



Phosphorus recovery from an igneous phosphate rock using organic acids and pyrolysis condensate



Akinson Tumbure^{a,b,*}, Mike B. Bretherton^a, Peter Bishop^a, Mike J. Hedley^a

^a Farmed Landscapes Research Centre, School of Agriculture and Environment, Massey University Palmerston North, New Zealand 4410

^b Faculty of Earth and Environmental Sciences, Marondera University of Agricultural Sciences and Technology, P.O. Box 35, Marondera, Zimbabwe

ARTICLE INFO

Article history:

Received 29 August 2021

Revised 7 December 2021

Accepted 25 January 2022

Editor DR B Gyampoh

Keywords:

Phosphorus

Apatite

Organic acids

Pyrolysis waste

Dissolution

ABSTRACT

Directly applied igneous phosphate rocks (PR) are agronomically ineffective because they are intrinsically unreactive. The main process by which PRs are solubilised in soils by microorganisms and plants is through the exudation of low molecular weight organic acids, which have a short lifespan in soils, thereby limiting the period of PR dissolution and agronomic effectiveness. This study measured the amount of P recovered from Dorowa PR (DPR) by suspension in water and sequential leaching with citric, acetic, oxalic acids, and pyrolysis condensate at various pH values. Of the dilute acids tested, oxalic acid was more effective at solubilising P from the DPR, cumulatively liberating 46% of total P from the DPR after 3 extractions at pH 3. However, aqueous phase pyrolysis liquid from maize stover pyrolysis was less effective at recovering P, yielding less than 14% of the total P despite maintaining a pH range of 3 to 3.8 in leachates after sequential extractions. The poor solubilisation was due to the low concentrations of chelating and complexing acids in the pyrolysis liquid, with the dominant acid being acetic acid and the high Ca content. Further research on improving the dissolution potential of pyrolysis liquid by removing cations in the liquid before leaching and other alternative processes to produce complexing acids such as oxalic acid is recommended.

© 2022 The Author(s). Published by Elsevier B.V. on behalf of African Institute of Mathematical Sciences / Next Einstein Initiative.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Introduction

Directly applied phosphate rocks (PR) of high chemical reactivity (carbonate substituted apatites) have proved to be effective P fertilisers for crops in acid soils [1]. Early studies by Bolan and Hedley [2] revealed that significant activity of microbial processes in soils that facilitate the oxidation of reduced carbon, nitrogen, and sulphur compounds in acid soils are often sufficient to maintain soil pH below the equilibrium pH at which carbonate substituted apatites dissolve. The less reactive PRs (e.g. igneous PR) such as the Kodjari PR from Burkino Faso [3] and the Dorowa PR (DPR) from Zimbabwe [4], however, do not dissolve sufficiently to provide plant available P when directly applied to soils. Therefore, where soluble P fertiliser manufacturing facilities are not available, or run at a high cost, researchers have evaluated biological acidulation

* Corresponding author at: Faculty of Earth and Environmental Sciences, Marondera University of Agricultural Sciences and Technology, P.O.Box 35, Marondera, Zimbabwe.

E-mail address: atumbure@muast.ac.zw (A. Tumbure).

processes, such as using phosphorus solubilising microbes [5–7] and composting [8–10] to assist with the solubilisation of PRs.

In-situ microbial solubilisation of PRs in soils has been of interest to researchers for a considerable time [11]. The effectiveness of microorganisms to solubilise PRs hinges on the production and exudation of organic acids, which is strongly influenced by environmental and nutritional parameters controlling microbial populations [12]. This presents great challenges in optimising microbial solubilisation in drier impoverished soils that support limited microbial diversity and activity. The major mechanism by which microorganisms solubilise P is through exudation of low molecular weight organic acids (LMWOA), which chelate those cations bound to phosphate [13]. These LMWOAs are readily available C substrates, have a low persistence in soil [14] and are as weak acids, generally neutralised by the soil's pH buffering capacity [15], rather than accelerating PR dissolution.

Ex-situ solubilisation of PRs with organic acids produced from separate optimised processes, such as fermentation [16] and pyrolysis [17,18] have the potential to solve the problems of in-situ solubilisation. In previous studies by Kpomblekou and Tabatabaie [19], the most effective low molecular weight organic acids that solubilised P from PRs were found to be citric, cis-aconitic, and oxalic acids. Recent work by Mendes et al. [20] found that oxalic acid was more efficient at solubilising P than sulphuric acid across a range of reactive and non-reactive PRs. With biochar production being promoted as a greenhouse gas (GHG) mitigation and soil nutrient loss-curbing technology [21], then pyrolysis condensate produced from the pyrolysis of biomass [18] may also be a significant source of low molecular weight organic acids. Pyrolysis is the thermochemical conversion of organic biomass to biochar (and its associated by-products) in the absence of oxygen [22]. The final products of the pyrolytic process are char (solid), condensate (liquid comprising various organic compounds and condensed gases), and non-condensable exhaust gases. Most pyrolysis research in agriculture has focused on obtaining biochar from slow-pyrolysis processes, with the final aim of soil amelioration [23]. Less research has focused on the beneficial use of the liquid fractions. For example, as a potential chelator of heavy metals in contaminated soils [24], and as potential plant and microbial stimulants [25].

Within the aqueous pyrolysis liquid fraction are dissolved organic compounds such as furfural, hydroxymethylfurfural (HMF), organic acids, aldehydes, and phenols [22,23]. The non-aqueous “oil” fraction contains insoluble organics (mainly aromatics) of high molecular weight [26]. Disposal or use of the aqueous phase is limited by the toxic nature of some of the products such as HMF, furfural, and aldehydes. The separation of these components is a daunting task, and the use of classic thermal separation processes, such as distillation, is ineffective [27]. Research to establish practical techniques to isolate undesirable chemicals from the liquid pyrolysis fraction is still in its infancy. Keskinen et al. [28] explains that effective methods have not yet been developed, and new ways to utilise pyrolysis by-products in the liquid phase are needed.

Using the pyrolysis condensate as an acid source for PR solubilisation would only require separating the oil and aqueous fraction. This study aimed to evaluate P recovery from Dorowa PR (DPR) using the aqueous phase of pyrolysis liquid produced from corn stover pyrolysis. The feasibility of P recovery from DPR was first evaluated using extraction and/or leaching with dilute acetic, citric, and oxalic acids to various pH endpoints. This was followed by sequential leaching experiments with diluted pyrolysis liquid. It was hypothesised that the extent of P release in the weak acid solution would depend upon the extent of proton supply to the phosphate at differing solution pH. The second hypothesis was that the mixture of organic acids in the aqueous phase of pyrolysis liquid could significantly solubilise P from DPR and sequential extractions would improve P recovery.

Materials and methods

Samples

The sampling and characterisation of the DPR and the maize residues used in this study are described elsewhere [29,30]. Briefly, DPR was obtained already milled (94% of particles $\leq 250 \mu\text{m}$) as a composite sample from Dorowa mine in Buhera, Zimbabwe (19° 03' 47" S, 31° 45' 45" E). The DPR had a P content of 16.5% with the P existing as non-water-soluble hydroxy-fluorapatite. The maize residues (stems + leaves) used to produce the pyrolysis condensate were obtained from Massey University, Hauronga Farm in Palmerston North, New Zealand when the crop had reached physiological maturity. They were then chipped using an electronic chipper before being dried to a constant mass in an oven at 70 °C and then ground in a crosscutting mill to a particle size of $<2 \text{ mm}$.

Initial dissolution / titration experiments using pure dilute acids

Suspensions of DPR: DI water (0.5 g/ 50 mL) were shaken overnight in 100 mL polyethylene screw top containers and left to stand for a further 48 h to ensure equilibration of the suspension. End point titrations were then performed using a TitraLab® 865 auto-titrator, with the temperature set at $25 \pm 0.5 \text{ }^{\circ}\text{C}$ and stirred at 600 rpm. The auto-titrator was programmed to allow 10 min for equilibration before initial pH was measured, and titration only began when a stable pH reading had been reached. The burette delivery speed was set between 0.01 and 0.02 mL/min, with proportional control employed to improve accuracy of the end point. An end point delay of 30 min was used to ensure equilibration at the final pH. The experiment was a two-factorial experiment with 20 treatments (5 pH points x 4 acid types) replicated three times. Endpoint pH values were set to 6, 5, 4, and 3, for the samples, and titrations were performed using 0.1 M of either sulphuric,

citric, acetic, or oxalic acid. All treatments (pH set point \times acid type) were replicated three times including suspensions of DPR: DI water that were not titrated serving as the control (referred to hereafter as initial pH). An acid concentration of 0.1 M was used to simulate the low concentration of organic acids in the diluted aqueous phase of the pyrolysis condensate. This concentration was in the mid-range of the study by Mendes et al. [20] to assess PR dissolution using various acids. When pH endpoint equilibria were reached, samples were immediately extracted and filtered through a 0.45 μm Millipore® Nitrocellulose filter paper under suction.

Selected cation concentrations in the filtrates obtained after each extraction were measured using atomic emission spectrophotometry (AES) on an Agilent® 4200 MPAES. To improve accuracy, matrix matching was employed for the standards, and spiked standards were included. The P content in the filtrates was measured following the addition of a vanadomolybdate reagent by UV-vis spectrophotometry after diluting a 10 ml aliquot of each filtrate into 250 mL volumetric flasks [31].

The acids were ranked according to how much they solubilised the DPR and the top 2 acids were selected for sequential titrations. For each of the 2 acids, a 5×3 factorial experiment with a total of 15 treatments with 3 replicates was run. The factors were pH set points (initial, 6, 5, 4, 3) and extraction sequence (1, 2, 3). For these titrations, the residue left on the filter paper was washed with DI water and then resuspended in 50 mL of DI water. The titration was then repeated to the same pH end point. Washing of residue, and re-suspension and titration to the same pH endpoint, was repeated three times. The control treatment consisted of suspensions of DPR: DI water that were not titrated but were sieved and sequentially resuspended in DI water thrice. The same leachate analytical procedures as previously mentioned for determination of P, and selected cations in leachates were employed.

Production, processing, and characterisation of pyrolysis condensate

A pyrolysis reactor composed of a rotating 25 L drum and LPG heating was used to produce pyrolysis condensate. Exactly 2 kg of maize stover (stem + leaves), previously dried at 70 °C and ground to less than 2 mm diameter, was placed in the reactor. Pyrolysis was performed by heating to 300 ± 10 °C and maintained until production of exhaust gases ceased, indicating completion of pyrolysis. This pyrolytic process produced biochar and pyrolysis condensate that was 39.2 and 35.6% respectively, of the initial maize stover mass (2 kg). The pyrolysis condensate was mixed with DI water in ratios of 1:4 and 1:1 (condensate/ water), and left overnight at 4 °C, after which the solutions were centrifuged at a relative centrifugal force (RCF) of $4696 \times g$ for 5 min, and then decanted to collect the aqueous phase pyrolysis liquid.

The pH of the aqueous phase pyrolysis liquid was measured using a Thermo Scientific Orion Star A214 pH metre, and the total acid number (TAN) was measured potentiometrically by titrating with 0.1 M KOH on a TitraLab® 865 autotitrator. The TAN analysis is an accepted method for pyrolysis condensate, originally developed (and adapted) from the measurement of the acidity of petroleum products [32]. Organic acids in the aqueous-phase pyrolysis liquid were identified and quantified by reversed phase liquid chromatography (RP-HPLC) using a Dionex ultimate 3000® HPLC. The HPLC was equipped with a Luna® C18 (2), 250 mm \times 4.6 mm column and a 25 mM KH_2PO_4 (at pH 2.5) mobile phase [33].

Column leaching of DPR with aqueous phase pyrolysis liquid

A column leaching study was performed using DPR that was mixed with acid washed sand at a ratio of 0.5 g DPR: 7.5 g sand per leaching tube. The experiment was run as a completely randomised design, 2×7 factorial experiment with type of condensate (1:1 and 1:4) and leaching time (2, 4, 6, 8, 12, 18, 26 h) as factors giving a total of 14 treatments. Leaching tubes were made of polythene, had a volume of 11.5 mL, a height of 130 mm, and an open-end internal diameter of 12 mm. The bottom of the column consisted of a fibreglass filter paper to prevent loss of the column contents during the leaching process. Leaching tubes were packed with the DPR/sand mixture to a constant bulk density, and all leaching tubes were initially moistened to approximately field capacity using 1.3 mL of pyrolysis liquid (diluted either 1:4 or 1:1) and left to stand for 2 h. Sequential leaching was then performed by delivering the aqueous phase pyrolysis liquid at a rate of 0.05 mL/min by means of a peristaltic pump. Leachate was collected into pre-weighed containers after 2, 4, 6, 8, 12, 18, and 26 h. A set of 4 replicates were run, with a blank consisting of acid washed sand only.

Chemical analysis of the pyrolysis liquid leachate

The pH of the collected leachates was measured using a Thermo Scientific Orion Star A214 pH metre. For analysis of P and other element concentrations in solution, a 2 mL aliquot of the leachate was first digested in 10 mL of 70% HNO_3 to remove organics which could interfere with measurements. The P, Ca, Mg, Na, Al, Fe, and Mn content of the digested leachates was then analysed by atomic emission spectrophotometry (AES) on an Agilent® 4200 MPAES.

Statistical analysis

Leachate element concentrations were analysed for variance (ANOVA) using the R statistical package (version 4.1.0) at 95% confidence interval. For multi-acid comparisons, two factors were considered: acid type and endpoint pH while for sequential extractions the factors were extraction sequence and endpoint pH. Significantly different means ($P < 0.05$) were

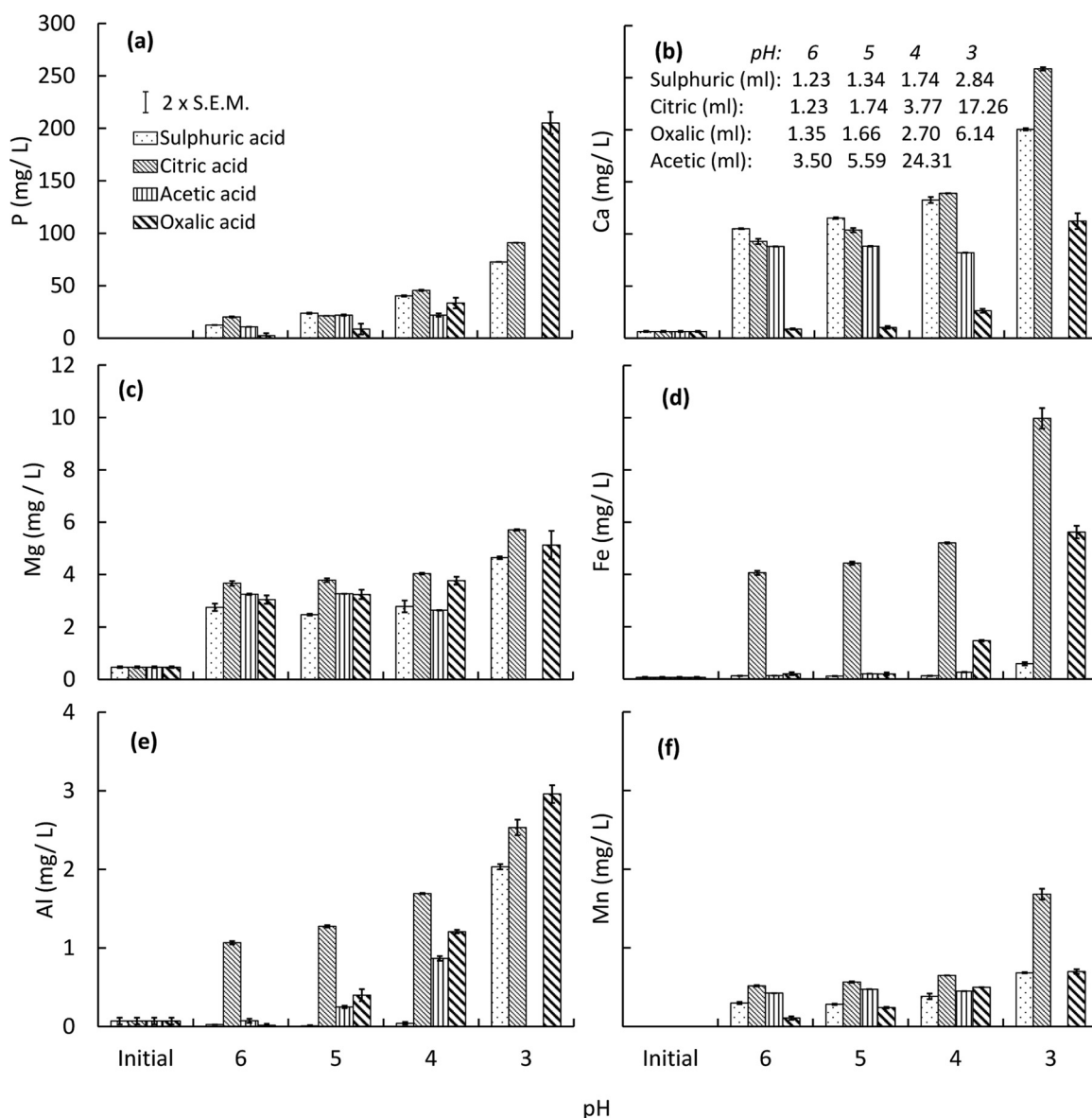


Fig. 1. Concentration of P (a), Ca (b), Mg (c), Fe (d), Al (e) and Mn (f) extracted from DPR using various dilute acids. Table in (b) shows volume of acid titrated to each pH end point.

separated by employing least significant differences. Normality and equal variance were assessed by plotting normal QQ plots before running ANOVA.

Results and discussion

Dissolved P and selected elements from single dilute acid extractions

The effect of acid type and pH set point on the amount of P that was solubilised were significant ($P < 0.001$). Irrespective of the type of extracting acid, when pH set points ranged from 6 to 4, less than 3% of the total P present in the DPR was solubilised (Fig. 1a). When the pH was lowered to 3 by titrating with oxalic, citric, and sulphuric acids, 14.0, 7.4, and 4.7% of the total P present in DPR was dissolved, respectively. Oxalic acid significantly liberated ($P < 0.001$) the highest amount of P compared to the other acids. When the pH was 3, the final concentration of oxalic acid in the PR suspension was 12 mmol/L, similar to the 10 mmol/L concentration used by Kpomblekou and Tabatabatai [19], who also found that oxalic acid mobilised the greatest amount of P (4 – 5 g kg⁻¹ PR) from Kodjari and North Florida PRs compared to a range of other organic and mineral acids.

With the exception of the oxalic acid extracts, the concentration of Ca in all acid extracts was at least 2.5 x higher than that for P from pH 6 to 3 (Fig. 1b). Oxalic acid extracts had similar P and Ca dissolution trends from pH 6 to 4, but at pH 3, the concentration of P was about twice that of Ca.

This trend is consistent with the chemical behaviour of Ca in oxalate solutions at low pH, in other studies where varied P sources such as PRs, sewage incineration ash, and pig manure ash, were reacted with oxalic acid, with the resulting precipitation of insoluble oxalate salts [13,34,35]. Other researchers explain that the ability of organic acids to remove Ca from the solution via precipitation is more significant for increasing P dissolution compared to chelation and/or protonation [13,36]. The removal of the reaction product Ca from solution as evidenced by the significant reduction of Ca concentration in oxalic acid titrated samples at pH 3 was responsible for driving the apatite solubilisation reaction forward.

In comparison to other acids, citric acid significantly ($P < 0.001$) had the highest concentration of dissolved Fe (Fig. 1d). Lazo et al. [37] report similar findings for iron phosphate where citric acid dissolved twice as much Fe phosphate compared to when oxalic acid was used.

Generally, the Ca:P molar ratios in sulphuric, citric, and acetic acids closely followed each other (Figure S1a). However, for oxalic acid, the Ca:P molar ratio was at least 3 times less than that of other acids from pH 6 to 3 (Figure S1a). Kpomblekou and Tabatabaie [19] also reported similar differences in the Ca:P molar ratio in solution when 10 mM citric and oxalic acid extractions were used to solubilise Kodjari and North Florida PR. A relatively higher Ca:P molar ratio was observed for all acids at pH 6 which gradually declined as the pH was reduced to pH 3. The high Ca:P molar ratio at pH 6 for all acids is because more calcite than apatite was solubilised at these higher pH values [30]. The lower Ca:P molar ratio at pH 3 which ranged 2.13 – 2.89 for all acids except oxalic acid was higher than that in the DPR (1.73 for apatite + free carbonate) indicating preferential Ca release.

The effects of different processes (protonation, chelation, complexation) in acid action were inferred from (Al or Fe): P molar ratios in the acid extracts. Protonation and/or chelation increased Al in solution for sulphuric and acetic acids, while insoluble or sparingly soluble Al-complex formation in oxalic acid reduced Al in solution.

Citric acid had the highest Fe:P molar ratios at each pH (Figure S1b), while acetic and sulphuric acids had very low Fe:P molar ratios. The ability of citric acid to chelate relatively more Fe into solution can be attributed to its β -hydroxyl group which forms chelated six-member ring structures with Fe [38]. Citric and oxalic acids had their highest Al:P molar ratios at pH 5 which steeply declined with a reduction of pH up to pH 3 (Figure S1c). This suggests that at pH 5 oxalic and citric acids dissolved Al not associated with P as confirmed by low P dissolution at that pH. At the same time, sulphuric acid had the lowest Al:P molar ratio at pH 6 to 4 which then increased at pH 3. This is because the mechanism by which sulphuric acid dissolves Fe and Al bound to P, or gangue minerals is through protonation which becomes less effective at higher pH values.

Dissolved P and selected elements from sequential dissolution in citric and oxalic acids

Following the multi-acid titration experiments reported previously in this study, citric and oxalic acids were selected for sequential extractions since they solubilised significantly ($P < 0.001$) more P than acetic and sulphuric acids at pH 3. Low amounts of P were solubilised by citric acid at pH > 4, resulting in solution concentrations of less than 20 mg/L (Fig. 2a).

At pH 3, about 7.4, 7.8, and 6.6% of the total P content in DPR was solubilised by the first, second, and third sequential citric acid extractions, respectively, giving a total P extraction value of 21.9%. The variation in solubilised P was significantly ($P < 0.01$) different per extraction sequence with the second extraction liberating the highest amount of solubilised P at pH 3. However, the relatively high amount of P that was solubilised by citric acid at each sequential extraction at pH 3 implies that further extractions beyond the third could continue to recover significant amounts of P, although at diminishing rates. Extraction of similar amounts of P from DPR have been previously reported after two sequential extractions with a fixed amount of 2% citric acid [30].

Concentration of Ca in citric acid extracts at pH 3 reduced by about 17 and 26% in the second and third sequential extractions, respectively (Fig. 2b). The amount of Ca observed in extracts at pH 3 was 9, 7, and 6% of the total Ca in DPR for the first, second and third sequential extractions respectively. The higher amount of Ca solubilised in the first extraction is because a part contribution of this is from calcite present in the DPR, which becomes much less in subsequent extractions.

Compared to other citric acid extractions, the first extraction gave significantly ($P < 0.001$) the highest concentration of Mg, Fe and Al from pH 6 to 3 (Fig. 2c, d, e). At pH 3 the amount of Mg and Al solubilised from the first extraction was >21% of the content in DPR while the second and third extractions solubilised about 3% of Mg and Al content in DPR. The amount of solubilised Fe showed the same trend at pH 3, with about 14% of Fe in DPR solubilised in the first extraction and 1% solubilised in succeeding extractions. The reason for this trend is that, in the first extraction, the dissolution of apatite, calcite, and other gangue minerals, all contribute to elements in solution, and non-apatite constituents in DPR may be relatively more rapidly dissolved during the first extraction.

When oxalic acid was used, the extraction sequence was not significant ($P = 0.862$) in affecting the amount of P that was solubilised. From pH 6 to 4, each oxalic acid sequential extraction did not exceed a P concentration of 35 mg P/L (Fig. 3a), which constituted, at each extraction, less than 2.2% of the total P in DPR.

As expected, the highest solubilised P was at pH 3, which maintained a concentration of at least 205 mg P/L at each sequential extraction (Fig. 3a). Sequential extractions of oxalic acid at pH 3 solubilised 14.0, 16.1, and 16.2% of the total P in DPR for the first, second, and third, sequential extractions, respectively, totalling 46.3% of the total P in DPR. Given that

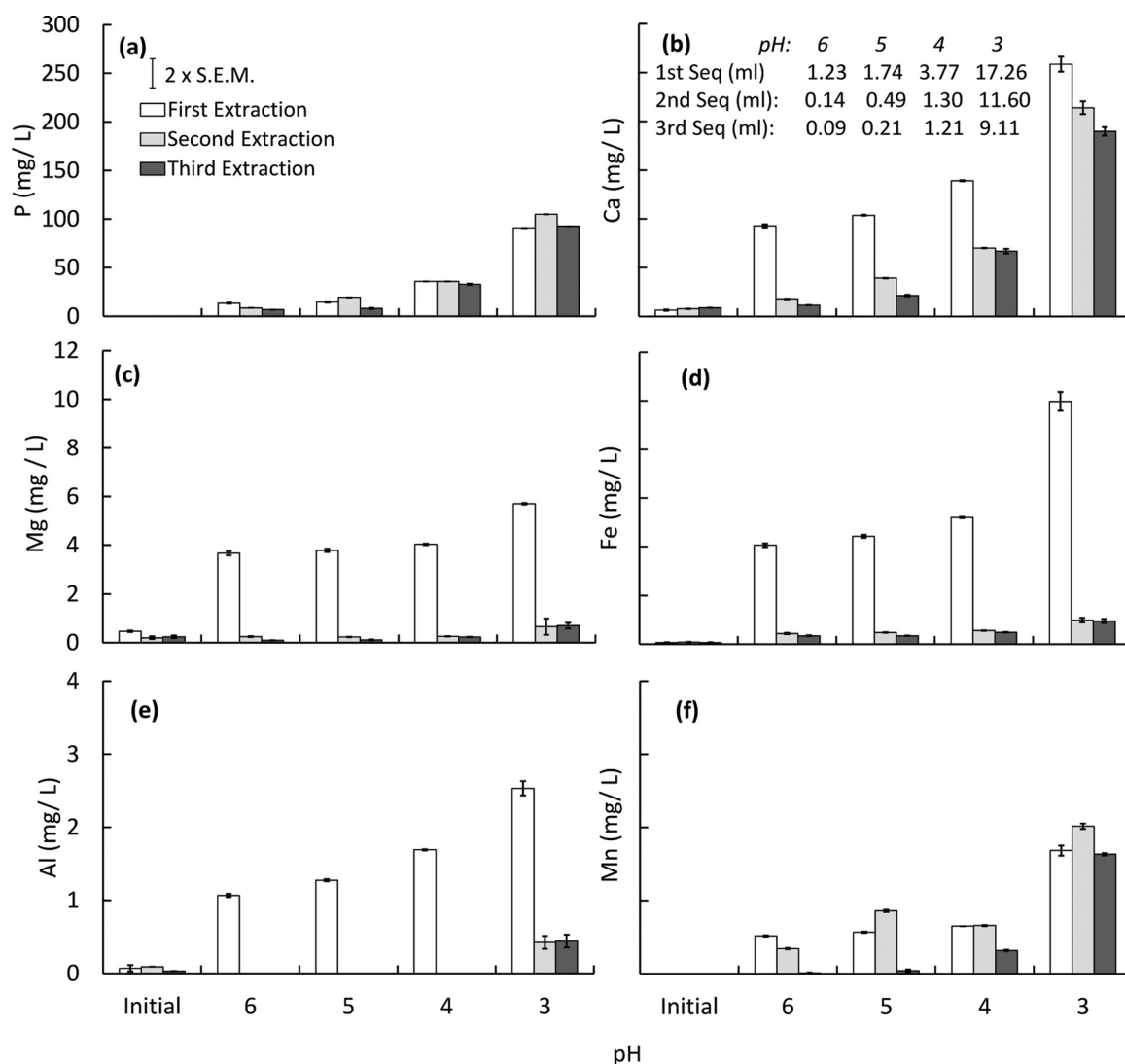


Fig. 2. Concentration of P (a), Ca (b), Mg (c), Fe (d), Al (e) and Mn (f) sequentially extracted from DPR by titrating against 0.1 M citric acid. Table in (b) shows volume of citric acid titrated to each pH end point.

the amount of P solubilised in the second and third oxalic acid extractions were the same, we speculate that if sequential extractions had been continued, nearly 100% of the P in the DPR could have been recovered, as has been observed when PR's were extracted with oxalic acid by Mendes et al. [20].

Solubilised Ca, Fe, Al, Mg, and Mn is described for pH 3 only since that is where the highest amount of P was solubilised. At pH 3, oxalic acid Ca had a concentration of between 112 – 144 mg Ca/ L for the three sequential extractions (Fig. 3b) which was about half the concentration of P in solution. The amount of Ca present in three sequential extractions of oxalic acid at pH 3 was 11.8% of the Ca amount in DPR (37.1%) [30]. The Ca:P molar ratio for the same three extractions ranged from 0.42 to 0.47. This shows that oxalic acid solubilised apatite P and Ca and was able to keep some of the Ca out of solution at the same level of effectiveness regardless of extraction sequence. The first extraction had higher concentrations of Mg, Fe, Al, and Mn, compared to subsequent extractions (Fig. 3c, d, e, and f). During the first oxalic acid extraction at pH 3, about 6.5, 19.5, 18.6, and 19.6%, of the total Fe, Al, Mg, and Mn was solubilised, respectively. This is likely from part contributions of gangue minerals in Dorowa PR which do not correlate with P dissolution. Both the second and third extractions solubilised less than 2.1% each of the total Fe and Al. Low levels of Fe and Al would be advantageous for soil application because of less risk of forming insoluble Fe and Al phosphates in soil. The Fe:P and Al:P molar ratio for each of the three extractions was less than 0.03.

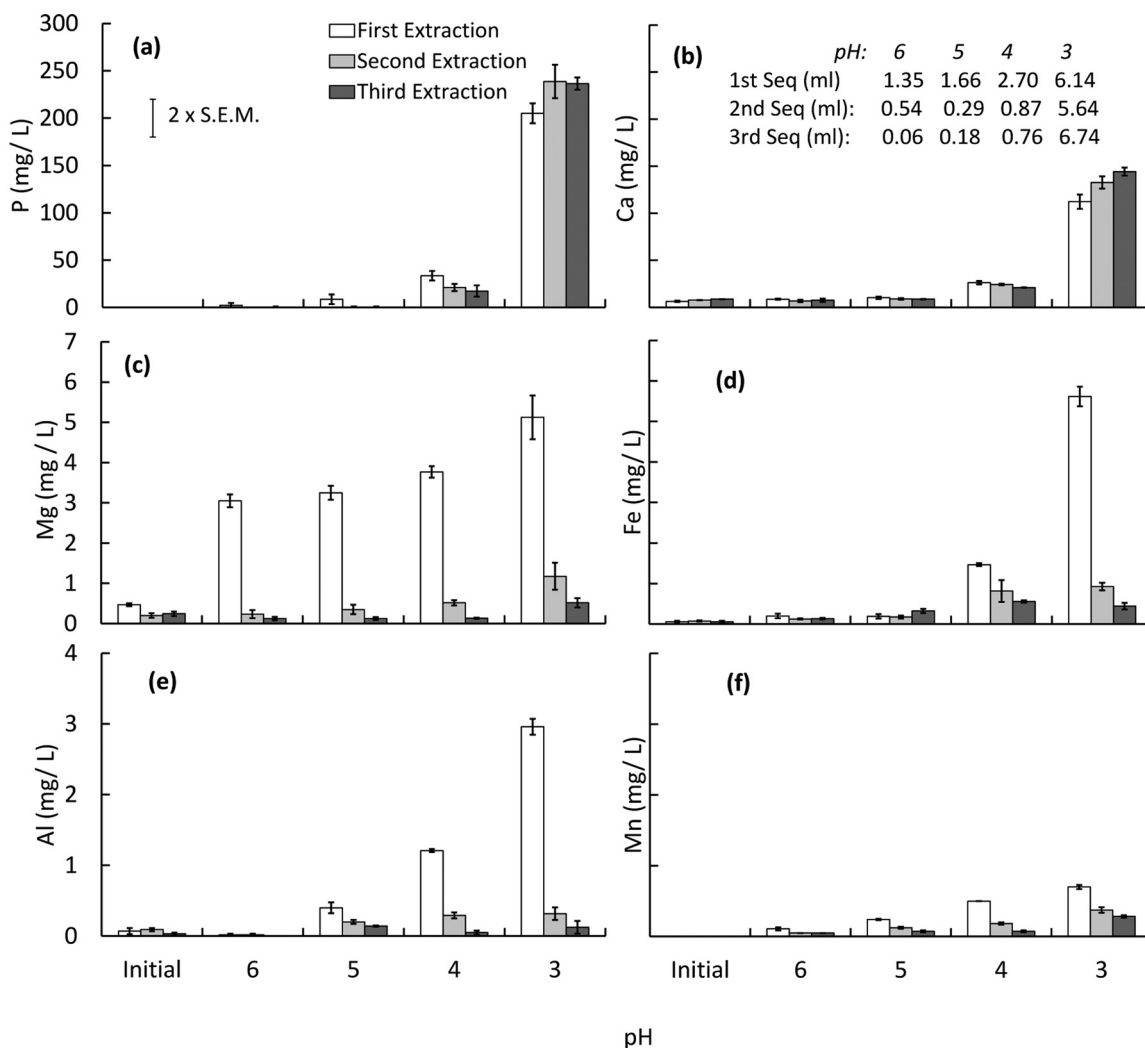


Fig. 3. Concentration of P (a), Ca (b), Mg (c), Fe (d), Al (e) and Mn (f) sequentially extracted from DPR by titrating against 0.1 M oxalic acid. Table in (b) shows volume of oxalic acid titrated to each pH end point.

Practicality of oxalic acid and citric acid sequential extractions

Hypothetically, a maize plant requires about 1 g of P per plant (45 kg P ha^{-1} ; [39], $45\,000 \text{ plants ha}^{-1}$). If plant recovery of applied P is about 33%, this means that 3 g of P/plant would need to be applied to the root zone. The oxalic acid titration mix, consisting of about 220 mg P/L, would require 13 L/plant of the mix which is about 20% of the water needed to grow a maize plant to physical maturity. It would be necessary to reduce the amount of water used in the leaching of DPR, so the initial water addition step could be omitted, and the concentration of oxalic acid increased to make volumes more practical. At 56 mL/0.5 g DPR and 3 oxalic acid extractions per 0.5 g DPR, a single maize plant would require 39 g of DPR and 1.6 L of 0.1 M oxalic acid (containing 13.5 g of pure oxalic acid). The general high cost of industrial oxalic acid ($\sim 800\text{€ /t}$) is four times that of sulphuric acid [13], and discourages the prospect of using oxalic acid. The mixture of organic acids in the pyrolysis liquid would be cheaper to produce and may provide significant protonation, chelation, and complexing processes, aiding the dissolution of P in the DPR. This provides the context for assessing the P-solubilisation power of aqueous phase pyrolysis liquid.

Selected organic acid composition and acidity of aqueous phase pyrolysis liquid

Collected crude pyrolysis condensate from the pyrolysis of maize stover was 35.6% of the initial feedstock mass, and the decanted aqueous phase pyrolysis liquid (1:4 crude liquid to water) had a pH of 2.94 and total acid number (TAN) of 25.7 mg KOH/g. The observed pH and TAN was in the range to that reported by other researchers (pH 3, TAN 20.1 – 30.1)

Table 1

Concentration of selected organic acids in aqueous phase pyrolysis liquid that was diluted at 1:4 (condensate/ water). Numbers after \pm are standard errors of means (SEM).

Organic acid	Concentration (moles/L)
Oxalic	0.038 ± 0.011
Tartaric	0
Malic	0.017 ± 0.005
Acetic	0.410 ± 0.022
Maleic	0.003 ± 0.0002
Citric	0
Succinic	0.099 ± 0.004

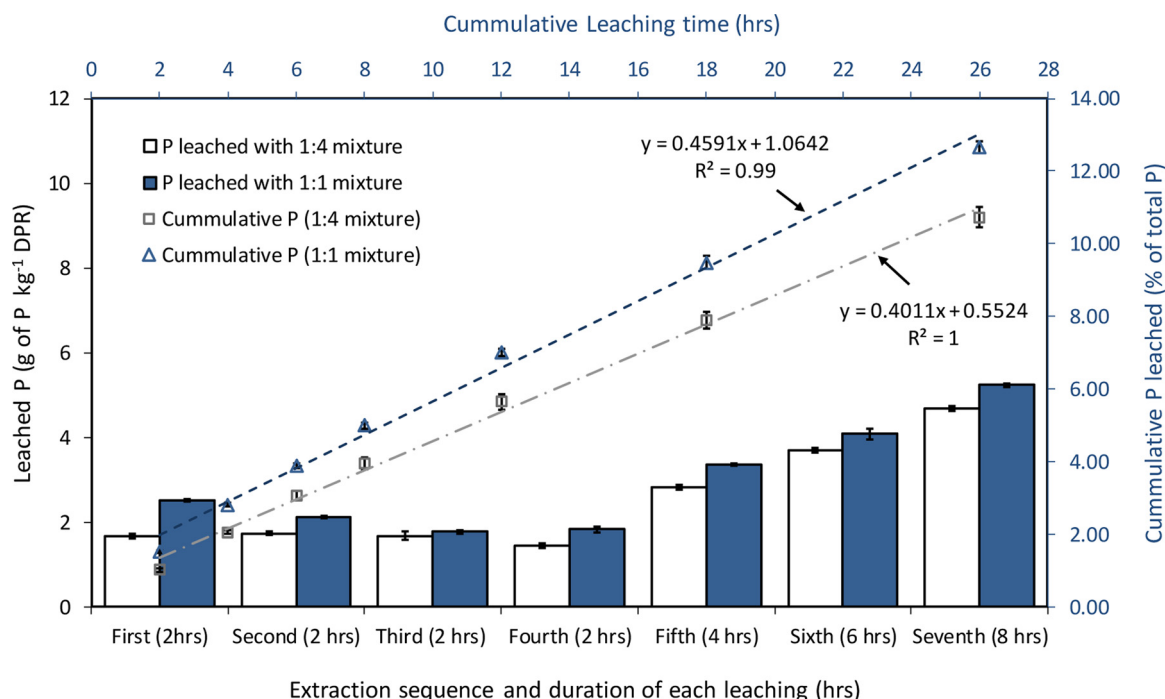


Fig. 4. Amount of P sequentially extracted from DPR using pyrolysis condensate mixed at 1:1 and 1:4 (condensate/ water) ratios. Error bars represent 2x standard errors of means ($n = 4$). Equations represent cumulative rate of leaching (%P/h).

for a crude pyrolysis condensate/ water mixture (1:4) obtained from switchgrass pyrolysis [40]. It should be noted that TAN can slightly overestimate total acid content because phenolic compounds are also neutralised with KOH [41].

An acetic acid concentration of 0.41 mol/ L was the highest of the seven organic acids analysed in the pyrolysis liquid (1:4 mixture) (Table 1). Other researchers report that acetic acid is usually the most dominant acid in pyrolysis condensate from fast pyrolysis or hydrothermal carbonisation of biomass [28]. Oh et al. [42] explains that acetic acid in pyrolysis condensate is derived from the breakdown of the hemicellulose component in the feedstock.

Citric and tartaric acids were not identified in the aqueous phase pyrolysis liquid, and oxalic acid concentrations were relatively low (0.04 M). The acetic acid concentration in the diluted pyrolysis condensate (1:4) was higher than the 0.1 M concentration of the laboratory-grade acid used in titrations while the concentration of oxalic acid was lower in the pyrolysis condensate. As a result, enhanced leaching with acetic acid in the condensate was expected.

Solubilised P and other selected elements after sequential leaching of DPR with aqueous phase pyrolysis liquid

The amount of P solubilised by the aqueous phase pyrolysis liquid at each leaching time/sequence was significantly different ($P < 0.001$). The concentration of P in pyrolysis liquid leachates ranged from 102 to 253 mg P/ L at each leaching stage for both the 1:1 and 1:4 pyrolysis liquid mixtures, representing about 0.87 to 3.17% of the total P solubilised from DPR after each stage (Fig. 4).

Compared to titrations with pure acids at pH 3, sequential leaching with aqueous phase pyrolysis liquid solubilised considerably less P while maintaining a pH of 3. There was a linear relationship ($R^2 > 0.99$) between the cumulative amount of P leached and the cumulative leaching time for both the pyrolysis liquid ratios. The aqueous phase pyrolysis liquid di-

Table 2Cation content and pH of pyrolysis liquid leachates after sequential leaching of DPR. Figures after \pm are standard errors of means (SEM), $n = 4$.

Leachate properties	Leaching time (hr)							Total (% of elemental content)
	2	4	6	8	12	18	26	
Leached with 1:1 aqueous phase pyrolysis liquid								
Mn (mg/L)	5.78 ± 0.20	0.63 ± 0.00	0.31 ± 0.00	0.31 ± 0.00	0.31 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	20.24
Al (mg/L)	8.36 ± 0.23	2.42 ± 0.27	1.64 ± 0.20	1.17 ± 0.15	1.02 ± 0.15	0.70 ± 0.20	0.16 ± 0.09	12.21
Fe (mg/L)	35.16 ± 0.92	9.45 ± 0.23	9.84 ± 0.37	5.00 ± 0.60	2.81 ± 0.26	2.58 ± 0.15	3.20 ± 0.35	9.18
Mg (mg/L)	28.13 ± 1.49	3.83 ± 0.15	1.88 ± 0.13	1.48 ± 0.08	0.78 ± 0.09	0.63 ± 0.00	0.70 ± 0.20	13.81
Ca (mg/L)	1416.56 ± 20.54	360.31 ± 9.11	303.20 ± 14.78	282.11 ± 2.36	263.75 ± 5.48	238.59 ± 1.52	204.30 ± 10.36	12.63
pH	3.39 ± 0.05	3.08 ± 0.01	3.03 ± 0.03	2.93 ± 0.03	2.99 ± 0.04	2.92 ± 0.01	3.03 ± 0.00	
Vol (mL)	5.01 ± 0.11	5.41 ± 0.10	5.64 ± 0.11	5.65 ± 0.12	11.83 ± 0.23	16.77 ± 0.77	19.41 ± 0.77	
Leached with 1:4 aqueous phase pyrolysis liquid								
Mn (mg/L)	5.23 ± 0.20	0.94 ± 0.13	0.31 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.31 ± 0.00	19.39
Al (mg/L)	3.67 ± 0.77	3.98 ± 0.41	2.58 ± 0.08	1.17 ± 0.08	0.94 ± 0.13	0.55 ± 0.08	0.47 ± 0.09	11.02
Fe (mg/L)	15.08 ± 1.19	10.23 ± 0.84	7.03 ± 0.30	3.67 ± 0.35	2.81 ± 0.34	1.80 ± 0.15	2.03 ± 0.39	5.89
Mg (mg/L)	29.30 ± 0.70	5.55 ± 0.23	2.19 ± 0.22	1.56 ± 0.00	1.02 ± 0.08	0.70 ± 0.08	0.70 ± 0.08	14.42
Ca(mg/L)	1242.42 ± 17.36	361.56 ± 16.48	289.61 ± 2.73	259.61 ± 5.16	249.84 ± 6.66	224.30 ± 4.61	194.30 ± 9.27	11.68
pH	3.84 ± 0.02	3.41 ± 0.13	3.19 ± 0.03	3.05 ± 0.04	3.17 ± 0.01	3.03 ± 0.01	3.14 ± 0.01	
Vol (mL)	4.62 ± 0.08	5.09 ± 0.14	5.37 ± 0.14	5.39 ± 0.12	11.24 ± 0.24	17.04 ± 0.37	23.26 ± 0.57	

luted at 1:1 leached about 18% more P than when a pyrolysis liquid mixture of 1:4 was used. Though statistically significant ($P < 0.001$), this cumulatively translated to only 2% more of the total P solubilised after 26 hrs (Fig. 4). This suggests that the effect of varying acid concentration (affecting H^+ supply) in the aqueous phase pyrolysis liquid extracts had a reduced effect on P dissolution. The low amount of P cumulatively leached over 26 h suggests that use of pyrolysis liquid to solubilise P from DPR may be ineffective. The low concentration of strong acid complexing agents such as oxalic and citric acids is likely the reason why P dissolution was low.

All leachates had low pH (2.99 – 3.84) with the highest pH recorded in the first 2 h of extraction (Table 2). A final pH of around 3 did not improve P dissolution compared to that observed during previous titrations with pure acids. The average cation content of pyrolysis liquid leachate run as blank during sequential leaching (Table S1) showed that the concentration of Ca was 9.9 and 17.2 mg/L for the 1:4 and 1:1 mixtures respectively. This Ca content in the pyrolytic liquid was already in the range of what other researchers report as equilibrium Ca concentrations obtained at pH 3 when igneous apatite is dissolved [43,44]. It is therefore likely that the cation chelating ability of citric and other organic acids in the pyrolysis liquid was already partially occupied by cations in the pyrolysis liquid thereby repressing its ability to extract P from apatite.

The highest concentration of Ca, Mg, Fe, and Mn were recorded after the first 2 h of leaching. An option to discard the first 2 h of leachate is therefore possible, to remove considerable quantities of Fe and Mn, which could react with P and make it unavailable upon soil addition. The concentration of Ca in the leachate collected in the first 2 h was at least 3.5x that of the succeeding leachates.

After 26 h of sequential leaching, at least 42, 12, 6, and 11% of the total content of Mg, Ca, Fe, and Al in DPR respectively, had been leached by both of the aqueous phase pyrolysis liquid/water mixtures used.

The Ca:P molar ratio of leachates at 2 h was > 4.3 for both pyrolysis liquids (Figure S2a). This indicated that considerable quantities of calcite were solubilised together with apatite in the first leaching [30]. Succeeding extractions had a Ca:P molar ratio that was around 1.5, a value that was less than that observed for dilute sulphuric and citric acids at pH 3, indicating relatively incongruent dissolution where P was preferentially released over Ca. This is likely because of Ca complexation reactions, albeit at a much lower degree than observed previously for oxalic acid titrations.

The succinic acid contained in the pyrolysis condensate is likely to have contributed a small percentage to Ca complexing reactions because it is a much weaker acid than oxalic acid (pK_{a1} 4.61 and 1.25 for succinic and oxalic acids, respectively).

Initially higher Fe:P molar ratios at 2 h suggest significant dissolution from non-P associated Fe probably from gangue minerals in the DPR sample. However, subsequent leachates from 4 h onwards had Fe:P ratios that were below the 0.059 value found in DPR (Figure S2b) but similar to when DPR was titrated with pure organic acids at pH 3 (Figure S1b).

Leachates from 2 h to 6 h had Al:P molar ratios that were higher than the 0.0097 value found in DPR (Figure S2c) indicating either some dissolution of non-P bound Al from gangue minerals, and/or preferential dissolution of Al over P from the apatite lattice. However, after 6 h the Al:P ratio of leachates reduced to either the same, or below that of the Al:P molar ratio in the DPR, as more P was solubilised with less Al solubilised. This was not due to exhaustion of the Al content in the DPR, as less than 14% of the total Al content was recovered after 26 hrs of sequential leaching using both pyrolysis liquid leaching ratios (Table 2).

Conclusions

Oxalic acid was more effective at solubilising total P from DPR, providing twice as much P in solution compared to citric acid at the same molar ratios, while maintaining the lowest Ca in solution. While three sequential extractions at pH 3 using

oxalic and citric acids were able to solubilise a total of 46 and 22% P respectively, sequential leaching extractions with aqueous phase pyrolysis liquid over 26 h solubilised less than 14% of the total P. Therefore, the use of pyrolysis condensate was relatively ineffective at solubilising total P from DPR. Leaching P from poorly soluble PRs remains an impractical pathway to plant available P, while the costs of biogenic organic acids remain high. Further studies are recommended to reduce these costs either from the production of higher oxalic acid concentrations in pyrolysis liquids, or low-cost processes that can be employed to produce oxalic acid in rural communities. Further research on improving the dissolution potential of pyrolysis liquid by removing cations in the liquid before leaching is also recommended.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful for funding received from New Zealand Developmental Scholarships for the first author's studies. Much appreciation is also expressed for technical assistance given by Massey University staff Pereira R. Calvelo, Jeya Jayakumar, Ian Furkert and Bob Toes.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.sciaf.2022.e01098](https://doi.org/10.1016/j.sciaf.2022.e01098).

References

- [1] S. Broom-Fendley, P.R. Siegfried, F. Wall, M. O'Neill, R.A. Brooker, E.K. Fallon, J.R. Pickles, D.A. Banks, The origin and composition of carbonatite-derived carbonate-bearing fluorapatite deposits, *Miner. Deposita* 56 (5) (2020) 863–884, doi:[10.1007/s00126-020-01010-7](https://doi.org/10.1007/s00126-020-01010-7).
- [2] N.S. Bolan, M. Hedley, Dissolution of phosphate rocks in soils. 2. Effect of pH on the dissolution and plant availability of phosphate rock in soil with pH dependent charge, *Fertil. Res.* 24 (1990) 125–134, doi:[10.1007/BF01073580](https://doi.org/10.1007/BF01073580).
- [3] S. Nakamura, S. Saidou, A. Barro, M. Fukuda, T. Kanda, D. Jonas, F. Nagumo, Kodjari phosphate rock for rain-fed lowland rice production in the Sudan Savanna, Burkina Faso, *Trop. Agric. Dev.* 64 (2) (2020) 97–106, doi:[10.11248/jsta.64.97](https://doi.org/10.11248/jsta.64.97).
- [4] A. Tumbure, P. Bishop, M.J. Hedley, M.R. Bretherton, Increasing phosphorus solubility by sintering igneous Dorowa phosphate rock with recycled glass, *J. Therm. Anal. Calorim.* 145 (6) (2021) 3019–3030, doi:[10.1007/s10973-020-10078-2](https://doi.org/10.1007/s10973-020-10078-2).
- [5] T.S. do Carmo, F.S. Moreira, B.V. Cabral, R.C.C. Dantas, M.M. de Resende, V.L. Cardoso, E.J. Ribeiro, Phosphorus recovery from phosphate rocks using phosphate-solubilizing bacteria, *Geomicrobiol. J.* 36 (3) (2019) 195–203, doi:[10.1080/01490451.2018.1534901](https://doi.org/10.1080/01490451.2018.1534901).
- [6] P. Magallon-Servin, H. Antoun, S. Taktek, Y. Bashan, L. de-Bashan, The maize mycorrhizosphere as a source for isolation of arbuscular mycorrhizae-compatible phosphate rock-solubilizing bacteria, *Plant Soil* (2019), doi:[10.1007/s11104-019-04226-3](https://doi.org/10.1007/s11104-019-04226-3).
- [7] Q. Wang, C. Xiao, B. Feng, R. Chi, Phosphate rock solubilization and the potential for lead immobilization by a phosphate-solubilizing bacterium (*Pseudomonas* sp.), *J. Environ. Sci. Health Part A* 55 (4) (2020) 411–420, doi:[10.1080/10934529.2019.1704134](https://doi.org/10.1080/10934529.2019.1704134).
- [8] L.T. Mupondi, P.N.S. Mkeni, P. Muchaonyerwa, H.A. Mupambwa, Vermicomposting manure-paper mixture with igneous rock phosphate enhances biodegradation, phosphorus bioavailability and reduces heavy metal concentrations, *Heliyon* 4 (8) (2018) 1–20, <https://doi.org/10.1016/j.heliyon.2018.e00749>.
- [9] E. Mwangi, C. Ngamau, J. Wesonga, E. Karanja, M. Musyoka, F. Matheri, K. Fiaboe, D. Bautze, N. Adamtey, Managing phosphate rock to improve nutrient uptake, phosphorus use efficiency, and carrot yields, *J. Soil Sci. Plant Nutr.* 20 (2020) 1350–1365, doi:[10.1007/s42729-020-00217-x](https://doi.org/10.1007/s42729-020-00217-x).
- [10] P. Poblete-Grant, P. Biron, T. Bariac, P. Cartes, M.d.L.L. Mora, C. Rumpel, Synergistic and antagonistic effects of poultry manure and phosphate rock on soil P availability, ryegrass production, and P uptake, *Agronomy* 9 (4) (2019) 191, doi:[10.3390/agronomy9040191](https://doi.org/10.3390/agronomy9040191).
- [11] H. Cicek, G.S. Bhullar, L.S. Mandloi, C. Andres, A.S. Riar, Partial acidulation of rock phosphate for increased productivity in organic and smallholder farming, *Sustainability* 12 (2) (2020), doi:[10.3390/su12020607](https://doi.org/10.3390/su12020607).
- [12] S.K. Jha, Z. Ahmad, D.E. Crowley, Fuzzy-genetic approaches for estimation of microbial rock phosphate solubilization in sandy clay loam textured soil, *Comput. Electron. Agric.* 150 (2018) 125–133, doi:[10.1016/j.compag.2018.04.014](https://doi.org/10.1016/j.compag.2018.04.014).
- [13] A.M.J. Kootstra, D.W.F. Brilman, S.R.A. Kersten, Dissolution of phosphate from pig manure ash using organic and mineral acids, *Waste Manage. (Oxford)* 88 (2019) 141–146, doi:[10.1016/j.wasman.2019.03.038](https://doi.org/10.1016/j.wasman.2019.03.038).
- [14] T. Roy, D.R. Biswas, S.C. Datta, A. Sarkar, Phosphorus release from rock phosphate as influenced by organic acid loaded nanoclay polymer composites in an Alfisol, *Proc. Natl. Acad. Sci. India Sect. B* 88 (1) (2016) 121–132, doi:[10.1007/s40011-016-0739-6](https://doi.org/10.1007/s40011-016-0739-6).
- [15] M.M. Aria, A. Lakzian, G.H. Haghnia, A.R. Berenji, H. Besharati, A. Fotovat, Effect of Thiobacillus, sulfur, and vermicompost on the water-soluble phosphorus of hard rock phosphate, *Bioresour. Technol.* 101 (2) (2010) 551–554, doi:[10.1016/j.biortech.2009.07.093](https://doi.org/10.1016/j.biortech.2009.07.093).
- [16] H. Qiao, X.R. Sun, X.Q. Wu, G.E. Li, Z. Wang, D.W. Li, The phosphate-solubilizing ability of *Penicillium guanacastense* and its effects on the growth of *Pinus massoniana* in phosphate-limiting conditions, *Biol. Open* 8 (11) (2019) 1–10, doi:[10.1242/bio.046797](https://doi.org/10.1242/bio.046797).
- [17] X. Li, T. Lei, Z. Wang, X. Li, M. Wen, M. Yang, G. Chen, X. He, H. Xu, Q. Guan, Z. Li, Catalytic pyrolysis of corn straw with magnetic solid acid catalyst to prepare levulinic acid by response surface methodology, *Ind. Crops Prod.* 116 (2018) 73–80, doi:[10.1016/j.indcrop.2018.02.049](https://doi.org/10.1016/j.indcrop.2018.02.049).
- [18] Y. Thepparat, A. Chandumpai, W. Leelasuphakul, N. Laemsak, Pyrolytic acids from carbonisation of wood and bamboo: their components and antifungal activity, *J. Trop. For. Sci.* 27 (4) (2015) 517–526, <http://www.jstor.org/stable/43596228>.
- [19] A. Kpombekou, M.A. Tabatabaie, Effect of organic acids on release of phosphorus from phosphorus rocks, *Soil Sci.* 158 (6) (1994) 442–453, doi:[10.1097/00010694-199415860-00006](https://doi.org/10.1097/00010694-199415860-00006).
- [20] G.O. Mendes, H.M. Murta, R.V. Valadares, W.B. Silveira, I.R. Silva, M.D. Costa, Oxalic acid is more efficient than sulfuric acid for rock phosphate solubilization, *Miner. Eng.* 155 (2020) 1–7, doi:[10.1016/j.mineng.2020.106458](https://doi.org/10.1016/j.mineng.2020.106458).
- [21] V. Yadav, T. Karak, S. Singh, A.K. Singh, P. Khare, Benefits of biochar over other organic amendments: responses for plant productivity (*Pelargonium graveolens* L.) and nitrogen and phosphorus losses, *Ind. Crops Prod.* 131 (2019) 96–105, doi:[10.1016/j.indcrop.2019.01.045](https://doi.org/10.1016/j.indcrop.2019.01.045).
- [22] J.A. Libra, K.S. Ro, C. Kammann, A. Funke, N.D. Berge, Y. Neubauer, M.-M. Titirici, C. Fühner, O. Bens, J. Kern, K.-H. Emmerich, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, *Biofuels* 2 (1) (2014) 71–106, doi:[10.4155/bfs.10.81](https://doi.org/10.4155/bfs.10.81).

- [23] A.B. Fuertes, M.C. Arbestain, M. Sevilla, J.A. Maciá-Agulló, S. Fiol, R. López, R.J. Smernik, W.P. Aitkenhead, F. Arce, F. Macías, Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover, *Soil Res.* 48 (7) (2010) 618–626, doi:[10.1071/sr10010](https://doi.org/10.1071/sr10010).
- [24] H.R.L. Benzon, S.C. Lee, Pyrolytic acids enhance phytoremediation of heavy metal-contaminated soils using mustard, *Commun. Soil Sci. Plant Anal.* 48 (17) (2017) 2061–2073, doi:[10.1080/00103624.2017.1406102](https://doi.org/10.1080/00103624.2017.1406102).
- [25] X. Luo, Z. Wang, K. Meki, X. Wang, B. Liu, H. Zheng, X. You, F. Li, Effect of co-application of wood vinegar and biochar on seed germination and seedling growth, *J. Soils Sediments* (2019), doi:[10.1007/s11368-019-02365-9](https://doi.org/10.1007/s11368-019-02365-9).
- [26] M.F. Demirbas, M. Balat, Recent advances on the production and utilization trends of bio-fuels: a global perspective, *Energy Convers. Manage.* 47 (15–16) (2006) 2371–2381, doi:[10.1016/j.enconman.2005.11.014](https://doi.org/10.1016/j.enconman.2005.11.014).
- [27] N.T. Machado, D.A.R. de Castro, M.C. Santos, M.E. Araújo, U. Lüder, L. Herklotz, M. Werner, J. Mumme, T. Hoffmann, Process analysis of hydrothermal carbonization of corn Stover with subcritical H₂O, *J. Supercrit. Fluids* 136 (2018) 110–122, doi:[10.1016/j.supflu.2018.01.012](https://doi.org/10.1016/j.supflu.2018.01.012).
- [28] R. Keskinen, J. Hyväluoma, H. Wikberg, A. Källi, T. Salo, K. Rasa, Possibilities of using liquids from slow pyrolysis and hydrothermal carbonization in acidification of animal slurry, *Waste Biomass Valorization* 9 (8) (2017) 1429–1433, doi:[10.1007/s12649-017-9910-4](https://doi.org/10.1007/s12649-017-9910-4).
- [29] A. Tumbure, P. Bishop, M. Bretherton, M. Hedley, Co-pyrolysis of maize stover and igneous phosphate rock to produce potential biochar-based phosphate fertilizer with improved carbon retention and liming value, *ACS Sustain. Chem. Eng.* 8 (10) (2020) 4178–4184, doi:[10.1021/acssuschemeng.9b06958](https://doi.org/10.1021/acssuschemeng.9b06958).
- [30] A. Tumbure, M.R. Bretherton, P. Bishop, M.J. Hedley, Updated characterization of Dorowa phosphate rock mined in Zimbabwe, *Nat. Resour. Res.* 29 (3) (2019) 1561–1570, doi:[10.1007/s11053-019-09567-5](https://doi.org/10.1007/s11053-019-09567-5).
- [31] Fertmark. (2016). Fertmark code of practice for the sale of fertiliser in New Zealand. The fermark code of practice. Retrieved 4 Feb 2017, from <https://fertqual.co.nz/?ddownload=747>
- [32] L.K.E. Park, J. Liu, S. Yiacoumi, A.P. Borole, C. Tsouris, Contribution of acidic components to the total acid number (TAN) of bio-oil, *Fuel* 200 (2017) 171–181, doi:[10.1016/j.fuel.2017.03.022](https://doi.org/10.1016/j.fuel.2017.03.022).
- [33] G.R. Cawthray, An improved reversed-phase liquid chromatographic method for the analysis of low-molecular mass organic acids in plant root exudates, *J. Chromatogr. A* 1011 (1–2) (2003) 233–240, doi:[10.1016/S0021-9673\(03\)01129-4](https://doi.org/10.1016/S0021-9673(03)01129-4).
- [34] S. Liang, H. Chen, X. Zeng, Z. Li, W. Yu, K. Xiao, J. Hu, H. Hou, B. Liu, S. Tao, J. Yang, A comparison between sulfuric acid and oxalic acid leaching with subsequent purification and precipitation for phosphorus recovery from sewage sludge incineration ash, *Water Res.* 159 (2019) 242–251, doi:[10.1016/j.watres.2019.05.022](https://doi.org/10.1016/j.watres.2019.05.022).
- [35] C.I. Sagoe, T. Ando, K. Kouno, T. Nagaoka, Relative importance of protons and solution calcium concentration in phosphate rock dissolution by organic acids, *Soil Sci. Plant Nutr.* 44 (4) (1998) 617–625, doi:[10.1080/00380768.1998.10414485](https://doi.org/10.1080/00380768.1998.10414485).
- [36] B.B. Basak, Phosphorus release by low molecular weight organic acids from low-grade indian rock phosphate, *Waste Biomass Valorization* 10 (11) (2018) 3225–3233, doi:[10.1007/s12649-018-0361-3](https://doi.org/10.1007/s12649-018-0361-3).
- [37] D.E. Lazo, L.G. Dyer, R.D. Alorro, Silicate, phosphate and carbonate mineral dissolution behaviour in the presence of organic acids: a review, *Miner. Eng.* 100 (2017) 115–123, doi:[10.1016/j.mineng.2016.10.013](https://doi.org/10.1016/j.mineng.2016.10.013).
- [38] D. Chatterjee, S.C. Datta, K.M. Manjaiah, Effect of citric acid treatment on release of phosphorus, aluminium and iron from three dissimilar soils of India, *Arch. Agron. Soil Sci.* 61 (1) (2015) 105–117, doi:[10.1080/03650340.2014.919449](https://doi.org/10.1080/03650340.2014.919449).
- [39] M. Camps-Arbestain, J.E. Amonette, B. Singh, T. Wang, H.P. Schmidt, A biochar classification system and associated test methods, in: J. Lehmann, S.D. Joseph (Eds.), *Biochar for Environmental Management*, 2 ed., Routledge, 2015, pp. 165–193.
- [40] S. Ren, X.P. Ye, Stability of crude bio-oil and its water-extracted fractions, *J. Anal. Appl. Pyrolysis* 132 (2018) 151–162, doi:[10.1016/j.jaap.2018.03.005](https://doi.org/10.1016/j.jaap.2018.03.005).
- [41] A. Oasmaa, D. Meier, Norms and standards for fast pyrolysis liquids, *J. Anal. Appl. Pyrolysis* 73 (2) (2005) 323–334, doi:[10.1016/j.jaap.2005.03.003](https://doi.org/10.1016/j.jaap.2005.03.003).
- [42] S.J. Oh, G.G. Choi, J.S. Kim, Production of acetic acid-rich bio-oils from the fast pyrolysis of biomass and synthesis of calcium magnesium acetate deicer, *J. Anal. Appl. Pyrolysis* 124 (2017) 122–129, doi:[10.1016/j.jaap.2017.01.032](https://doi.org/10.1016/j.jaap.2017.01.032).
- [43] M.W. Guidry, F.T. Mackenzie, Experimental study of igneous and sedimentary apatite dissolution, *Geochim. Cosmochim. Acta* 67 (16) (2003) 2949–2963, doi:[10.1016/S0016-7037\(03\)00265-5](https://doi.org/10.1016/S0016-7037(03)00265-5).
- [44] N. Harouiya, C. Chairat, S.J. Köhler, R. Gout, E.H. Oelkers, The dissolution kinetics and apparent solubility of natural apatite in closed reactors at temperatures from 5 to 50°C and pH from 1 to 6, *Chem. Geol.* 244 (3–4) (2007) 554–568, doi:[10.1016/j.chemgeo.2007.07.011](https://doi.org/10.1016/j.chemgeo.2007.07.011).