54	2.00	44.5	210.98	143.6	198.2
Swine waste	9.0	9.74	6.09	12	758.6	713.5	705.5

<sup>a</sup>Data taken from Gadekar and Pullammanappallil 2009

over that of the Visual Minteq ( $R^2=0.33$ ) in predicting struvite (Table 4). The prediction from Polymath may be because the simulation model was tailored specifically for magnesium-related mineral such as struvite. However, to validate the accuracy of the  $R^2$  values, the use of RMSE and index of agreement ( $d$ -statistics) were obtained. The RMSE was used to differentiate the model having the most significant influence, since  $R^2$  may indicate inaccuracy when used as a measure of accuracy (Willmott 1982). A lower value of 293.2 RMSE for Polymath suggests that the model fits the data well in terms of struvite predictions (Table 4). Furthermore, index of agreement or  $d$ -statistics was also evaluated to measure the degree to which the models predictions are error-free. Polymath showed a greater  $d$  value of 0.78 as compared to 0.69 for Visual Minteq, suggesting that the model is better in agreement for struvite prediction. The inability of Visual Minteq to predict struvite well may be due to greater stability of calcium ions, such as calcium phosphate and hydroxyapatite, or due to Ca ions which compete with Mg for phosphate ions in solution (Kristell et al. 2005; Bouropoulos and Koutsoukos 2000). In addition, struvite formation is affected by precipitation kinetics and wide degree of variabilities such as chemical species, pH, EC, and ion activity products (Celen et al. 2007). These factors may have accounted for the large amount of RMSE

**Table 4** Statistical parameters for model prediction with coefficient of determination ( $R^2$ ), root-mean-square error (RMSE), and index of agreement ( $d$ )

Statistics	Polymath	Visual Minteq
$R^2$	0.57	0.33
RMSE	293.2	355.7
D	0.78	0.69

$RMSE = \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}}$ , where  $n$ =number of observations,  $P_i$ =predicted value for the  $i$ th measurement, and  $O_i$ =observed value for the  $i$ th measurement.

$d = 1 - \left[ \frac{\sum_{i=1}^n (P_i - O_i)^2}{\sum_{i=1}^n (|P_i| + |O_i|)^2} \right]$ ,  $0 \leq d \leq 1$ , where  $n$ =number of

observations,  $P_i$ =predicted value for the  $i$ th measurement,  $O_i$ =observed value for the  $i$ th measurement,  $O$ =the overall mean of observed values,  $P'_i = P_i - O$  and  $O'_i = O_i - O$  (Willmott 1982)



observed. Polymath simulation model, on the other hand, was custom-made for prediction of struvite. The tailoring of Polymath for Mg–P solid phases (e.g., struvite) may have accounted for saturation indexes of phosphate minerals and other amorphous forms when Ca ions are greater than Mg into its formulations, thus a lower reduction of errors observed in the model predictions.

### 3.2.2 Solid-phase equilibria of co-blended soil with Visual Minteq

Simulation results of soil (control) and co-blended samples were calculated using Visual Minteq and Polymath models and are presented in Tables 5 and 6, respectively. Although co-blended samples were assumed to be thoroughly mixed, we recognized the complexities and the uncertainties associated with non-equilibrium nature of soil samples, as well as the inherent kinetic effects in chemical speciation. Bearing the uncertainties in mind, we restrict our interpretation to major significant trends in the modeling results.

Phosphorus chemical speciation was calculated for the leachates collected from the samples soil [Soil+MgO (2%), Soil+Slag (2%), Soil+Al-WTR (2%), Soil+Al-WTR+MgO (1+1%), Soil+Al-WTR+Slag (1+1%)]. Visual Minteq was used to predict the saturation indices for possible solid minerals formation. Table 5 indicates the soil solution saturation indices for phosphate minerals whose dissolution–precipitation reactions may control P activity of the soil. For the control, major fraction of P was associated with Ca–Mg~60%, followed by  $\text{HPO}_4^{2-}$ ~30%, and  $\text{H}_2\text{PO}_4^-$ ~4% of negatively charged complexes (data not shown). The control soil solution was undersaturated with respect to Mg–P minerals of farringtonite [ $\text{Mg}_3(\text{PO}_4)_2$ ] and newberryite [ $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ], but were saturated with Ca–P minerals of hydroxyl apatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ],  $\beta$ -tricalcium phosphate [ $\beta\text{-Ca}_3(\text{PO}_4)_2$ ], and octacalcium phosphate [ $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ], except that of dicalcium phosphate dihydrate [ $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ] and dicalcium phosphate [ $\text{CaHPO}_4$ ] whose mineral phases were almost at equilibrium with the soil. The results suggest that phosphate solubility and activity in soil solutions from manure-impacted soils, without any amendment, were dominated mainly by the dissolution–precipitation reactions of undersaturated Ca- and Mg–P solid phases ( $\text{SI} < 0$ ). The above observation with the control soil without any amendment is

**Table 5** Saturation indices calculated using Visual Minteq for treatments with and without co-blending

Treatments	Predicted minerals							
	$\beta$ -TCP	OCP	DCP	DCPD	HA	FNT	NBT	
Soil (control)	2.58	2.60	0.27	-0.01	10.66	-1.05	-0.16	
Soil+MgO (2%)	6.04	5.37	-0.42	-0.70	18.27	2.02	-0.98	
Soil+Slag (2%)	3.59	2.81	-0.54	-0.82	13.49	-0.69	-1.19	
Soil+Al-WTR (2%)	3.54	3.43	0.14	-0.14	12.71	-1.12	-0.63	
Soil+WTR+MgO (1+1%)	4.31	3.39	-0.67	-0.95	15.05	2.29	-0.56	
Soil+WTR+Slag (1+1%)	3.54	2.92	-0.37	-0.65	13.22	-1.12	-1.15	

Saturation index Log ion activity product (IAP)-log solubility product ( $K_s$ ), ( $\beta$ )- $\text{Ca}_3(\text{PO}_4)_2$   $\beta$ -tricalcium phosphate ( $\beta$ -TCP),  $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$  octacalcium phosphate (OCP),  $\text{CaHPO}_4$  dicalcium phosphate (DCP),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  dicalcium phosphate dihydrate (DCPD),  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  hydroxyapatite (HA),  $\text{Mg}_3(\text{PO}_4)_2$  farringtonite (FNT),  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  newberryite (NBT)

**Table 6** Calculated values of solid (mg) found per litter of residual leachate as determined by Polymath model

Treatments	Predicted mineral										
	β-TCP	HA	DCPP	DCP	MHO	NBT	MP22	MP8	Struvite (%Purity)	Total (Solid)	
Control	26.9	1.35E-9	622.3	280.9	22.5	23.2	0.15	1.135	12.24(1.2)	989.3	
Soil+MgO (2%)	377.6	9.60E-7	173.4	78.3	22,295.9	3.64	0.37	2.86	119.0(3.9)	3,051.2	
Soil+Slag (2%)	14.3	4.95E-10	484.4	218.6	96.7	87.9	9.2	70.2	90.29(8.4)	1,071.7	
Soil+Al-WTR (2%)	48.1	4.96E-9	544.4	245.7	96.0	36.9	1.61	12.28	37.18(3.6)	1,022.2	
Soil+WTR+MgO (1+1%)	9.2	6.58E-08	150.3	67.8	2,080.7	8.79	1.98	15.1	199(7.4)	2,610.9	
Soil+WTR+Slag (1+1%)	8.8	8.23E-11	1,092.6	493.0	19.0	324.1	24.6	187.4	353.1(14.1)	2,502.6	

(β)-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> β-Tricalcium phosphate (β-TCP), Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH hydroxyapatite (HA), CaHPO<sub>4</sub>·5H<sub>2</sub>O dicalcium phosphate pentahydrate (DCPP), CaHPO<sub>4</sub> dicalcium phosphate (DCP), Mg(OH)<sub>2</sub> magnesium hydroxide (MHO), MgHPO<sub>4</sub>·3H<sub>2</sub>O newberryite (NBT), Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·22H<sub>2</sub>O magnesium orthophosphate (v) dicosahydrate (MP22), Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O magnesium orthophosphate (v) octahydrate (MP8), MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O struvite

consistent with results from Immokalee soil, a spodosol (Silveira et al. 2006; Agyin-Birikorang et al. 2009).

Co-blending the soil with Slag, Al-WTR, and MgO at 2% rate had similar mineral predictions under Visual Minteq modeling. All treatments were undersaturated with newberryite [MgHPO<sub>4</sub>·3H<sub>2</sub>O], farringtonite [Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] except that of Soil+MgO, indicating supersaturation of newberryite. The supersaturation with respect to newberryite supports the fact that Mg–P bearing minerals maybe responsible for controlling P solubility in manure-impacted soils. On the other hand, addition of Slag and Al-WTR co-blended soil had similar solid phases with Mg–P minerals but with undersaturation indices (Table 5). In addition, undersaturation was also observed with some calcium mineral phases of [CaHPO<sub>4</sub>·2H<sub>2</sub>O] and [CaHPO<sub>4</sub>], thus indicating the role of Ca and Mg in controlling P solubility, which is consistent with the conclusions of other studies involving manure-impacted soils (Josan et al. 2005; Silveira et al. 2006; Agyin-Birikorang et al. 2009).

Co-blended samples with Soil+WTR+Slag and Soil+WTR+MgO at 1% +1% amendments had solid phase similar to either Soil+MgO or to Soil+Slag at 2%, respectively. Although, the solid solution of the co-blended samples were thoroughly mixed, it was suggested that the chemical activity of solid phases in the soil system dissolve nonstoichiometrically, thereby creating inhomogeneity and disequilibrium between the solid’s surface and that of the interior (Bohn and Bohn 1987). Consequently, the true equilibrium in soil suspensions maybe extremely difficult, and applying strict thermodynamics may be less effective for co-blended samples. In all treatments, the most thermodynamically stable solid phase observed appeared to be that of hydroxyapatite with SI > 0. Furthermore, the presence of DOC, which are usually high in manure-impacted soils (Table 2), have been reduced due to co-blending effects. This may be explained due to the neutralizing effects of alkaline nature introduced by Ca–Mg amendments.

### 3.2.3 Solid-phase equilibria of co-blended soil with Polymath model

The types of solid phases identified by polymath model were identical to those predicted by Visual Minteq (Table 6). However, major differences revealed from

Polymath were solid phases of dicalcium phosphate pentahydrate (DCPP), magnesium hydroxide (MHO), magnesium orthophosphate (v) docosahydrate (MP22), magnesium orthophosphate (v) octahydrate (MP8), and struvite. Polymath model shows clearly the prediction of magnesium-based solids. Struvite precipitation was observed to follow the following order: Soil+WTR+Slag>Soil+Slag>Soil+WTR+MgO>Soil+MgO>Soil+WTR>control. The order of struvite precipitation might suggest a combined effect of magnesium availability and pH. This is because in struvite formation, magnesium ion and pH play a major role. The importance of struvite cannot be overemphasized. Struvite as a sparingly soluble mineral can slowly release its nutrients in the long run. The slow release of struvite may offer great advantage to forage growers who are faced with excess laden of manure. The conventional school of thought in addressing soil P pollution is to permanently fix the P with a sorbent in the soil. However, with the identification of struvite in the amendment application which is aimed to immobilize the P, the unconventional thinking should be fixing the P and release it later for future use. This unconventional school of thought is beneficial in cost terms as well as for sustainable environmental management. Struvite is produced at industrial scale and used as a slow release fertilizer. It can release the P and N at a slower rate which can be controlled by adjusting the pH if needed. The released N and P can be beneficial to plant growth. However, struvite is not used alone, but rather used by mixing with other forms of inorganic and organic fertilizers (Ueno and Fujii 2001). The presence of struvite as revealed by the Polymath simulation model may help in evaluating the slow release in soils. The release by struvite is so slow and is a function of prevailing pH (Bhuiyan et al. 2009). The slow release of struvite may lead to saving cost to ranchers whose soils are heavily laden with manure. The dwindling phosphate reserve in Florida is of great concern, thus suggesting that cycling and reuse of excess P in soil through co-blending techniques of amendments may be a safe practice.

#### 4 Conclusions

Loss of phosphorus (P) is a major concern for many areas laden with manure. It is confirmed that co-blending

of Al-based materials with Ca–Mg-based materials may help to reduce offsite release of P. The use of chemical equilibrium models of Visual Minteq and Polymath model revealed various solid phases formed in the soil. Polymath model, however, was observed to add new information to that revealed by Visual Minteq. The results suggest that Polymath model revealed solid phases of DCPP, MHO, MP22, MP8, and struvite, which were lacking in the modeling from Visual Minteq. Notably, the solid phase that is difficult to predict in soils is struvite. Struvite precipitation in soil suggests that the immobilized P can be reused. Residual leachate from the co-blended amendments, Soil+WTR+Slag, Soil+WTR+MgO, Soil+MgO, Soil+Slag, Soil+WTR, and the control (without amendment), had struvite of 353, 199, 119, 90, 37, and 12 mg l<sup>-1</sup> respectively. The slow release of struvite to leach P may be harnessed for future plants' uptake. Such a process of P immobilization and release may help in promoting the sustainability of environmental nutrient.

#### References

- Agyin-Birikorang, S., O'Connor, G. A., & Bonzongo, J.-C. (2009). Modeling solid phase control of solubility of drinking water treatment residuals-immobilized phosphorus in soils. *Communications in Soil Science and Plant Analysis*, 40(11), 1747–1769.
- Arias, M. J., Da Silva-Carballal, L., Garcia-Rio, J., Mejuto, & Nunez, A. (2006). Retention of phosphorus by iron and aluminum oxide-coated quartz particles. *Journal of Colloid and Interface Science*, 295(1), 65–70.
- Bhuiyan, M. I. H., Mavinic, D. S., & Beckie, R. D. (2009). Dissolution kinetics of struvite pellets grown in a pilot-scale crystallizer. *Canadian Journal of Civil Engineering*, 36(4), 550–558.
- Bohn, H. L., & Bohn, R. K. (1987). Solid activities of trace elements in soils. *Soil Science*, 143(6), 398–403.
- Bouropoulos, N. Ch., & Koutsoukos, P. G. (2000). Spontaneous precipitation of struvite from aqueous solutions. *Journal of Crystal Growth*, 213(3–4), 381–388.
- Celen, I., Buchanan, J. R., Burns, R. T., Robison, R. B., & Raman, D. R. (2007). Using chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. *Water Research*, 41(8), 1689–1696.
- Chang, A. C., Page, A. L., Sutherland, F. H., & Grgurevic, E. (1983). Fractionation of phosphorus in sludge affected soils. *Journal of Environmental Quality*, 12(2), 286–290.
- Cucarella, V., & Renman, G. (2009). Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments—a comparative study. *Journal of Environmental Quality*, 38(2), 381–392.

- Dayton, E. A., & Basta, N. T. (2005). A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. *Journal of Environmental Quality*, 34(3), 1112–1118.
- Dayton, E. A., Basta, N. T., Jakober, C. A., & Hattey, J. A. (2003). Using treatment residuals to reduce phosphorus in agricultural runoff. *Journal of American Water Works Association*, 95(4), 151–158.
- Gadekar, S., & Pullammanappallil, P. (2009). Validation and applications of chemical equilibrium model for struvite precipitation. *Environmental Modeling and Assessment*, 15(3), 201–209. doi:10.1007/s10666-009-9193-7.
- Grubb, D. G., Guimaraes, M. S., & Valencia, R. (2000). Phosphate immobilization using an acidic type F fly ash. *Journal of Hazardous Materials*, 76(2–3), 217–236.
- Güngör, K., & Karthikeyan, K. G. (2005). Probable phosphorus solid phases and their stability in anaerobically digested dairy manure. *Transactions of the ASABE*, 48(4), 1509–1520.
- Güngör, K., Jürgensen, A., & Karthikeyan, K. G. (2007). Determination of phosphorus speciation of dairy manure using XRD and XANES spectroscopy. *Journal of Environmental Quality*, 36(6), 1856–1863.
- Hieltjes, A. H. M., & Lijklema, L. (1980). Fractionation of inorganic phosphates in calcareous sediments. *Journal of Environmental Quality*, 9(3), 405–407.
- Josan, M. S., Nair, V. D., Harris, W. G., & Herrera, D. (2005). Associated release of magnesium and phosphorus from active and abandoned dairy soils. *Journal of Environmental Quality*, 34(1), 184–191.
- Kennedy, V. H., Rowland, A. P., & Parrington, J. (1994). Quality assurance for soil nutrient analysis: A case study. *Communications in Soil Science and Plant Analysis*, 25(9), 1605–1627.
- Kristell, S. C., Le, E., Valsami-Jones, P., Hobbs, & Parsons, S. A. (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth*, 283(3–4), 514–522.
- Lindsay, W. L. (2001). *Chemical equilibria in soils*. Caldwell, NJ, USA: Blackburn Press.
- Makris, K. C., & O'Connor, G. A. (2007). In D. Sakar, R. Datta, & R. Hannigan (Eds.), *Currents perspectives in environmental geochemistry*. Denver, CO, USA: Geological Society of America Press.
- Miyittah, M. K., Stanley, C. D., Mackowiak, C., & Rechcigl, J. E. (2011). Developing a remediation strategy for phosphorus immobilization: Effect of co-blending Al-residual and Ca-Mg amendments in a manure-impacted spodosol. *Soil and Sediment Contamination: An International Journal*, 20(4), 337–352.
- Moore, P. A., Daniel, T. C., & Edwards, D. R. (1999). Reducing phosphorous runoff and improving poultry production with alum. *Poultry Science*, 78(5), 692–698.
- Moore, P. A., & Miller, D. M. (1994). Decreased phosphorus solubility in poultry litter with aluminum, calcium and iron amendments. *Journal of Environmental Quality*, 23(2), 325–330.
- Nair, V. D., Graetz, D. A., & Portier, K. M. (1995). Forms of phosphorus in soil profiles from dairies of South Florida. *Soil Science Society of America Journal*, 59(5), 1244–1249.
- Rabenhorst, M. C. (2009). Making soil oxidation-reduction potential measurements using multimeters. *Soil Science Society of America Journal*, 73(6), 2198–2201.
- Ruttenberg, K. C. (1992). Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography*, 37(7), 1460–1482.
- Sharpley, A. N., McDowell, R. W., & Kleinman, P. J. A. (2004). Amounts, forms and solubility of phosphorus in soils receiving manure. *Soil Science Society of America Journal*, 68(6), 2048–2057.
- Silveira, M. L., Miyittah, M. K., & O'Connor, G. A. (2006). Phosphorus release from a manure-impacted spodosol: Effects of a water treatment residual. *Journal of Environmental Quality*, 35(2), 529–541.
- Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry: Chemical equilibria and rates in natural waters* (3rd ed.). New York: Wiley.
- Toor, G. S., Hunger, S., Peak, J. D., Sims, J. T., & Sparks, D. L. (2006). In D. L. Sparks (Ed.), *Advances in agronomy vol. 89* (pp. 1–72). Boston: Academic Press.
- Ueno, Y., & Fujii, M. (2001). Three years operating experience selling recovered struvite from full scale plant. *Environmental Technology*, 22(11), 1373–1381.
- USEPA. (1996). Acid digestion of sediments, sludges and soils. Cincinnati, OH: USEPA. [Online]. <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3050b.pdf>. Accessed 6 December 2009.
- USEPA. (2000). National water quality inventory 2000 report. Washington, DC: USEPA. <http://www.epa.gov/305b/2000report/>. Accessed 22nd July 2009.
- Visual Minteq. (2009). Visual Minteq version 2.61. <http://www.lwr.kth.se/English/Oursoftware/Vminteq/index.html>. Accessed 6 September 2009.
- Willmott, C. J. (1982). Some comments on the evaluation of model performance. *Bulletin of the American Meteorological Society*, 63(11), 1309–1313.
- Zhu, C., & Anderson, G. (2002). *Environmental applications of geochemical modeling*. Cambridge: Cambridge University Press.