An Investigation of the Role of Organic Amendments on the Availability of Phosphorus in an Acidic Soil

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Abstract

The recovery of P from organic waste streams (known as organic amendments, OA) is becoming increasingly popular. Besides a source of P, OA have also been reported to increase soil P availability and reduce P adsorption in acidic soil. The main mechanism involves the reduction in the soil P adsorption sites (especially Al and Fe) by the organic anion producing compounds of the OA. Organic anions form organometallic complexes in the soil to reduce P adsorption. The potential representative organic anion producing compounds of the OA are phenolic and carbonyl compounds. The phenolic and carbonyl compounds usually represent the aromatic (such as benzoic, hydroxybenzoic, protocatechuic acids etc) and aliphatic (such as oxalic, malic, citric etc) organic acids, respectively. This study aimed to investigate if these signature phenolics and carbonyl compounds of the OA can be used to predict their role in soil P availability for future prescriptive applications.

An acidic soil (Red Chromosol) from the Rutherglen, northeast of Victoria, Australia was collected and waste from two different streams namely food waste and biosolid and their three different processed forms (untreated or raw, biochar and compost) were utilized as sources of OA in this study. Nuclear magnetic resonance (NMR) spectroscopy was utilized to identify forms of C (solid-state ^{13}C NMR) and P compounds (solution-state ^{31}P NMR) in the OA. The effect of OA on soil P availability was studied in a 110-day laboratory incubation study. Further, some selected representative compounds of phenolic and carbonyl C of OA (aromatic and aliphatic organic acids) were tested against soil P availability in another 110-day laboratory incubation experiment. Finally, a plant bioassay experiment with Triticale (genus *Triticosecale*) was conducted to understand the effect of both OA and organic acid on soil P availability and plant P uptake with or without the addition of external P.

Results from incubation of OA with soil showed an increase in soil P availability (Olsen P) and a decrease in soil P buffering capacity, (PBC). An additional increase in soil Olsen P was observed above the total amount of Olsen P from OA that was added. It might imply that this additive increase of the soil Olsen P was due to the substitution of previously fixed P by the action of organic anions (coming from the dissociation of phenolic and carbonyl compounds) and formation of the stable organometallic complexes. This was further supported by a strong and positive correlation between the ∆Olsen P (difference between observed and expected Olsen P) and phenolic and carbonyl C content of the OA. The phenolic and carbonyl C content of the OA also showed a significant correlation with the decrease of soil PBC (∆PBC, the difference between treatment and control). In both correlation studies, the ratio of phenolic to carbonyl C compounds of OA showed a strong correlation with soil P availability compared to their total abundance. The contrasting nature of phenolic and carbonyl compounds was speculated as to the reason why there was a high correlation between soil P availability and the ratio of phenolic to carbonyl C content of OA. The OA with a nearly equal abundance of phenolic to carbonyl C content showed a maximum increase in soil P availability. Therefore, it was concluded that the ratio of phenolic and carbonyl C content of OA could be used to predict P availability in acidic soil.

In the next study, some naturally occurring aromatic organic acids (representative of the phenolic compounds) and aliphatic organic acids (representative of the carbonyl compounds) were added either individually or in combination (at 1:1 ratio of aliphatic and aromatic organic acids). The experimental results suggested that aliphatic organic acids were more effective in increasing soil P availability and decreasing soil PBC compared to aromatic organic acids. However, the effect of aliphatic organic acids on increasing soil P availability was prolonged when applied in combination with aromatic organic acids at 1:1 ratio. Therefore, this study concluded that the effect of an OA can be predicted based on their phenolic and carbonyl C content.

Finally, the results from the plant bioassay experiment showed that the addition of OA increased the soil P availability irrespective of addition of external P to the soil. As hypothesized in the previous study, this increase in soil P availability after OA addition was expected to show a strong correlation with the ratio of phenolic to carbonyl C content of the OA. The correlation study between the soil P availability and the ratio of phenolic to carbonyl C content of the OA showed a moderate to weak correlation. The differences in those studies (laboratory incubation vs pot) were speculated as to the reason for obtaining this moderate to week correlation between the soil P availability and ratio of phenolic to carbonyl C content of the OA. In the plant bioassay experiment, OA and P were added simultaneously to the soil. Therefore, a competition between organic anions (which was coming from dissociation of organic acid compounds of OA) and P and was expected to increase P availability in the soil by reducing P adsorption. However, the preferential sorption of P by Al and Fe compared to organic anions was speculated as the main reason for observed moderate correlation. The phenolic and carbonyl C content of OA would correlate strongly with the soil P availability if OA were added first (which might reduce P sorption by forming organometallic complexes) and then P to the soil as also observed in previous study. Therefore, it was concluded that the phenolic and carbonyl C content of the OA would predict soil P availability better if OA was first added (which would form organometallic complexes) and then P added to the soil rather than adding both simultaneously.

The addition of OA significantly increased the plant P uptake and showed a positive correlation with soil Olsen P. There it was concluded that soil Olsen P was a good indicator of plant P availability.

In the plant bioassay experiment, organic acid treatments showed no significant effect on soil P availability and plant P uptake compared to the control. This might be due to the addition of organic acids at 10 times lower concentration in this experiment compared to the previous incubation experiment.

In conclusion, this thesis showed that the ratio of the phenolic to carbonyl C content of the organic amendments could be used to predict the role of organic amendments on increasing soil P availability. The availability of fertilizer P could also be predicted by phenolic and carbonyl C content, if OA added first and then P added to the soil compared to their simultaneous addition. The OA with a nearly equal abundance of phenolic and carbonyl C content would have a maximum effect on increasing soil P availability. This knowledge would be beneficial for farmers, agricultural landholders and especially OA producers to assess the impact of their organic waste products on soil P availability in the quickest possible time based on the abundance of the signature C compounds (phenolic and carbonyl).

Declarations

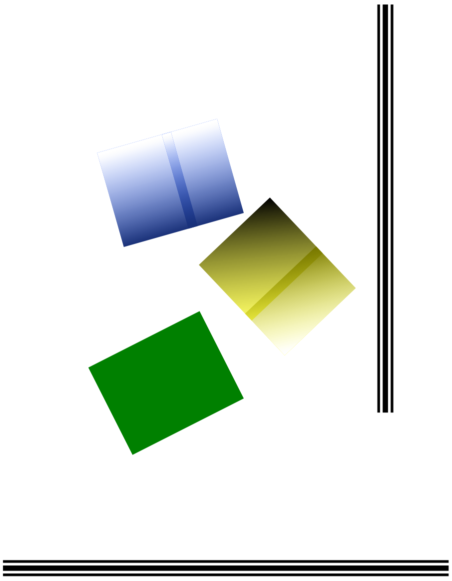
This is to certify that:

I. This thesis comprises only my original work.

II. All other materials used have been acknowledged.

III. This thesis contains less than 80,000 words, exclusive of tables, illustrations, bibliography and appendices.

Md. Shahinur Rahman
Date: 11.06.2020



I dedicate this
thesis to
My
Beloved Parents
and
All the hard
working Farmers
around the world

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Sincerely yours,
Md. Shahinur Rahman

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Chapter 1: Introduction

1.1 Background

Concomitant with growth in global population there is a greater generation of waste, which includes both organic and inorganic sources. Cities in both the developed and the developing world are facing great problems in managing these wastes. A recent study by Guerrero et al. (2013) illustrated the challenges faced by 22 developing countries in regards to solid waste management which included place for dumping of waste and lack of recycling facilities, and the off-site impacts such as greenhouse gas emissions and eutrophication.

In general, inorganic wastes are convenient to recycle and reuse, whereas the organic waste (such as food waste and biosolid) mainly goes to landfill and partially to recycling through composting, biochemical materials production (bioplastic, biopolymers) (Mirabella et al., 2014) and energy recovery (biofuel, biogas) (Pham et al., 2015, Guo et al., 2014, Ezeji et al., 2007). Of the total food waste generated in Australia in 2016-17, about 76% went to landfills and only 18% was recycled (Pickin et al., 2018). About 50-60% of biosolid generated from the USA in 1999 were disposed of via land dumping (USEPA and Response, 1999).

There has been an increasing amount of interest in the reuse of organic waste in agriculture as a source of nutrients (N, P, K etc), with the associated benefits of increased microbial activity, greater water infiltration and storage, and enhanced nutrient cycling. Around 40% of the produced dry solids applied to agricultural land in the European Union (Roig et al., 2012). In Australia, about 83% of the generated biosolid were recycled by direct land application in agriculture or used in the production of compost products (Pickin et al., 2018).

Furthermore, a move toward sustainable agricultural production systems requires closing the nutrient loop, farm to cities and return to farm. Next to nitrogen, phosphorus (P) is the most limiting plant nutrient and its supply is reliant on a finite source of phosphate rock (PR), with some predictions of shortages within the next few hundred years (Van Kauwenbergh, 2010, Smit et al., 2009). Besides, the plant availability of P in soil is generally very low with only about 5-30% of the applied P fertilizer taken up by the plants in the first year after application depending on soil properties (pH, cation concentration, phosphate buffering capacity) (Price, 2006, Glendinning, 2000). This P becomes unavailable to the plant by the precipitation with oxides and hydroxides of cations (Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}) in soil solution (also known as P adsorption/fixation) (Juo and Franzluebbers, 2003, White, 1981). A step-change in phosphorus use efficiency is required to extend the life of these limited resources.

In addition to the supply of P, processed organic waste (popularly known as organic amendments, OA) addition to soil has been reported to increase P availability both by releasing native soil fixed P (Siddique and Robinson, 2004) and by decreasing the sorption of added P (Ch'ng et al., 2017, Agegnehu et al., 2016, Zhai et al., 2015, Slavich et al., 2013, Opala et al., 2012, Gaskin et al., 2010, Elias et al., 2009, Halajnia et al., 2009). The substitution and complexation reactions were reported as the key mechanism for increasing P availability in soil through OA addition. The organic acid-producing compounds (phenolic and carbonyl) of OA have been reported as main compounds to dissociate into the organic anions and took part in those substitution and complexation reactions to increase soil P availability (Hu et al., 2005b, Hue, 1991, Violante et al., 1991, Hue et al., 1986). Organic acids can be produced during the decomposition of OA (Jones et al., 2003) or through the direct addition of organic acid-producing compounds from OA.

There are many methods for processing organic waste to an organic amendment before agricultural application including dehydration, incineration, aerobic and anaerobic digestion, composting, pyrolysis (production procedure of biochar) (EPA, 1999). Composting is an ageold process that can reduce pathogens and produce a chemically mature product. Pyrolysis, on the other hand, requires energy input and a high level of engineering to produce an optimal product with the recovery of useful byproducts. Research has shown that organic amendments are a complex mixture of carbon compounds in which their abundance is dependent on the processing method (Eldridge et al., 2013, Spaccini et al., 2012, Albrecht et al., 2008, Baldock and Smernik, 2002).

Many studies have shown that soil P availability changes with the addition of different types of OA (Ch'ng et al., 2017, Agegnehu et al., 2016, Zhai et al., 2015, Slavich et al., 2013, Opala et al., 2012, Gaskin et al., 2010, Elias et al., 2009, Halajnia et al., 2009). This change is due to the P content (both inorganic and organic) or C content (phenolic and carbonyl) added from OA. It is important to understand which mechanism is dominant in OA and specifically how this alters soil P availability.

It is common to test the effectiveness of OA systematically through laboratory incubation, pot/greenhouse and field experiments. These traditional approaches are expensive, time-consuming and laborious. It is estimated that compost, biochar, dehydrated product, manures of plant and animal originated OA are marketed worldwide, with many new ‘formulations’ entering the market every year and in many cases their efficacy is unknown. Although highly technical, the C and P signature of an OA could be used to screen organic amendments that may be suitable for varying environmental situations.

Therefore, this study proposes to identify the P and C compounds of OA created through stepwise processing (oven drying vs composting vs pyrolysis) of two main forms of organic waste (food and biosolid). These materials will then be evaluated through incubation experiments to determine their impact on soil phosphorus availability and fixation. A further study will determine the effect of OA and organic acids on soil P availability and plant growth.

1.2 Experimental approaches to this study

A meta-analysis was initially carried out using 473 observations from 40 research articles to determine the types of amendments that had a measurable effect on P availability. This study included food waste and biosolid as two different sources of organic amendments and their three different processing forms; oven-dried (raw), pyrolysed (biochar) and compost. Signatures of the C and P compounds for all the amendments were obtained using solid-state ^{13}C NMR (Nuclear Magnetic Resonance) and solution-state ^{31}P NMR spectroscopy along with some chemical characterization.

The effect of organic amendments on P availability was evaluated in a laboratory incubation study with acidic soil. An acidic soil was selected because around 50% of the world's agricultural lands are acidic (Von Uexküll and Mutert, 1995) and many of these lands exist in developing countries. The same soil was used to evaluate the effect of common organic acids on P availability. The final experiment involved a plant bioassay study, to determine if the chemical signature of OA was indicative of potential plant P uptake.

A number of smaller tests were carried out to test the methodologies and to determine appropriate rates of organic amendments and organic acids to be added in incubation and bioassay studies.

1.3 Organization of this thesis

This thesis contains eight chapters, including an introduction, literature review, meta-analysis and four experimental chapters and one summary and conclusion chapter and four appendices. Chapter 1 is the introduction which includes background, approaches of this study, organization of thesis and significance of this study. Chapter 2 is a comprehensive literature review that leads to the identification of the research gaps, research questions, aims and hypothesis of this study. Chapter 3 is the meta-analysis which demonstrates the effect of OA on soil P availability. Chapter 4 includes characterization (both NMR and chemical) of the organic amendments. Chapter 5 is an incubation experiment with soil and OA and other associated chemical analysis. In chapter 5 the P availability results were correlated with the signature C compounds of the OA to determine their relation with soil P availability. Chapter 6 is the follow-up work from chapter 5 which includes an incubation experiment with the soil and signature C compounds (original compounds) against soil P availability. Chapter 7 is a plant bioassay experiment where all the organic amendments and selected original organic acid compounds were applied in a pot to understand their effect on plant uptake of P. Chapter 8 summarizes results from all the experiments, with the discussion of applications, limitations and future direction of this research. Among four appendices, Appendix 1 is the characterization results of some selected OA using GCMS (Gass Chromatography-Mass Spectroscopy), FTIR (Fourier-Transform Infrared Spectroscopy) and LCMS (Liquid Chromatography-Mass Spectroscopy) to identify different types and forms of organic compounds. Appendix 2 is the incubation experiment with the OA to test a hypothesis and methodologies used in Chapters 5, 6 and 7. Appendix 3 is an incubation study with one of the organic acid used in Chapter 6 for determining their rate of addition. Appendix 4 is a proposal that was submitted for the synchrotron study at the Australian synchrotron but was unsuccessful.

1.4 Significance of this study

Declining reserves of rock phosphate (the main source of inorganic P fertilizer) require greater recovery of P from waste streams and/or greater efficacy of P reserves that currently exist in soil, which will decrease the dependency on rock phosphate reserves and through the application of organic waste materials return valuable nutrients to agricultural land, including carbon to the soil.

While research into the benefits of the organic amendment to agricultural lands has been ongoing for many years, this research has predominantly assessed individual products, with the research findings relevant to specific products from specific sources, produced through a specific process. Therefore, the broader applicability of these findings is somewhat limited. Moreover, this research has generally relied upon assessing the organic amendments upon the addition to selected soils, through laboratory and glasshouse experiments.

This study has developed a refined approach to assessing the relative value of specific organic amendments in increasing plant-available P, prior to the investment in soil-based experiments. Such an approach would allow screening of amendments for their ‘fit for purpose’ across a range of sources and processing streams, potentially then generating opportunities to blend amendments to create ‘designer’ products for specific agricultural applications.

Chapter 2: Literature Review

2.1 Organic waste generation

With the global population expected to grow by another 2 billion people in the next 20 years (UNPD 2019), there is a requirement for increases in the production of food and fiber. Concomitant with this it is likely to increase in the quantity of waste and associated problems in managing those wastes.

According to the Food and Agricultural Organization (2009), about 32% of all food produced globally was wasted (including pre and after consumption during preparation and processing) (Buzby and Hyman, 2012). The National Waste Report 2011, from state-based authorities in Australia, estimated that the amount of food waste was produced was nearly equivalent to one-third of Municipal Solid Waste (MSW) and one-fifth of Commercial and Industrial (C&I) waste streams. About 4 million tons (MT) of annual food waste generation has been reported in Australia.

The solid organic materials produced from the urban wastewater treatment processes are commonly known as biosolid (historically also known as sewage sludge) (EPA, 1999). The annual generation of dry biosolid is around 6.5 MT in the USA (LeBlanc et al., 2009) and 9 MT in Europe (EUROSTAT, 2014). Australia and New Zealand together produce around 4 MT of dry biosolid every year (LeBlanc et al., 2009). The annual generation of food waste and biosolid from some selected countries is presented in Table 2.1.

Table 2.1: The annual food waste and biosolid generation in selected countries.

Food waste generation		Biosolid generation		
Country	Million Tons (MT)/year	Country	Million Tons (dry weight) (MT)/year	Year
USA[1]	61	USA[8]	6.5	2004
Australia[2]	4	Australia and New Zealand[8]	0.4	2008
South Korea[3]	6	China[8]	3	2006
China[4]	92	Japan[8]	2	2006
Japan[5*]	21[a]	EU-27[9]	9	2010
Europe[6]	90	Iran[8]	0.7	2008
UK[7*]	14[b]	Jordan[8]	0.3	2008
		Turkey[8]	0.6	2004
		Canada[8]	0.6	2008
		Brazil[8]	0.4	2005
		Norway[8]	0.1	2008

[*]Year of food waste production [a] 2010 and [b] 2013 Source: [1](Waste, 2012), [2](Dee, 2013), [3](Hou, 2013) [4](Lin et al., 2011) [5](Kojima and Ishikawa, 2013) [6](Monier et al., 2010) [7](Thi et al., 2015) [8](LeBlanc et al., 2009) [9](EUROSTAT, 2014).

2.1.1 Management approaches for organic waste

Management of waste materials is a global concern due to the effect of waste on public health and the environment such as greenhouse gas emission and eutrophication. In many developing countries, waste is usually dumped through landfilling or in the river or seawater, which causes environmental pollution such as eutrophication. A recent study by Guerrero et al. (2013) demonstrated challenges faced by 22 developing countries in regards to solid waste management such as a place for the dumping of waste or lack of recycling facilities which resulting in environmental pollution such as greenhouse gas emission and eutrophication.

In the year 2016-17, about 76% of the total food waste generated went to landfill and only 18% were recycled in Australia (Pickin et al., 2018). About 50 to 60% of biosolid produced in the USA in 1999 were disposed of via land dumping (USEPA and Response, 1999). Around 40% of the produced dry solids applied to agricultural land from the European Union (Roig et al., 2012)

Land application or agricultural application involves the spreading of organic waste on the soil surface or incorporating or injecting into the soil. Application of organic wastes directly to land without processing is the lowest cost option although transport cost is likely to be high owing to the entrained water, about 95% for biosolid, and about 70% for food waste. Besides, waste may contain hydrophobic oil and may also emit unpleasant odors during decomposition. Food waste from the C&I is likely to have contaminants from food processing. Biosolid may contain different pathogens and contaminants which may require further processing. The animal manure and plant residues can be directly added to the land for agricultural activities but not for leafy vegetables (Reiman et al., 2008). In most cases, organic waste receives an initial treatment or processing before landfilling or agricultural application. This processing is necessary to meet regulatory requirements for hazardous organic compounds and pathogens.

2.1.2 Processing of organic waste prior to land and agricultural application

Dehydration/ Pelletising

Pelletising involves physical drying and compression of feedstock to produce dry organic waste (Zafari and Kianmehr, 2014, Härdtle et al., 1987). It reduces the volume and mass of organic waste and offers cheap transport and application to the land (López-Fernández et al., 2007). However, this process is not recommended for land application due to reduced efficiency in removing pathogens (Hutchison et al., 2005) and also for the compactness which may determine irregular distribution, incorporation and consequent variable degradation behaviour.

This pelletized product of organic waste can be used for energy production during recycling (Rao et al., 2007) and also can be used during composting processes.

Incineration

In this process, organic waste is burnt in a combustion device at a high temperature in the presence of oxygen to produce ash (Adam et al., 2009). In the USA, biosolid are commonly treated through an incineration process (EPA, 1999). The produced ash can be directly added to the land and contain few hazardous organic compounds and pathogens (EPA, 1999). The ash materials are rich in plant available nutrients like P and potassium (K) (Adam et al., 2009) and suitable for agricultural application. However, this process would release a considerable amount of smoke, gas, and dust to the environment (EPA, 1999).

Pyrolysis

Pyrolysis is the process of producing solid char (commonly called biochar) through thermal decomposition of organic waste under high temperature (300-800 °C) and pressure in an oxygen-limited environment (Oliveira et al., 2013). The biochar materials are recalcitrant (aromatic rich compounds), highly porous and possess large surface area (Li et al., 2013), thus could act as useful exchange sites for plant nutrients when added to the soil (Knowles et al., 2011). Biochar can be produced from any organic waste such as animal manure, plant residue, food waste, biosolid, wood residues, etc with changes in their properties and nutrient content (especially P) (Rose et al., 2019). It has also been promoted as an excellent tool for mitigating climate change through C sequestration in soil (Sohi et al., 2009).

Besides the origin of organic waste, the combustion temperature can significantly affect the biochar yield and production. In general, higher temperature produces more recalcitrant materials compared to the lower temperatures of combustion (Li et al., 2013).

Depending on the heating process there are different techniques available for biochar production, such as conventional heating and microwave heating (Mokhtar et al., 2012). The conventional heating technique involves the production of char using a furnace at a desired temperature. This technique requires heating of the furnace first and then conductive heating transfer to the organic materials in the furnace (Miura et al., 2004). Therefore, a greater residence time (Wang et al., 2009) and a slow increase in the temperature are required (Tsai et al., 2006).

In contrast, the microwave heating technique involves energy transfer through the penetration of the surface of the organic materials to quickly reach the core of the materials (Miura et al., 2004). The microwave heating process saves time and offers higher efficiency for char production (Brodie, 2012). The most significant advantage of microwave heating process over the conventional heating process is better to control the temperature and reduced equipment size (Jones et al., 2002).

Digestion

The digestion process involves the biological stabilization of the organic waste materials in a closed (anaerobic) or open tank (aerobic) environment to reduce the organic carbon, mass, odor and pathogen content (EPA, 1999). It involves both aerobic and anaerobic microorganisms depending on the digestion conditions which consume part of the organic portion. Both aerobic and anaerobic digestion is typically conducted at a temperature of 35° C but can be increased up to 55° C (EPA, 1999). A more extensive range of organic waste can be processed through both aerobic and anaerobic digestion and further used as a soil amendment for agricultural activities (EPA, 1999).

Composting

Composting is a biological process where organic materials are decomposed into simpler forms of C compounds by the action of microorganisms (Bernal et al., 2009). Many factors affect the composting process, including C:N ratio, the size and porosity of the compost pile. The composting process leads to an increase in temperature typically from 50° to 60° C and destroys most of the pathogens (EPA, 1999). The composting process requires regular aeration, mixing and 4 to 6 weeks to complete the decomposition process of the organic materials. Composting can be achieved using windrow composting, aerated static piles and in-vessel composting (EPA, 1999). Windrow composting is when mixed materials are formed into a long, open-air pile and regularly turned to introduce the oxygen and water to the pile. Aerated static piles are formed into a rectangular shape and with a connected oxygen blower under the pile. In-vessel composting is conducted in enclosed containers with air and moisture supplying capacity to the pile. The temperature and moisture content of the compost pile can be easily monitored in an in-vessel composting setting.

2.2 Benefits of adding organic waste/amendments to the soil

The addition of organic amendments (OA) to the soil offers various beneficial effects. The OA have been reported to increase soil organic matter content (Diacono and Montemurro, 2011, Peng et al., 2015), soil physical structure (Aggelides and Londra, 2000) and soil nutrient supply, retention and improve availability. In the following sections, the capacity of OAs on nutrient supply, retention and availability in soil will be discussed.

2.2.1 Nutrient content of the organic amendments

The OA can supply both macro (N, P, K, Ca, Mg and S) and micronutrients to soil. Common amounts of macronutrients for OA derived from different sources and processing are presented in Table 2.2. In the following section, the total C, N and P content of OA is discussed.

Table 2.2 lists the total C content (%) of OA across a wide range of sources and processing. In general, biochar materials contain a higher total amount of C content compared to the manure, compost, food waste and biosolid irrespective of source.

OA contains different amounts of N to the soil depending on the sources and processing (Table 2.2). The inorganic portion of N is considered as plant-available N in the soil and the organic portion goes through mineralization processes to produce inorganic forms of N. By far the largest amount of N is in the organic form.

The C and N content of the OA are also essential to control soil microbial activity, which regulates the mobilization and immobilization of the plant nutrients in the soil. A higher C: N ratio (usually more than 10:1), the higher microbial activity in the soil and immobilization of N will occur. However, the abundance of mineralizable forms of C (simple carbohydrates such as sugars) and N in OA is also important for microbial activity. For instance, a study by Calbrix et al. (2007) found a large variation in the quantity and diversity of the soil bacterial community when turkey manure (with C:N ratio 9.1 and mineralizable C 82%) and sewage sludge was added (with C:N ratio 5.9 and mineralizable C 99%) compared with composted turkey manure (with C:N ratio 11.7 and mineralizable C 9%) suggesting that C form was more important compared to C:N ratio in terms of microbial activity in the soil.

The P content of OA varies based on sources and processing. In general, animal originated OA have a higher P content compared to plant originated OA presented in Table 2.2. The total P content of the OA is not high (mostly ranged from 1-2% (Table 2.2) when the P contents of commercial fertilizers are considered (SSP 9%, MAP 22% and DAP 20%). However, the P content of OA varies depending on the country of origin of the materials. For instance, poultry manure originated from Pakistan has a P content of 5.5 % (Arif et al., 2017) and poultry manure originated from Australia and South Africa has a P content of 1.8% (Belyaeva and Haynes, 2012) and 1.5 % (Azeez and Van Averbeke, 2010), respectively.

OA contains both inorganic and organic P and P and could contribute to the soil P availability. Studies have shown the increase of available soil P from the inorganic P content of OA (Jin et al., 2016) and also from the mineralization of the organic P after OA addition (Parmjit et al., 2005). The continuous availability of organic P from cattle manure in soil has been reported by (Halajnia et al., 2009). Furthermore, immobilization of more than 90% of poultry, cattle and goat manure P were reported from 120 days of incubation experiment with acidic soil (Azeez and Van Averbeke, 2010). A detailed discussion on the different forms of organic and inorganic P in OA, their fate and role in soil P availability is needed and discussed in section 2.3.

In conclusion, the nutrient content of OA (such as N and P) is not as high as chemical fertilizer. Moreover, nutrient contents are in both organic and inorganic forms in the OA. Inorganic forms of nutrients are considered as readily plant available depending on their chemical nature and organic forms of P need to go through mineralization processes to convert into inorganic forms before becoming available to the plant. The effect of OA on soil nutrient retention and availability is discussed in the following sections.

Table 2.2: Nutrient concentrations of organic amendments.

Categories	Source	Organic materials	Country	Total C (%)	Total N (%)	Total P (%)	Total K (g/kg)	Total Ca (g/kg)	Total Mg (g/kg)	References
Manure	Animal	Goat	South Africa	49.8	2.6	0.2	22.7	39.3	22.7	(Elias et al., 2009)
		Cattle	Iran	22.7*		1.2				(Halajnia et al., 2009)
		Cattle	South Africa		1.6	0.4				(Azeez and Van Averbeke, 2010)
		Poultry			3.7	1.5				
		Goat			2.2	0.4				
		Pig	China	21.9	2.5	2.7				(Yin and Liang, 2013)
		Cattle	Idaho, USA	26.4	2.2	0.4	13.5	22.0	8.2	(Lentz and Ippolito, 2012)
		Swine solids	Italy	48.2	1.8	1.7				(Marchetti et al., 2012)
		Poultry	Pakistan	68.3*	2.6	5.5				(Arif et al., 2017)
		Liquid swine	USA		9.9	2.3	48.3			(Laboski and Lamb, 2003)
		Poultry	Australia	29	2.7	1.8	17.5	9.9	7.1	(Belyaeva and Haynes, 2012)
		Cow	Italy		2.8	2				(Baldi et al., 2010)
		Beef cattle	Canada	36.7	1.7	0.6				(Zvomuya et al., 2006)
		Chicken litter straw	Australia	38.4	3.9	1.7				(Mackay et al., 2017)
		Chicken litter sawdust		36.9	3.3	1.4				
		Pig straw litter bedding		38.6	1.8	0.6				
	Plant	Farm yard	Pakistan	47.3*	1.5	3.4				(Arif et al., 2017)
		Farm yard	Kenya	36	1.8	0.4	22.0	9.0	5.0	(Opala et al., 2012)
Compost	Animal	Pig manure	China	33.3*	6.2	1.8	16.7			(Bin et al., 2009)
		Poultry manure	China			1.7				(Yu et al., 2013)
		Beef cattle	Canada	19.8	1.8	0.9				(Zvomuya et al., 2006)
	Plant	Green vegetables	Australia	19		0.3				(Schefe et al., 2008
		Pineapple leaves	Malaysia	45.8	2.3	0.5	26.7	4.0		(Ch'ng et al., 2014)

Categories	Source	Organic materials	Country	Total C (%)	Total N (%)	Total P (%)	Total K (g/kg)	Total Ca (g/kg)	Total Mg (g/kg)	References
		Bark	Germany	12.9	0.8	0.2				(Qayyum et al., 2015)
		Green waste	Australia	28.3	1.4	0.5	6.3	11.8	3.1	(Belyaeva and Haynes, 2012)
		Organic waste	Italy	22.8^{*}	2.4	0.6	9.0			(Baldi et al., 2010)
Biochar	Animal	Chicken litter	Malaysia	63.7	2.8	2.6	39.0	59.0	0.2	(Ch'ng et al., 2014)
		Swine solids	Italy	51.1	2.1	3.9				(Marchetti et al., 2012)
		Poultry manure	Australia	27.6	9.1	3.1	31.3	108.6	8.9	(Belyaeva and Haynes, 2012)
		Poultry litter	USA	27	2.3	4.3	47.1	55.0		(Revell et al., 2012)
	Plant	Maize straw	China	76	5.0	0.1	40.0	10.0		(Zhai et al., 2015)
		Willow wood	Australia			-				(Agegnehu et al., 2016)
		Sawdust	USA	66.2	0.3	0.03	3.4	3.7	1.5	(Lentz and Ippolito, 2012)
		Wood chip	Italy	72	1.1	0.1				(Marchetti et al., 2012)
		Wood	Saudi Arabia	76.2		0.1	9.6			(Usman et al., 2016)
		Feedlot manure	Australia	44	0.6	0.7	21.0	15.0		(Slavich et al., 2013)
		Green waste		76	0.2	0.02	1.7	1.7		
		Pine locust	China	66.7	0.2	0.1				(Han et al., 2016)
		Pea nut hull	USA	72.8	1.9	0.2	19.3	5.4	2.7	(Gaskin et al., 2010)
		Pine chip		76.9	0.2	0.1	2.8	4.0	1.2	
		Corn cob	USA	81.1	0.6	0.1	0.4	1.6	0.3	(Nelson et al., 2011)
		Wheat residue	Sweden	63.7	2.9	0.9	18.1	24.9	5.1	(Parvage et al., 2013)
		Eucalyptus green waste	Australia	79	0.3	0.04				(Abujabhah et al., 2016)
		Willow	Australia	9.24	0.04	0.2	15.4	15.2	4.4	(Agegnehu et al., 2015)
		Acacia		5.9	0.04	0.02	0.1	3.9	0.1	
Food waste		Food waste		46.8	3.2	0.5				(Zhang et al., 2007)
		Food waste	San Francisco	51.4	3.5	-				(Han and Shin, 2004)

Categories	Source	Organic materials	Country	Total C (%)	Total N (%)	Total P (%)	Total K (g/kg)	Total Ca (g/kg)	Total Mg (g/kg)	References
Food waste		Food waste		46.67	3.5	0.15				(Zhang et al., 2011)
		Food waste	Korea	47-54.1	1.5-3.4	1.9-4.2				(Bouallagui et al., 2003)
		Fruit and vegetable waste	Ohio, USA	10.5	1.1	0.2				(Alvarez and Lidén, 2008)
		Household waste	Bolivia	31.9	1.0					(Suthar, 2007)
		Vegetable waste	India	39	1.5					
		Food waste vermi-compost	Tunisian	19.5	1.3	2.7		1.9	0.4	(Arancon et al., 2004)
		Food waste compost		25.7	1.9	0.3				(Stutter, 2015)
		Meat and bone waste	France			18.4				(Deydier et al., 2005)
		Meat Bone meal	Spain	46	11.1	2.7				(Cayuela et al., 2009)
		Meat and bone waste	Poland			16.5				(Kowalski and Krupa-Żuczek, 2007)
		Fish bone	India			17.2				(Logesh et al., 2012)
						10.8				
		Egg Shell				< 5				(Yasothai and Kavithaa, 2014)
Biosolid		Sewage sludge	India		1.6	0.2				(Mohanty et al., 2006)
		Sewage Sludge	Japan	24.3	4.4	1.7				(Wickramatilake et al., 2010)
		Biosolid	India			0.7				(Hosseinpur and Pashamokhtari, 2013)
		Sewage sludge	UK			2.1		42.0		(Siddique and Robinson, 2004)
		Municipal waste compost	Australia	22.01	1.4	0.3				(Mackay et al., 2017)
		Municipal waste compost	Iran	20.5*		0.3				(Hosseinpur et al., 2012)
		Municipal solid waste compost	Pakistan		1.0	0.5				(Iqbal et al., 2015)
		Sewage sludge biochar	Germany	26.5	3.4	3.8				(Qayyum et al., 2015)

Categories	Source	Organic materials	Country	Total C (%)	Total N (%)	Total P (%)	Total K (g/kg)	Total Ca (g/kg)	Total Mg (g/kg)	References
		Biosolid Biochar	USA	42.2	5.7	1.3				(Gonzaga et al., 2017)
Others		Lignite	Australia	40		0.01				(Schefe et al., 2008)
		Decaying rice straw	China	41.7	1.0	1	0.6			(Bin et al., 2009)
		Tithonia	Kenya	42	3.1	0.3	41.0	20.0	6.0	(Opala et al., 2012)
		Organic fertilizer	China			0.7				(Yu et al., 2013)

*Informing total organic C of the OA materials.

2.2.2 Effect of organic amendments on soil nutrient retention and availability

The OA have been reported to increase nutrient availability in the soil especially N and P. The losses of N in the soil system occur through leaching, ammonia volatilization and return of N to the atmosphere in the forms of N_2O, NO and N_2 as a result of the denitrification process (Dowdell, 1982). OA addition such as biochar has been reported to reduce N leaching and volatilization from soil through increased adsorption by the organic materials and microbial immobilization (Sun et al., 2017). The addition of compost and charcoal have been reported to increase soil N retention and plant uptake on a Ferrosol (Steiner et al., 2008). Furthermore, the addition of OA such as dairy waste, sewage sludge compost and manure, has shown an increase in soil total N content (Habteselassie et al., 2006, Zaman et al., 2004, Eghball et al., 2004).

Unlike N, the P is less mobile in the soil and expected to have less leaching (unless in sandy soil) and no volatilization or atmospheric losses (Blume et al., 2010a, Finck, 2007). The adsorption of P by the soil cations (such as $Fe^{2+ \text{ or } 3+}$, Al^{2+}, Ca^{2+}, Mg^{2+} etc.) is the main reason for the limited availability of P from added P fertilizer (Margenot et al., 2016, Finck, 2007, Reddy et al., 2005). Only 5-30% of the added P becomes available to the plant in the first year of application to the soil from P fertilizer (Price, 2006, Glendinning, 2000).

Mechanisms of P adsorption in soil

The dissolution of P fertilizer applied to soil results in phosphate ions ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in soil solution (Gerke, 2015, Blume et al., 2010a) and depending on soil pH, plants take up P in the orthophosphate form ($H_2PO_4^-$ and HPO_4^{2-}). In acidic soil, the dominant form of P ion is $H_2PO_4^-$ which is readily adsorbed and precipitated by oxides and hydroxide of Al and Fe ions and becomes unavailable to the plant.

The availability of P to the plant depends on the mechanism of the sorption process. If the sorption process is physisorption or non-specific sorption due to quick electrostatic attraction between two opposite electric charges (Equation 2.1), the sorbed P can readily be replaced by the ions of similar charge and value (DeLaune and Reddy, 2008) and this is considered as labile P.

$$[\mathrm{Al\,(OH)}^{2+}]\,\mathrm{OH} + \mathrm{H_2PO_4^-} \leftrightarrow [\mathrm{Al\,(OH)}^{2+}]\,\mathrm{H_2PO_4} + \mathrm{OH^-} \quad \text{---------} \ (2.1)$$

If the sorption is chemisorption or specific sorption due to strong coordinate bonding between ions (Equation 2.2), P is considered moderately or less available (Mnthambala et al., 2015, Blume et al., 2010b, Samadi, 2006).

$$\mathrm{Al\,(OH)_3} + \mathrm{H_2PO_4^-} \leftrightarrow \mathrm{Al\,(OH)_2\,H_2PO_4} + \mathrm{OH^-} \quad \text{------------} \ (2.2)$$

OA have been reported to increase soil P availability by supplying P from OA (Parmjit et al., 2005), releasing native P from soil (Siddique and Robinson, 2004), reducing added P adsorption (Ch'ng et al., 2017, Agegnehu et al., 2016, Zhai et al., 2015, Slavich et al., 2013, Opala et al., 2012, Gaskin et al., 2010, Elias et al., 2009, Halajnia et al., 2009) and also by some biological processes (phosphate solubilizing bacteria and enzymes) (Rahman et al., 2014, Elias et al., 2009, Nèble et al., 2007, Ayaga et al., 2006, Guppy et al., 2005, Iyamuremye et al., 1996).

Although OA increased N and P availability in the soil, this study will be focused on the effect of OA on soil P availability. While N fertilizer is produced from atmospheric N_2 with the atmosphere N content of about 78%, the primary source for P fertilizer production is phosphate rock (PR), which is a finite natural resource and estimated to be declining soon, with predictions ranging from few to hundreds of years (Table 2.5) and is also considered to be a geopolitically isolated resource.

2.3 Forms of P in Organic amendments

The inorganic forms of P in the OA are orthophosphate and pyrophosphate. Pyrophosphate is formed through the polymerization of orthophosphate. Orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}) is considered as readily available to the plant and unlike orthophosphate, pyrophosphate is considered as a less effective form of plant-available P owing to its chemical structure and stability ($P_2O_7^{4-}$) in soil (Sutton and Larsen, 1964).

Organic P includes orthophosphate monoesters (Phytic acid and other monoesters), orthophosphate diesters (phosphonates, DNA and phospholipids) and polyphosphates (Stutter, 2015, Li et al., 2014, Hansen et al., 2004). These organic forms of P need to be mineralized to orthophosphate before they can become available to plants.

The orthophosphate monoesters release phosphorus in soil through a slow hydrolysis process with a half-life of hundreds of years (Hutzinger and Craig, 1980). In contrast, orthophosphate diesters are degraded to orthophosphate monoesters within 24 hours in an alkaline environment, (Turner et al., 2003b, Makarov et al., 2002). Due to their high charge density orthophosphate monoesters form stable complexes with cations and strong binding to clay and organic matter in the soils (Leytem and Maguire, 2007, Turner et al., 2005, Celi et al., 1999) and are thus considered as less bioavailable. Polyphosphate can be hydrolyzed completely into pyrophosphate and partially to orthophosphate under alkaline conditions (Reitzel et al., 2006, Ahlgren et al., 2005) with a half-life of 0.8 years in the soil (Zhang et al., 2013).

Therefore, organic P content of the OA is not likely to contribute to plant P availability in soil immediately after application. The inorganic orthophosphate content of the OA is more likely to predict the P fertilization value of the OA.

2.3.1 Abundance of different forms of P in organic amendments

The abundance of different forms of P in OA is presented in Table 2.3. A significant portion of P that is present in OA is inorganic P (ranging from 24.8 to 100%) followed by orthophosphate monoester ranging from (0 to 74.9%) and orthophosphate diesters ranging from (0 to 10.5%) depending on their source and processing form.

Due to limitations to the data, it is difficult to predict the change of P abundance in OA with different processing. However, from the existing data, in general, manure and compost contain both inorganic (orthophosphate) and organic P (orthophosphate monoesters (phytic acid and orthophosphate diesters) while biochars contain mostly inorganic orthophosphate (Table 2.3). Manures contain more organic P than inorganic P (Table 2.3). Compost contains more inorganic P than organic P, which may be due to the extended mineralization of organic P during the composting process (Stevenson, 1967). It is also very evident that the pyrolysis of organic materials converts most of the organic P to the inorganic P. It is also noticeable that pyrolysis resulted in the synthesis of more pyrophosphate in biochars compared to manure and compost (Table 2.3).

Moreover, a recent study of P speciation by X-ray Absorption Near-Edge Structure (XANES) spectroscopy demonstrated the major forms of P in biochars were Al-phosphate (variscite) while originated from sugarcane trash, sugarcane bagasse and cow manure and non-apatite Ca-phosphates (monocalcium phosphate or dicalcium phosphate) when originated from papermill sludge, green waste, poultry litter, sugarcane mill mud, wheat chaff and rice husk biochars (Rose et al., 2019). These compounds are expected to be less bioavailable and therefore, the bioavailability of the inorganic orthophosphate from biochar would be highly dependent on its chemical association.

Table 2.3: Abundance (%) of different forms of P in organic amendments identified by ^{31}P solution-state NMR. All the percentages were calculated based on total extractable P from NMR extracts.

		Inorganic P		Ortho-P monoesters		Ortho-P diesters					
	Organic material	Ortho-P	Pyro-P**	Phytic acid	Other monoesters	Phospho lipids	DNA	Phos phonates	Poly-P	Country	Ref
Manures	Lagoon manure	58.4	7.1	10.8	20.1	1.8	1.8	0		USA	(Hansen et al., 2004)
	Solid manure	63.3	3.5	15.6	14.4	1.8	0.9	0.5			
	Organic manure	79.7	1.6	9.8	6.5	0	0.8	1.6	0	USA	(He et al., 2009)
	Dairy manure	68.2	1.5	9.2	13.6	3	1.5	0	3		
	Chicken straw	65.2	0.5	23.5	4.4	2.6	3.9			Australia	(Mackay et al., 2017)
	Chicken Saw dust	54.4	0.1	31.7	5.7	3.4	4.7				
	Pig straw	77.3	1.3	6.4	4.6	6.4	4.1				
	Chicken Manure	47.9	0.4	51.7			0			Norway	(Stutter, 2015)
	Dairy manure	59.3	0	37.7			3			China	(Li et al., 2014)
	Swine manure	41.7	0.7	57.6			0				
	Broiler litter	23.8	1	74.9			0.3				
	Broiler litter	34.1	0	65.9			0			USA	(Turner, 2004)
	Cattle manure	65	3.8	15.2			10.5		5.5		
	Swine manure	87.1	0.4	10.3			2.2		0.01		
	Dairy manure	63-77	1.6-2.5	5-14	6.1-12.5	2.4-5	0.8-1.7	0.8-1.6		USA	(Toor et al., 2005)
Compost	Sewage sludge compost	92.5	0.5	8.2		0.4	0.1			Spain	(Galvez-Sola et al., 2010)
	Com manure compost	87.1	0.8	14.5		0.1	0.6				
	Poultry manure compost	86.6	0.4	15.3		0.2	0.4				
	Food waste compost	88.4	0	11.6			0			Norway	(Stutter, 2015)
	Green waste compost	91.8	0	8.2			0				

Biochar	Cotton seed hull biochar @ 650	46	54							USA	(Uchimiya and Hiradate, 2014)
	Broiler litter biochar @ 650	100									
	Wheat straw biochar @ 600	94	6							China	(Xu et al., 2016)
	Maize straw biochar @ 600	91	9								
	Peanut husk biochar @ 600	78	22								
	Biochar	100								Norway	(Stutter, 2015)
Others	Sewage sludge from 13 location	49-87	4-19%	13-31			6-8%			China	(Peng et al., 2010)
	Sewage sludge	95.3	0.4	4.3			0			Norway	(Stutter, 2015)
	Anaerobic digest	92.8	0	5.4			1.8				
	Sea weed	72.2	0	27.8			0				
	Forest litter	27.5	1.8	57.3	0.0	1.9	4.8	5.8	1.0	Italy	(Li et al., 2015)

Here, *Ortho-P: Orthophosphate, Pyro-P: Pyrophosphate, Poly-P: Polyphosphate. Phytic acids represent all the phytate and inositol phosphates.*

*** Pyrophosphate is considered an ineffective inorganic form of P, which may source from microbial biomass or produced during the extraction process or processing of OA.*

2.3.2 Methods for determination of P forms in organic amendments

Nuclear Magnetic Resonance (NMR) spectroscopy is widely used to identifying different forms of P in soil, plants, organic amendments, sediment and water. Both solid and liquid state ^{31}P NMR spectroscopy can identify different forms of P. However, liquid state ^{31}P NMR spectroscopy has widely been used for the identification of the P compounds in OA.

Liquid state ^{31}P NMR spectroscopy techniques involve the extraction of both organic and inorganic P from OA using ‘selective’ solvents. Sodium hydroxide and ethylene-di-amine tetra acetic acid (NaOH and EDTA) are the most widely used due to their capacity to enhance P extraction and minimize hydrolysis of organic P to inorganic P during extraction (Koopmans et al., 2007). The function of EDTA is to release P from paramagnetic ions to decrease line broadening in the NMR spectroscopy (Cade-Menun, 2005).

A list of different extraction techniques of different forms of P from OA using solution-state ^{31}P NMR cited in the literature is presented in Table 2.4. In the extraction process, different concentrations of NaOH (ranged from 0.25 M to 0.5 M) and extraction time (ranged from 1 to 24 hr) have been used in previous studies. According to Turner (2004), using a high concentration of NaOH may assist only to quantify phytic acid accurately, but for complete characterization and comparison among different types of OA diluted NaOH would work better. Moreover, in an experiment on the effect of different extraction times, there was no significant difference between 4 to 16 hr in recovering P from OA (Turner, 2004).

Finally, to identify different organic P compounds in the OA, all the spectra obtained from ^{31}P NMR spectroscopy were referenced to an external standard like orthophosphoric acid or Methylene-di-phosphonic acid (MDPA).

Table 2.4 P extraction techniques for OA using solution-state ^{31}P NMR

Concentration of NaOH	
0.25M	(Mackay et al., 2017) (Xu et al., 2016) (Li et al., 2015) (Stutter, 2015) (Uchimiya and Hiradate, 2014) (Uchimiya and Hiradate, 2014) (Uchimiya and Hiradate, 2014) (Uchimiya and Hiradate, 2014) (Gatiboni et al., 2013) (Galvez-Sola et al., 2010) (Peng et al., 2010) (Toor et al., 2005) (Turner, 2004)
0.5 M	(Li et al., 2014) (Turner, 2004) (Hansen et al., 2004)
Extraction time	
1 hr-4 hr	(Gatiboni et al., 2013) (Turner, 2004)
4.1hr to 24 hr	(Xu et al., 2016) (Li et al., 2015) (Li et al., 2014) (Uchimiya and Hiradate, 2014) (Gatiboni et al., 2013) (Galvez-Sola et al., 2010) (Peng et al., 2010) (Toor et al., 2005) (Turner, 2004) (Hansen et al., 2004)
External standard	
Orthophosphate (H_3PO_4, 85%)	(Xu et al., 2016) (Uchimiya and Hiradate, 2014) (Li et al., 2014) (Gatiboni et al., 2013) (Galvez-Sola et al., 2010) (Peng et al., 2010) (He et al., 2009) (Toor et al., 2005) (Turner, 2004) (Hansen et al., 2004)
MDPA	(Mackay et al., 2017) (Li et al., 2014) (Stutter, 2015)

2.4 Limited and geopolitical distribution of Phosphate Rock reserves

Phosphate rock (PR) is a naturally occurring resource, rich in the phosphate bearing mineral apatite, with the general formula of $Ca_{10}(PO_4)_6(OHF)_2$. It is the primary source of P for agricultural and industrial activities around the world. Around 82% of world mined PR is used for agricultural activities and 18% for industrial process (PRud'hoMMe, 2010). The low water solubility of P from apatite necessitates the processing of PR to achieve plant-available forms.

The primary process involves acidification of PR with either sulfuric, phosphoric or nitric acids to produce single superphosphate (SSP), wet-process phosphoric acid (WPA), triple superphosphate (TSP), di and mono ammonium phosphate (DAP and MAP) and some other nitro-phosphates (Figure 2.1) (Van Kauwenbergh, 2010). The P concentration in these water-soluble fertilizers ranges from 18 % (SSP) to 46 (TSP) % as P_2O_5 (Van Kauwenbergh, 2006). According to the International Fertilizer Industry Association (IFA), globally DAP, MAP and TSP accounted for half of the total P based fertilizer application in 2013 (Van Kauwenbergh, 2010).

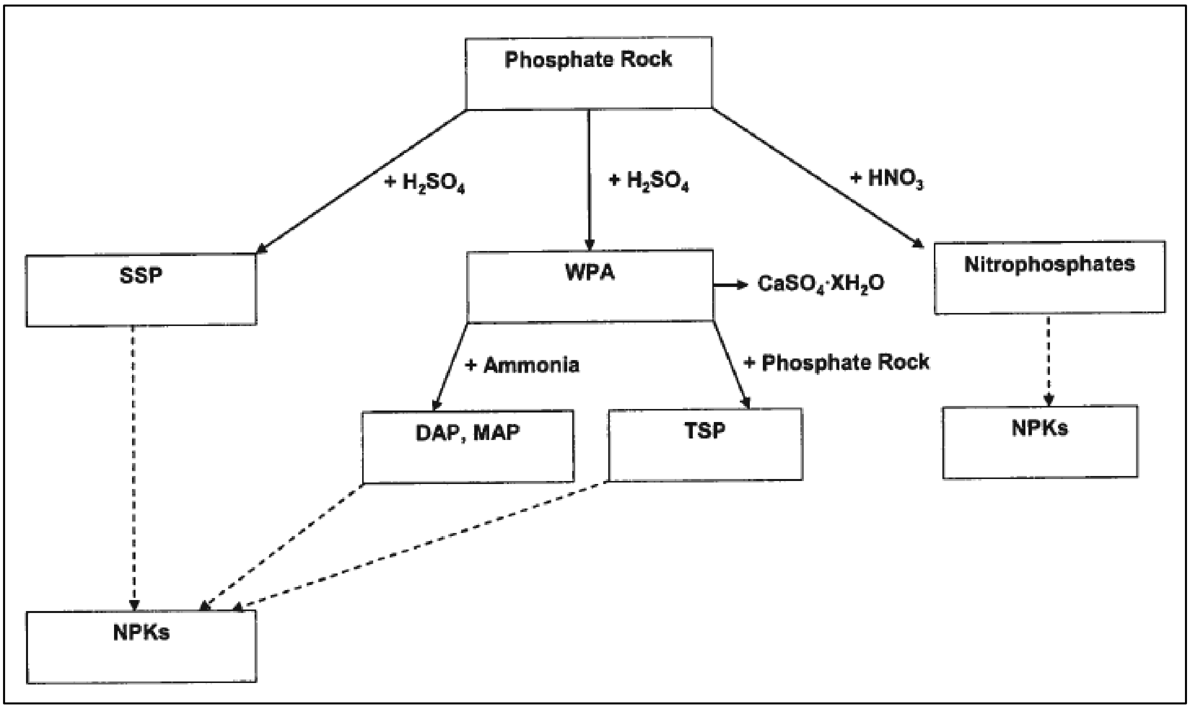

Figure 2.1: Production of different forms of P fertilizer from phosphate rock. Sourced from IFDC (Van Kauwenbergh, 2010). Single superphosphate (SSP), wet-process phosphoric acid (WPA), triple superphosphate (TSP), diammonium phosphate (DAP) and mono ammonium phosphate (MAP).

The reserves of phosphate rock are finite and estimates vary from 16,000 Mt (according to US Geological Survey) (Vaccari, 2009) to 60,000 Mt (according to International Fertilizer Development Centre) (Van Kauwenbergh, 2010). Recent studies suggest the lifetime of the current world PR reserve varies from a few to hundreds of years (Table 2.5) with a peak phosphorus production occurring around 2033 (Figure 2.2) (Cordell and White, 2011). The US

Geological Survey in 2017 reported the existing extractable phosphate rock reserve may last for 260 years.

Table 2.5: Estimates of the lifetime of current world phosphate rock reserve by different authors, sourced from (Cordell and White, 2011).

References	Lifetime of reserve (years)	Depletion year*	Assumptions
(Tweeten, 1989)	61	2050	If demand increased by 3.6%.
(Runge-Metzger, 1995)	88	2083	If demand increased by 2.1%
(Steen, 1998)	60-130	2058-2128	If demand increased by 2% and 0% after 2020 due to recycling and efficient measurement.
(Smil, 2000)	80	2080	If extracted at current rate
(Fixen, 2009)	93	2102	If production rate remained constant as were in 2007–2008
(Smit et al., 2009)	69-100	2078-2109	Considered 0.7–2% increase until 2050, and then no increase
(Vaccari, 2009)	90	2099	If extracted at current rate
(Van Kauwenbergh, 2010)	300-400	2310-2410	If extracted at current rate

* From the date of publication the lifetime estimation calculation was conducted

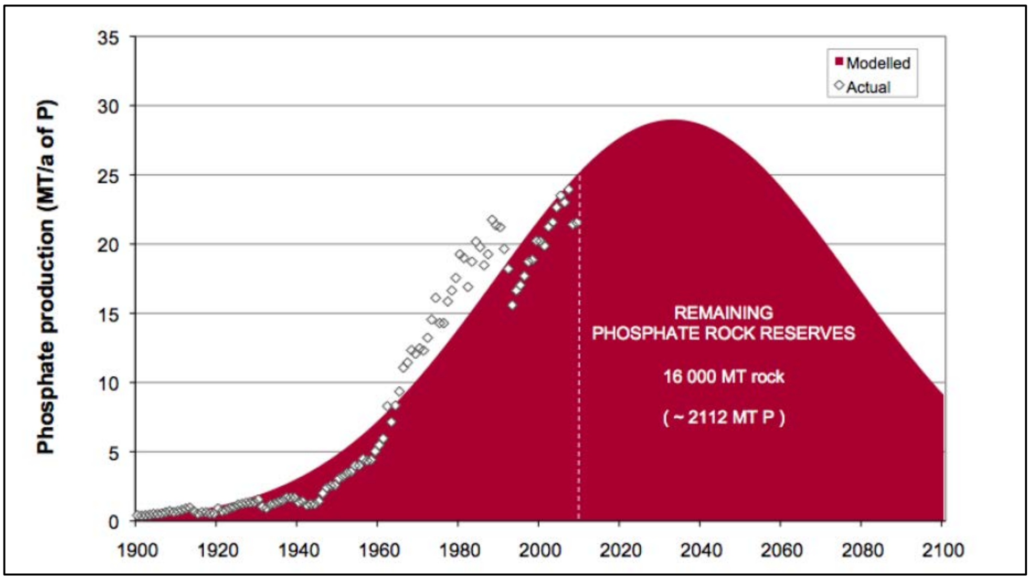

Figure 2.2: The peak P production curve, derived from the US Geological Survey and industry data. Sourced from (Cordell and White, 2011).

The existing PR reserve is mostly concentrated in the Morocco and Western Sahara region (72%) (Figure 2.3). Due to the non-renewability and high economic value of the PR, the concentrated reserve in selected countries may lead to political and social tension in the future (Shim et al., 2019).

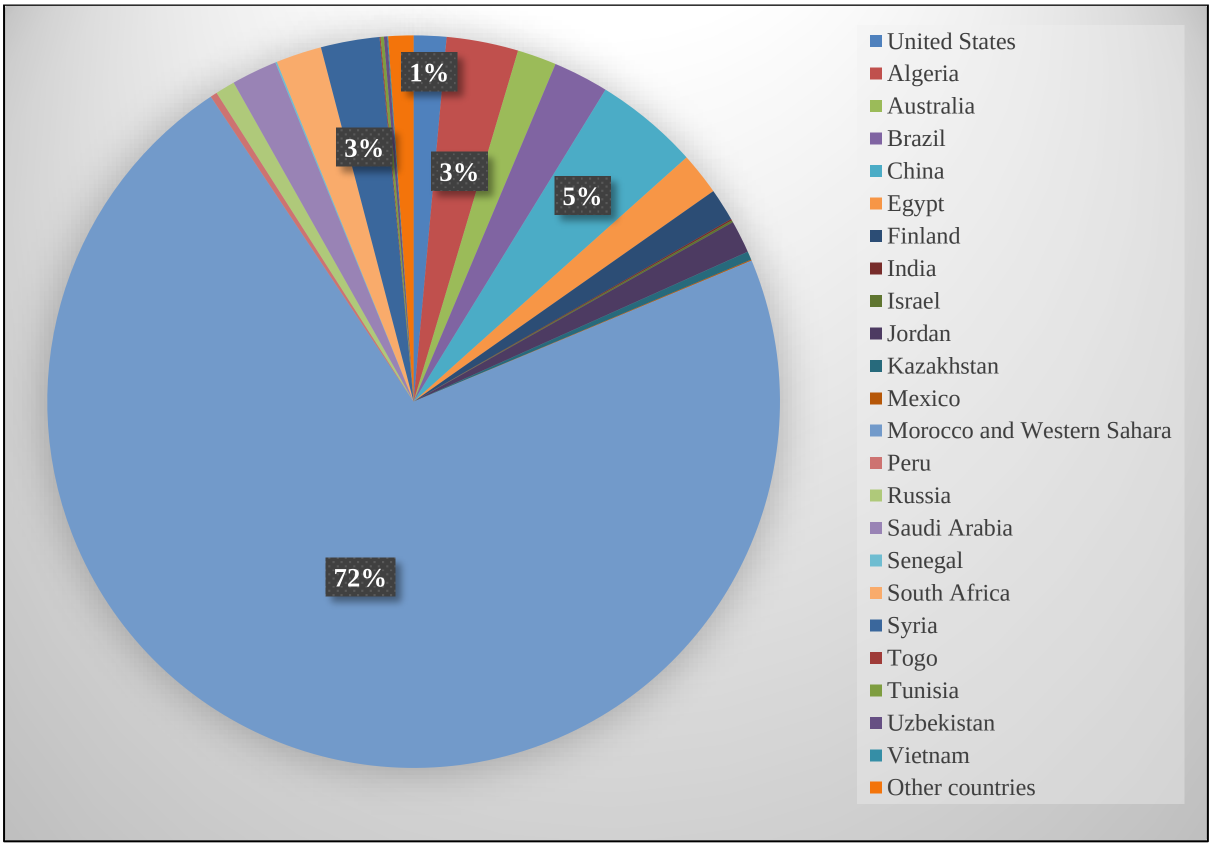

Figure 2.3: The world Phosphate Rock reserve, derived from the U.S. Geological Survey, Mineral Commodity Summaries, January 2020.

Therefore, alternative sources of the P are needed to be explored to reduce PR mining and increase it's longevity. Organic amendments that are generating from organic wastes could be served as an alternative source of P fertilizer (Mackay et al., 2017). The benefit of using OA is that besides supplying P, it reduces the sorption of the added P in the soil.

2.5 Possible mechanisms for increases in soil P availability with OA addition

2.5.1 By releasing sorbed P

In addition to supplying P to the soil, OA have been reported to increase P availability by releasing adsorbed or labile P in soil. The release of P from the soil after the addition of sewage sludge, poultry litter, and cattle slurry have been reported from a 100 days soil incubation experiment (Siddique and Robinson, 2004). The increase in soil solution P concentration by the release of poorly soluble P from soil with the addition of green waste compost and lignite from a 26-day soil incubation study also reported by (Schefe et al., 2008).

2.5.2 By reducing P adsorption

The addition of OA is reported to increase soil P availability by reducing P adsorption in the soil by blocking P fixing sites through complexation with soil cations or by competing with phosphate ions to be fixed. For instance, the addition of manure prior to P addition in a soil incubation experiment has been suggested to increase P availability by shielding phosphate ions from the direct interactions with soil surfaces (Agbenin and Igbokwe, 2006). The addition of lignite and green waste compost increased P availability by the likely formation of organic-metal complexes as reported by (Schefe et al., 2008). Furthermore, the addition of compost and biochar reported increasing soil P availability by fixing soil Al and Fe (Huck Ywih et al., 2014).

Many studies have identified that organic acids from OA (oxalic, malic, citric acids) form organic-metal complexes in soil by the organic ligands produced during the degradation process (Cheng et al., 2008, Agbenin and Igbokwe, 2006, Hu et al., 2005b, Kwabiah et al., 2003, Geckeis et al., 2002, Iyamuremye et al., 1996, Sibanda and Young, 1986, Hue et al., 1986, Mnkeni and MacKenzie, 1985, Borie and Zunino, 1983, Levesque and Schnitzer, 1967).

Studies also found a positive correlation with the dissolved organic C content of the OA in reducing soil P adsorption and increasing P availability (Schreeg et al., 2013, Bin et al., 2009).

To investigate the role of organic carbon compounds (which derived from OA) in increasing soil P availability, extensive research has been conducted in the past, especially with organic acids (both aliphatic and aromatic). Research outcomes have shown the positive effect of organic acids to increase soil P availability by complexing with soil cations (Hu et al., 2005b, Hue et al., 1986), competing with P for sorption sites (Hue, 1991, Violante et al., 1991) and by mobilizing/substituting P from poorly soluble fractions (Bolan et al., 1994). A summary of the effect of organic acids derived from the OA on soil P availability presented in Figure 2.4.

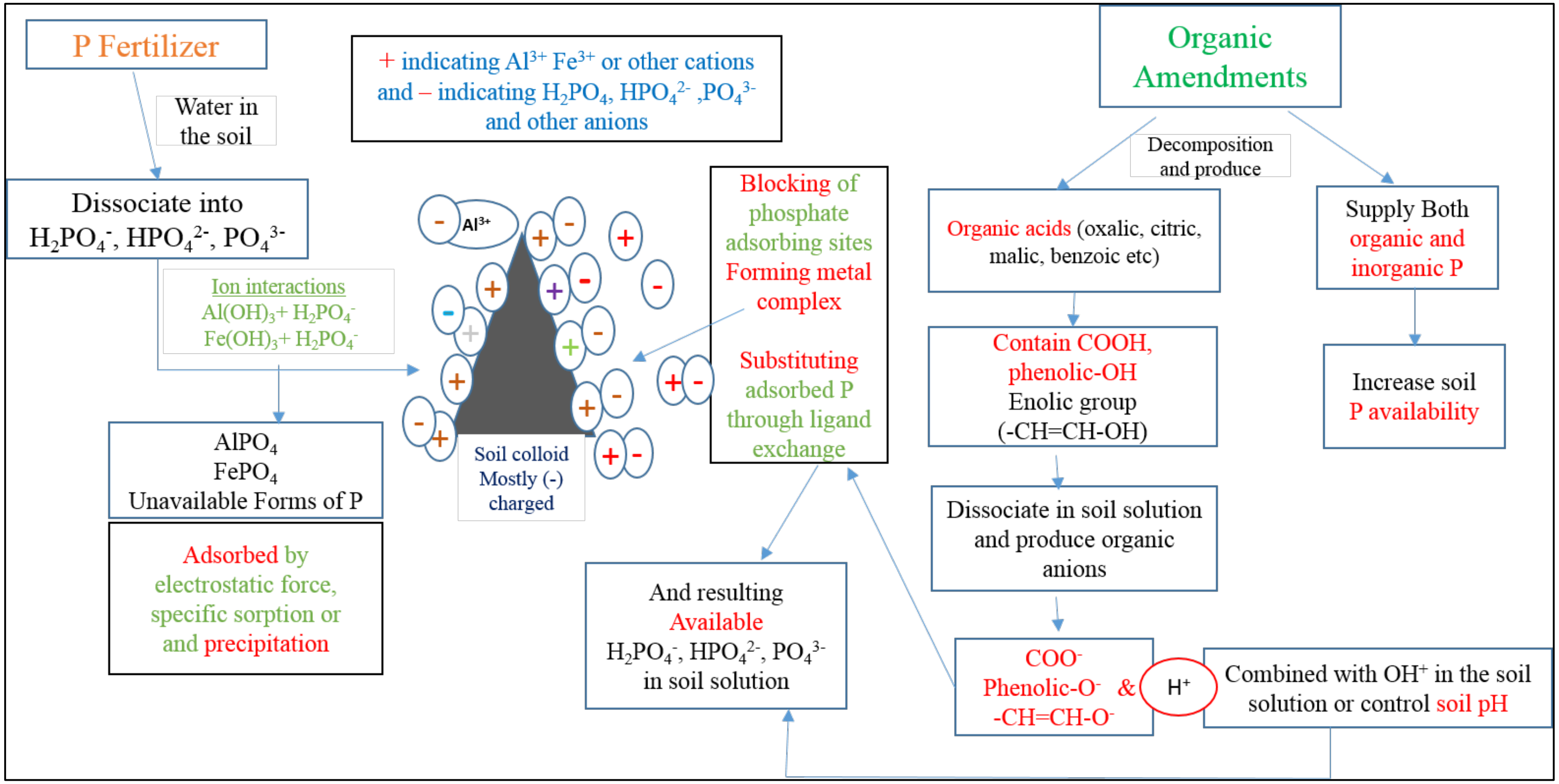

Figure 2.4: A diagram of the fate of organic amendments in soil and their impact on P availability

2.6 Forms of C in organic amendments

The main forms of carbon compounds identified by solid-state ^{13}C NMR spectroscopy are alkyl-C, methoxyl, O-alkyl C, di-O-alkyl, Aryl-C, O-aryl C, and carbonyl C (Kavdır et al., 2005, Ivanova and Randall, 2003, Faz Cano et al., 2002, Baldock and Smernik, 2002). The presence of alkyl-C indicate straight-chain methylene/aliphatic C compounds, O-alkyl and di-O-alkyl indicate cellulose, hemicellulose and other polysaccharide compounds (Preston et al., 2009), Aryl-C and O-aryl C represent aromatic and phenolic compounds, respectively and carbonyl C represent carboxylic and amide compounds (Eldridge et al., 2013, Spaccini et al., 2012, Albrecht et al., 2008).

2.6.1 Abundance of different forms of C in organic amendments

Due to the limited availability of information, it is difficult to establish the effect of processing on different C forms in OA, a table of different forms of C in OA with their abundance is presented in Table 2.6. The most abundant forms of C compounds are carbohydrate, polysaccharide and protein in OA with a mean highest abundance of 78.7% in unprocessed OA followed by manure (76.9%), compost (75.2%) and biochar (50.5%). In contrast, the highest abundance of aromatic and phenolic compounds appeared in biochar compared to compost, manure and unprocessed organic materials. To understand the total organic anion producing capacity of OA, a sum of phenolic and carbonyl C compounds has been derived (Table 2.6). It appears, except for biochar, all the other processed materials have similar amount of organic anion producing compounds with a mean abundance value of 25.9%, 16.7%, 14.9% and 14.8% in biochar, manure, compost and unprocessed OA, respectively. To understand how the abundance of the different forms of C is changing after different processing further work is required where OA needed to be processed from similar feedstock materials.

Table 2.6: Forms and abundance (%) of C compounds in organic amendments identified by solid-state ^{13}C NMR

Processing form	Organic materials	Alkyl C (0-45)*	Methoxyl and N alkyl C (45-65)	O-Alkyl C (65-90)	Di-O-Alkyl C (90-110)	Aryl and unsaturated C (110-145)	O-Aryl C (Phenolic and Furan) (145-165)	Carbonyl and amide C (165-190)	Ketone C (190-215)	Total Carbohydrate, Polysaccharide and proteins	Total phenolic, carbonyl, amide and ketone	References
Manure	Cow manure	22.8	8	34.3	8.4	8.1	3.8	14.6		73.5	18.4	(Eldridge et al., 2013)
	Swine Manure	22.8	6.2	40.8	9.2	5.3	1.6	14.1		79	15.7	
	Broiler litter	15.2	6.7	45.4	10.8	6.1	3.9	12		78.1	15.9	
Compost	Sewage sludge and green waste compost	18.5		57.4		11.5	4.8	7.8		75.9	12.6	(Albrecht et al., 2008)
	Fermented manure (Cow)	21.2	13.5	40.6^{b}		12.8	5	6.9^{d}		75.3	11.9	(Spaccini et al., 2012)
	Organic waste compost	45.3^{a}		37.6^{b}		9.6^{c}		7.4		82.9	-	(Spaccini and Piccolo, 2007)
	Broiler litter compost	18.2	7.6	39.6	9.2	8.9	5	11.6		74.6	16.6	(Eldridge et al., 2013)
	Cow manure compost	17.9	9.1	38.7	9.3	8	5.2	11.7		75	16.9	
	Green waste compost	22.4	10.7	32.3	8.1	8.2	6.3	12		73.5	18.3	
	Municipal solid waste compost	23	7.6	39.8	8.9	7.3	3.6	9.8		79.3	13.4	
	Municipal waste Compost	19.5	8.7	28.9	8.3	18	7.5	7	2.1	65.4	14.5	(Mackay et al., 2017)
Biochar	Pine wood Char	10	7.7	38	9.2	22.2	8.8	5.8	2.1	64.9	14.6	(Baldock and Smernik, 2002)
	Green waste Char	19.7	6.1	14.4	6.7	25	8.6	19.6		46.9	28.2	(Eldridge et al., 2013)
	Poultry manure char	15.5	3.7	16.7	3.8	25.3	7.3	27.7		39.7	35	
Others/ Without processing	Biosolid	34.2	11.9	23.7	4.8	5	2.1	18.3		74.6	20.4	(Eldridge et al., 2013)
	Blood and Bone	35.8	17.8	13.2	2.4	3.8	1.8	25.2		69.2	27	
	Pinewood shavings	9.6	7.4	51.3	10.7	7.9	4.8	8.3		79	13.1	
	Wheat straw	10.6	5.8	52.4	12.7	6.3	3.4	8.8		81.5	12.2	
	Grease trap waste	59	6.3	13	2.2	4.5	1.8	13.1		80.5	14.9	
	Chicken Straw bedding	18.3	7	48.3	10.6	5.2	3	7.2	0.3	84.2	10.2	(Mackay et al., 2017)
	Chicken Saw dust bedding	15.2	7.9	50.1	10.3	7.2	3.1	6.1	0.1	83.5	9.2	
	Pig straw	8.4	5.5	51.2	12.3	10	5.2	6.5	1	77.4	11.7	

*represents chemical shifts and a: representing chmichal shift from 0-65, b: 65-110, c: 110-145, and d: 165-190 ppm

2.6.2 Understanding the fate and role of organic carbon compounds in soil

Organic carbon compounds have different roles and fate in the soil. For instance, carbohydrate (including simple saccharides and polysaccharides) compounds are considered to be the most labile compounds in the soil, while aromatic compounds are the most recalcitrant.

Polysaccharides (cellulose, hemicellulose, starch, pectin, and chitin) are the primary source of carbon for microorganisms in the soil (Gunina and Kuzyakov, 2015). Polysaccharides undergo a decomposition process by exoenzymes (cellulases, xylenes, glucosidases, hydrolases, chitinases) to produce oligo and monosaccharides and other sugars (Gunina and Kuzyakov, 2015), which further mineralize to CO_2 (Werth and Kuzyakov, 2008). The decomposition time of cellulose and hemicellulose ranges from months (Blagodatskaya et al., 2014) to years (Zech et al., 2012). Another critical function of all the poly-, oligo- and monosaccharides is the formation of micro aggregates in the soil due to their sticky nature (Six et al., 1999, Oades, 1984). No sorption and desorption with soil cations have been reported due to lack of surface charge or ability to form hydrophobic ligand interactions except weak hydrogen bonds (Olsson et al., 2011).

The aromatic and phenolic compounds are primarily sourced from lignin, lignin-cellulose complexes, flavonoid and tannins in the organic materials (Berg and McClaugherty, 2008, Siqueira et al., 1991). Though the aromatic and phenolic compounds are considered to be very stable, a 6-month laboratory incubation experiment revealed 56~68% of lignin was transformed to CO_2 in soil (Stott et al., 1983). Ready degradation of phenolic compounds in a biologically active soil has also been reported (Elliott and Cheng, 1987).

Degradation of lignin compounds involves different steps and processes. Firstly, all the lignin and other phenolic compounds undergo microbial degradation to produce smaller polyphenolic units, methoxy-phenols and intermediate phenols (Kassim et al., 1982, Haider et al., 1975). These hydroxylated phenols then take part in the polymerization or oxidation, hydroxylation and decarboxylation reactions (Kassim et al., 1982, Haider et al., 1975, Dagley, 1967). Alternatively, they go through oxidation or decomposition to produce simpler molecules such as phenolic acids or produce phenolic radicals through auto-oxidation and polyphenol oxidase enzyme activity (Siqueira et al., 1991).

Aliphatic carboxylic acids are highly soluble and sorption, biodegradation and metal complexation been reported as the primary fate in the soil (Jones et al., 2003) with a half-life of 1 to 12 hours (Jones and Brassington, 1998). However, the organic anions that are derived from the dissolution of aliphatic organic acids are firmly held by soil cations reported as less susceptible to bio-degradation (Ström et al., 2001, Jones and Edwards, 1998).

Organic acids have also been reported to mobilize and solubilize poorly soluble nutrients such as Mn, Cu, Zn, Fe and P in soil (Micales, 1997, Marschner, 1995, Delhaize et al., 1993, Hoffland, 1992). About 65% of P mobilization was observed in an experiment of 20 different soil types with organic acids (Jones et al., 2003). The role of carboxylic compounds seems to have a direct effect on soil P mobilization and sorption.

2.6.3 Understanding the magnitude of the effect of aliphatic versus phenolic compounds

Interestingly, the effect of both aliphatic and phenolic compounds has been well established concerning soil P availability, but the combined effect of both aliphatic and phenolic compounds are less often evaluated. However, both of these compounds have unique characteristics in dissociation, formation of stabile organometallic complexes and degradation.

In general, aliphatic compounds are more able to dissociate and are capable of forming stable organometallic complexes in the soil due to a lower pKa value compared to phenolic compounds. In previous studies in most of the cases, the aliphatic compounds generally had a greater effect compared to phenolic compounds in soil P release, sorption, dissolution and availability (Lindegren and Persson, 2009, Hu et al., 2005a, Hu et al., 2005b, Ron-koul et al., 2004).

On the other hand, the microbial degradation of the aliphatic compounds is much quicker (due to straight-chain structure) ranging from 3 hr to days (Ström et al., 2001) than the phenolic compounds in soil. The ring structure of phenolic compounds makes them resistant to microbial degradation and result in longer residence time in the soil compared to aliphatic compounds.

During the degradation process, phenolic compounds go through a series of different steps (Kassim et al., 1982, Haider et al., 1975, Dagley, 1967). The degradation steps of relatively simple phenolic compounds such as coumaric acid was described by Shindo and Kuwatsuka (1976) to hydroxybenzoic acid and then rapidly to protocatechuic acid before entering the TCA (tetracarboxylic acid) cycle.

Phenolic acids have also been reported to be toxic to soil microbes (Wu et al., 2016, Hu et al., 2005b), which may delay the degradation and prolong the effect of aliphatic carboxylic compounds when added together. Phenolic compounds were more readily adsorbed onto soil clay minerals than carboxylic compounds in an experiment by Schefe and Tymms (2013). Thus, the combined addition of phenolic and aliphatic carboxylic compounds in soil may have a significant effect in increasing soil P availability than solo addition due to their heterogeneous nature as also recommended by Schefe and Tymms (2013) and Chittleborough (2004).

2.6.4 Effect of phenolic and aliphatic organic acid compounds on soil P

A range of different types of carbon compounds (Table 2.7) based on the presence of carboxylic (-COOH), hydroxyl (-OH) and phenolic (aromatic-OH) functional groups have been evaluated in the past for their effect on soil P solubilization, release, mobilization and availability (Yang et al., 2013b, Harrold and Tabatabai, 2006, Hu et al., 2005a, Bolan et al., 1994, Fox et al., 1990), P sorption (Lindegren and Persson, 2009, Hue, 1991) P fertilizer dissolution (both organic and inorganic) (Ron-koul et al., 2004, Kpomblekou-A and Tabatabai, 2003), P fertilizer use efficiency (Schefe and Tymms, 2013, Hue, 1991) and plant growth and phyto-availability P (Chatterjee et al., 2015, Liptzin and Silver, 2009, Kpomblekou-A and Tabatabai, 2003, Bolan et al., 1994, Hue, 1991).

All of these studies indicated a positive effect of phenolic and carboxylic compounds on increasing soil P availability by elucidating the following three possible mechanisms described by Traina et al. (1986) as (i) competition for P adsorption sites (Lindegren and Persson, 2009, Hu et al., 2005b, Hue, 1991); (ii) dissolution/substitution of adsorbents (Chatterjee et al., 2015, Fox et al., 1990) and (iii) changes in the surface charge on the adsorbents (Liptzin and Silver, 2009) by the organic anion produced through the dissociation of organic acids.

Differences in the magnitude of the effectiveness of different compounds for increasing soil P availability have also been reported depending on the number and position of the carboxylic and phenolic functional group, dissociation constant (pKa value) and stability constant (logK value). In general, the effectiveness of organic acids on soil P availability increased as the number of carboxylic groups increased (Harrold and Tabatabai, 2006, Hu et al., 2005b, Kpomblekou-A and Tabatabai, 2003, Hue, 1991). This is due to an increase in competing ability with $PO4^{3-}$ ions to be fixed (Hu et al., 2001, Parfitt, 1979).

The alpha (α) and beta (β) position of carboxylic functional group in carboxylic compounds and ortho position of hydroxyl functional group in phenolic compounds have been reported to be more effective in rapid dissolution of inorganic P and chelate metal ions in the soil solutions (McColl and Pohlman, 1986, Pohlman and Mc Coll, 1986, Stevenson, 1967).

The release of P has been reported to be mostly dependent on the stability constants of organic compounds (logK value) to form organic-metal-complexes. A significant positive correlation has been reported between the stability constant of organic compounds forming organic complexes with Al, Fe and Ca (log K_{Al}, Log K_{Fe} and log K_{Ca} values) and release of P in soil (Harrold and Tabatabai, 2006). In contrast, a study by Fox et al. (1990), reported no correlation between the stability constant of organic compounds and the release of soluble organic P in the soil which may lead to the importance of understanding the strength of organic compounds depending on their dissociation constant (pKa value).

The release of P has been reported to be more dependent on the strength of acid compared to the ability to form organo-metal complexes (Manley and Evans, 1986). The strength of organic compounds is directly related to its first dissociation constant (pKa value). An inverse relationship has been reported between pKa value of organic compounds and P release in the soil.

Table 2.7: Previous studies of the effect of phenolic and aliphatic organic acids on soil P availability.

Compounds	Experiment type	References
Aliphatic: Acetic, formic, lactic malic, tartaric, oxalic and citric acid	Laboratory and Pot	(Bolan et al., 1994)
Aliphatic: Formic, acetic, propionic, glycolic, pyruvic, n-butyric, lactic, n-Valeric, oxalic, malonic, fumaric, maleic, succinic, oxaloacetic, malic, ketoglutaric, tartaric, cis-aconitic, citric **Phenolic:** Salicylic, hydroxybenzoic, protocatechuic, phthalic, vanillic, gallic	Incubation	(Harrold and Tabatabai, 2006)
Aliphatic: Citric acid **Phenolic:** Caffeic and protocatechuic	Incubation	(Hu et al., 2005a)
Aliphatic: Citric **Phenolic:** Caffeic acid, p-coumaric acid, protocatechuic acid and vanillic acid	Incubation	(Hu et al., 2005b)
Aliphatic: Acetic and Malic **Phenolic:** Protocatechuic	Sorption and bioassay	(Hue, 1991)
Aliphatic: Oxalate, citrate and butanetetracarboxylic **Phenolic:** Mellitate	Sorption	(Lindegren and Persson, 2009)
Humic acid extracted from lignite	Solubilization	(Martinez et al., 1984)
Aliphatic: Acetic, lactic, melonic, malic, tartaric, oxalic and citric **Phenolic:** Hydobenzoic and salicyclic acid	Dissolution experiment	(Ron-koul et al., 2004)
Aliphatic: Acetic, aconitic, citric, formic, fumaric, lactic, maleic, malic, maleic, malonic, oxalic, phthalic, succinic, tartaric and vanillic **Phenolic:** Hydroxybenzoic, Salicylic	Dissolution experiment	(Fox et al., 1990)
Aliphatic: Citric	Applied to the soil column	(Chatterjee et al., 2015)
Humic acid (derived from coal)	Incubation experiment (15 Days) and pot	(Wang et al., 1995)
Aliphatic: Oxalic, tartaric, cis-aconitic and citric	Incubation experiment (45 days) and pot	(Kpomblekou-A and Tabatabai, 2003)
Acetate	Incubation experiment (27 days)	(Liptzin and Silver, 2009)
Fulvic acid (extracted from weathered coal)	Incubation experiment (21 days)	(Yang et al., 2013b)
Oxalic, malic, citric, **Phenolic:** 4-hydroxybenzoic, protocatechuic, 4-hydroxycinnamic, and caffeic acids	Short-term adsorption and desorption experiments	(Schefe and Tymms, 2013)
Humic acid (extracted from peat and weathered coal)	Incubation study (90 days)	(Yang et al., 2013a)

2.7 General conclusions

This literature review has identified that the addition of OA increase soil P availability and the C (carbonyl and phenolic) and P (orthophosphate) compounds as the key elements. It also finds that NMR spectroscopy is a robust way to identify forms and abundance of C and P in OA. The key research gaps were identified as-

i) Limited studies to understand the changes in the forms of C and P compounds in OA across different processing (such as raw, compost and biochar) when originated from similar feedstock.

ii) No study was available to understand if the signature C and P compounds can be used to screen OA for determining their capacity to increase soil P availability and plant P uptake.

iii) Both aliphatic and aromatic organic acids have been reported to increase soil P availability when added individually but there are no studies to date to understand the effect of combined addition of aliphatic and aromatic organic acids on soil P availability and plant P uptake.

2.7.1 Research aims, questions and hypotheses

The aim of this study was: (i) to identify the forms and abundance of C and P compounds in organic amendments across different sources and processing, (ii) to screen OA for their effect on soil P availability and plant P uptake and to investigate if the signature C and P compounds of OA can be used to predict the increase of soil P availability and plant P uptake and (iii) to examine the combined addition of aliphatic and aromatic organic acids on soil P availability and plant P uptake.

The following research questions were answered to achieve the aims of this study-

1. How does the abundance of different forms of C and P change with different processing of OA (raw, compost and pyrolysis) when derived from a similar waste stream?

2. Can OA be screened based on C and P signature compounds for their ability to increase soil P availability and plant P uptake?

3. How do aliphatic and aromatic organic acids behave in relation to P availability and plant P uptake in an acidic soil when added in combination?

The following hypothesis were set-

i) Phenolic and carbonyl compounds of OA would determine the release of soil native or fixed P and sorption of added P in the soil by supplying organic anions.

ii) The combined addition of aliphatic and aromatic organic acid would prolong soil P availability and plant P uptake in an acidic soil compared to individual addition due to their heterogeneous nature and complementary effect on each other.

Chapter 3: The effect of organic amendments on soil P availability: A Meta-Analysis

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3.1 Introduction

The beneficial role of OA have been reviewed in a variety of situations, such as for soil reclamation (Larney and Angers, 2012), soil management (Laghari et al., 2016) and use (Quilty and Cattle, 2011). The use of composted materials as organic fertilizer has also been reviewed (Senesi, 1989). Different studies covered the use of biochar (animal origin) and biosolid (TORRI et al., 2017) as an alternative to phosphate rock. The effect of aerobically digested materials was also reviewed on crop growth and yield (Möller and Müller, 2012). However, to date, there have been no reviews where the role of OA on soil P availability and comparisons made according to source and processing. The following meta-analysis was carried out to address this gap with an objective to understand the general effect of OA on soil P availability, plant biomass, P uptake and content across different sources and methods of processing of OA.

3.2 Materials and Methods

3.2.1 Collection of information

All the data on the effect of OA on soil P availability was collected from peer-reviewed journal articles using Google Scholar, Web of Science, Scopus and The University of Melbourne library database. The keywords used for searching articles were “effect of organic amendments”, “compost”, “biochar”, “biosolid” and “manure” on soil P availability and sorption, plant biomass and P uptake.

40 peer-reviewed research articles were found with 473 observations of differently processed OA on soil P availability; among them, 218 observations were animal originated OA and 147 were plant originated OA. For reviewing the effect of OA on plant biomass, plant P uptake and plant P content, information was collected from 12, 14 and 16 peer-reviewed research articles with 100, 104, 126 observations. Observations include different types of OA, different rates of OA addition, different duration of sample collections and effect on different soil types from laboratory/field incubation, pot, greenhouse/glasshouse and field experiments.

3.2.2 Categories of Organic Amendments

All the OA were categorized according to their source and processing. OA were categorized based on plant and animal originated sources. OA from poultry, cattle, pig/swine, goat and dung sources was considered as the animal originated and OA from green waste, food waste, plant straw/direct plant, plant residues such as leaves, nut hull, corn cob, farmyard manure, sawdust and wood/wood chip were considered as plant originated OA. All the OA were categorized into five different processing forms such as manure, compost, biochar, mix (includes mixes of compost and biochar or compost and manure or biochar and manure or mixer of compost, biochar and manure) and others (includes direct plant materials and straw, farm residues, sewage sludge, biosolid and lignite).

Definition of P availability

In this study, P availability refers to the conventional extraction processes, which are usually practiced to understand the plant P availability from the soil. On a global scale a wide range of methods are used to evaluate P availability, such as Bray-P extraction, Resin P extraction, Olsen P extraction, Colwell P extraction, $CaCl_2$ extractable P, Mehlich-3 extractable P, Strip extractable P, water extraction and available P (extractant unknown).

Plant biomass, P uptake and P content

For plant biomass, only the dry weight of plant samples was considered. Plant P concentration data included total P content of the plant extracted following both wet acid digestion and dry combustion. In the case of wet oxidation, different types of extraction procedures with different ratios and types of acids were included. Plant P uptake was calculated from plant P concentration and plant dry biomass data (when data were not available) following the Equation 3.1.

$$\text{Plant P uptake} = \text{Plant biomass} \times \text{Plant P concentration} \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (3.1)$$

3.2.3 Meta-analysis

The meta-analysis was conducted following the method described in Lam et al. (2012). The MetaWin 2.1 software was used to calculate the mean effect sizes at 95% confidence intervals following a bootstrapping technique (Rosenberg et al., 2000). The effect of OA (both animal and plant originated OA) on soil P availability, plant biomass, plant P uptake and P content based on their different processing forms were calculated as a percentage of control treatment.

The negative percentage indicates a decreasing effect and positive values indicate an increase relative to the control. The control treatment includes effect without OA addition. The effect of OA was considered significant compared to control if their 95% confidence interval did not overlap with zero. Means of the effects of differently processed OA were considered significant from one another if their 95% confidence interval did not overlap.

3.3 The outcome of the meta-analysis

3.3.1 Effect of organic amendments on soil P availability

The meta-analysis result showed the addition of OA independent of source and processing significantly (at 95% level of confidence interval) increased soil P availability compared with control (Figure 3.1a). At this level, the effect of processing was statistically non-significant. The extent of increasing soil P availability varied among the different processed forms. The compost and biochar had a similar increase in soil P availability with a mean of 140 and 150 percent increase, respectively. Similarly, manure and other processed forms of OA also had a similar effect on soil P availability with a mean of 214 and 234 percentage increase, respectively. The highest increase in soil P availability was observed with mixed OM (including mixes of compost and biochar or compost and manure or biochar and manure or mixer of compost, biochar and manure) with a mean of 287 percent increase. The overall effect ranged from 164 to 204 percent increase in soil P availability with a mean of 183 percent (Figure 3.1a).

The animal originated OA were categorized into three different processing forms such as manure, compost and biochar. Compared to control all the OA significantly (at 95% level of confidence interval) increased soil P availability and showed no significant difference among different processing forms (Figure 3.1b). The highest increase was observed by animal originated biochar with a mean value of 310% followed by animal originated manure and compost with a mean of 239% and 151%, respectively. The overall increase ranged from 187% to 326% with a mean of 246%.

The plant originated OA were categorized based on different processing forms such as manure, compost, biochar and others. All the processed forms of plant originated OA significantly (at 95% level of confidence) increased soil P availability compared to control. However, the compost significantly increased soil P availability compared to all other processed forms of OA except manure (Figure 3.1c). The overall mean increase was 66%, whereas the highest increase was observed by compost with a mean value of 199% and the lowest increase was observed by biochar with a mean value of 31%. The mean increase by the plant originated manure and others were 99% and 59%, respectively.

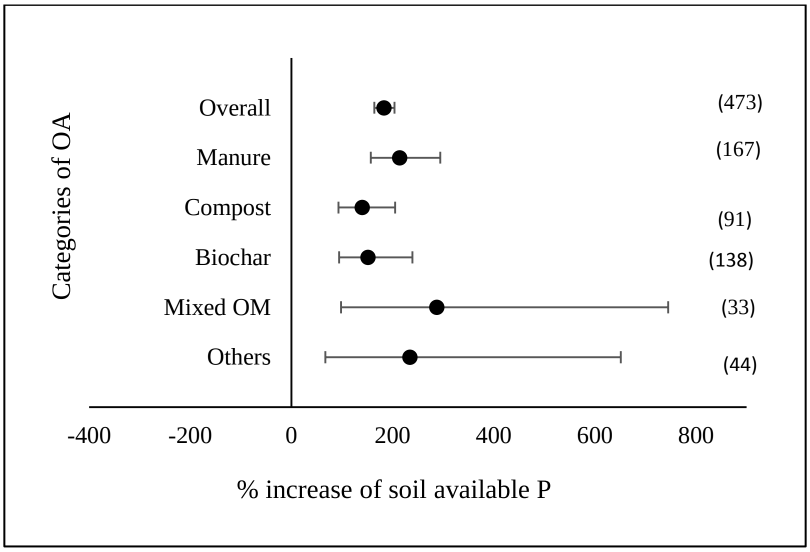


Figure 3.1 a: Meta-analysis results showing the effect of OA (independent of source) on soil P availability. The value in the parentheses indicates total observations. The dot indicating the mean value and the left and right bar indicating the lower and upper value of the 95% confidence intervals, respectively. Overlapping of the 95% confidence intervals indicates statistically non-significant.

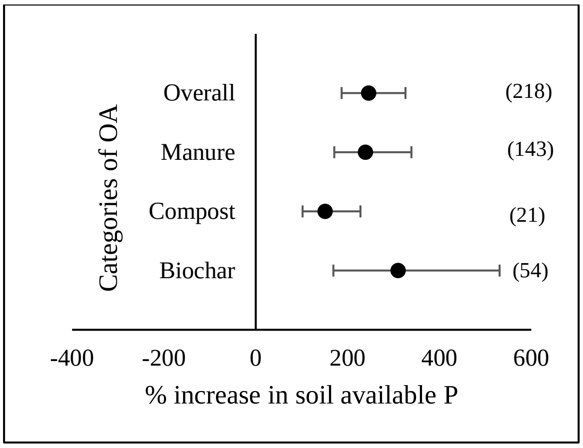


Figure 3.1 b: Meta-analysis results showing the effect of animal originated OA on soil P availability.

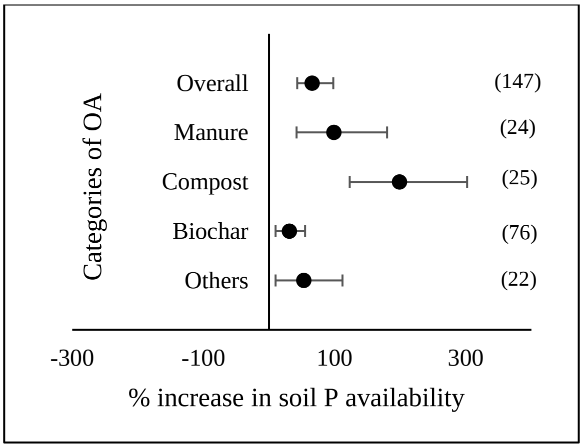


Figure 3.1 c: Meta-analysis results showing the effect of plant originated OA on soil P availability.

3.3.2 Effect of organic amendments on plant biomass, P uptake and P content

OA were categorized into 5 different categories based on processing such as manure, compost, biochar, mixed OM and others, including both plant and animal originated source. The meta-analysis result showed that all the processed forms of OA significantly increased plant biomass, P uptake and P content.

The addition of OA significantly (at 95% level of confidence interval) increased plant biomass, P uptake and content compared to control (Figure 3.2 a, b and c). The highest increase in plant biomass was observed by manure and compost with a mean value of 53% and 54%, respectively (Figure 3.2 a). Biochar had the lowest effect on the plant biomass increase compared with other processed forms of OA with a mean value of 23% increase. The mixed OM and other processed form increased the plant biomass of 44% and 33%, respectively.

The highest plant P uptake was obtained by the other processed form of OA (includes direct plant materials and straw, farm residues, sewage sludge, biosolid and lignite) with a mean increase value of 293% (Figure 3.2 b). Whereas manure, compost, biochar and mixed OM showed a similar increase value in plant P uptake. The overall mean value was 153% with a range of 121% to 192%.

Similar to plant P uptake, the highest plant P content was attained by other processed forms of OA with a mean value of 196% (eg biosolid) and the rest of the processed forms showed a similar increase in plant P content (Figure 3.2 c).

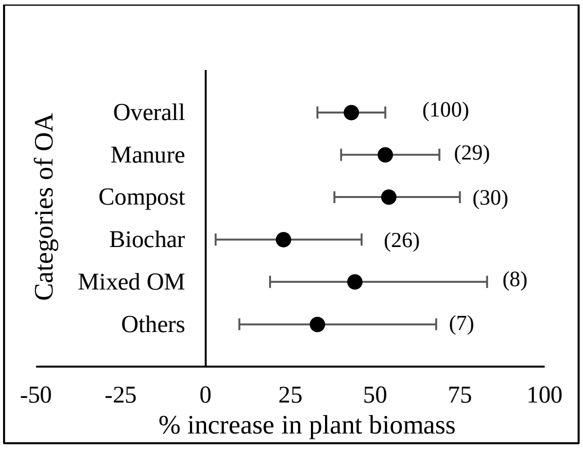


Figure 3.2 a: Meta-analysis results showing the effect of OA (independent of source) on plant biomass. The value in the parentheses indicates total observations. The dot indicating the mean value and the left and right bar indicating the lower and upper value of the 95% confidence intervals, respectively. Overlapping of the 95% confidence intervals indicates statistically non-significant.

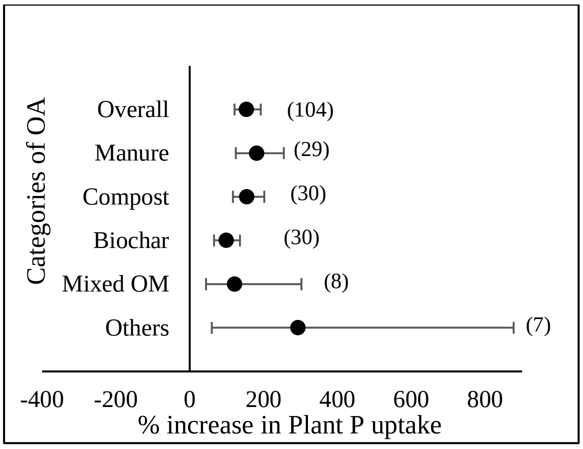


Figure 3.2 b: Meta-analysis results showing the effect of OA (independent of source) on plant P uptake.

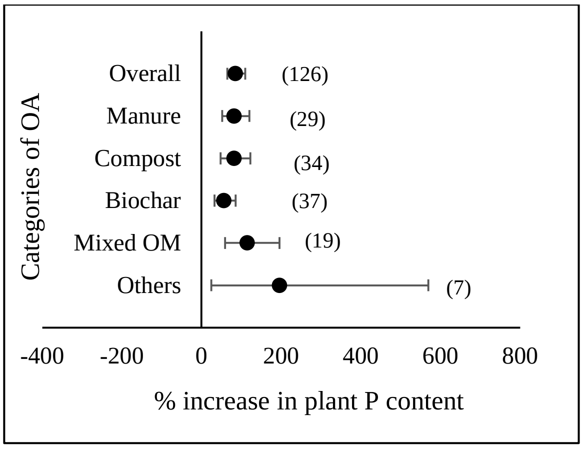


Figure 3.2 c: Meta-analysis results showing the effect of OA (independent of source) on plant P content.

3.4 General conclusions from the meta-analysis

The meta-analysis showed a significant positive effect of the OA on soil P availability, plant growth (dry weight), plant P uptake and plant P concentration compared with soil where no OA were added (control). Generally, the animal originated OA were more effective in increasing soil P availability compared to plant originated OA. This was may be due to the high P concentration in the animal originated OA compared to the plant originated OA (Table 2.2)

The meta-analysis showed a broad range of increase in soil P availability after OA addition. This was due to the inclusion of observations both with and without P fertilizer addition in this meta-analysis. P fertilizer addition with OA would have a higher soil P availability compared to no fertilizer addition.

The meta-analysis did not show any significant difference among different processing forms of OA in increasing soil P availability. The obtained effect of increasing soil P availability is very general and did not take into consideration different rates of OA addition and different duration of the experiments while compared among different processed forms. This may be the reason why no significant differences were observed among different processing forms of OA.

However, the meta-analysis showed the positive effect of OA in increasing soil P availability and plant P uptake compared to no OA addition. In the following section 2.5 the mechanisms of increasing soil P availability by OA addition have been discussed.

Chapter 4: Characterization of the organic amendments

4.1 Introduction

In order to understand the effect of organic amendments (OA) on soil P availability, we need to understand their chemical characteristics. In this chapter, a comprehensive chemical characterization of the OA were conducted including nuclear magnetic resonance (NMR) spectroscopy analysis to identify the abundance of different forms of P (solution-state ^{31}P NMR spectroscopy) and C (solid-state ^{13}C NMR spectroscopy) compounds. Samples from two waste streams, food waste and biosolid were used to prepare material with potentially different forms of P and C compounds through composting and pyrolysis. Their properties were contrasted with those of untreated waste.

In this chapter, I examine the changes in the chemical composition and forms of P and C compounds generated in these new OA. The characterization results were further utilized to understand the effect of selected OA on soil P availability (Chapter 5) and plant P uptake (Chapter 7) in a P limited acidic soil.

4.2 Materials and Methods

4.2.1 Collection of organic amendments

Food waste and biosolid and their different processed forms: oven-dried (raw), biochar and compost, were used in this study. Food waste was collected from the student union of the University of Melbourne, Parkville campus from a centralized waste collection point from eateries. The collected food waste was separated as best as possible to determine the food groups present. The waste contained on a dry weight basis: mixed vegetables (34%), leafy vegetables (1%), capsicum waste (6%), fruit peel waste (55%), some bread and dairy (2%) and some unidentifiable food waste (2%).

Biosolid was collected from the wastewater treatment plant of North East Water, Wodonga, Victoria, Australia. The biosolid was collected into a drying pan on-site and left to air dry to approximately 75% solid and stockpiled for at least 7 years before use. The biosolid used in this study was classified as T1-C2 grade, which meets the guideline provided by the Environmental Protection Authority, Australia. T1 represents the accepted microbial quality and C2 represents the chemical contamination level especially heavy metals.

4.2.2 Processing of food waste and biosolid

Oven drying (raw): Food waste and biosolid were dried in an oven at 80° C overnight, cooled and ground to less than 2 mm with a cutting mill and cylinder sieve grinder, respectively and thereafter considered as raw food waste (FWR) (Figure 4.1 A) and raw biosolid (BSR) (Figure 4.1 B). The ground materials were thoroughly mixed and stored in an airtight box/ bucket for future use.

Collection of food waste

Drying in an oven

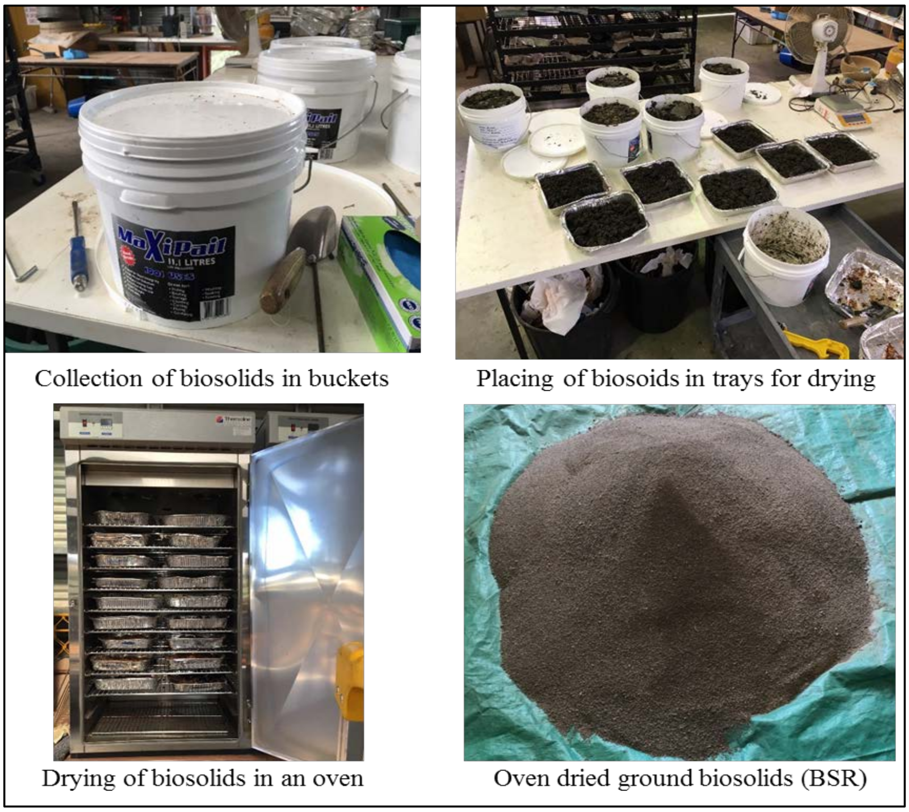
Oven dried food waste

Cutting mill for grinding

Ground food waste

Storing of ground food waste (FWR)

Figure 4.1 A: Steps of collection and processing of food waste



Collection of biosolids in buckets

Placing of biosoids in trays for drying

Drying of biosolids in an oven

Oven dried ground biosolids (BSR)

Figure 4.1 B: Steps of collection and processing of biosolid

Pyrolysis: The FWR and BSR materials were pyrolyzed at 550-600° C for about 30 minutes in an oxygen-limited condition using microwave pyrolysis setting at the University of Melbourne, Dookie campus following the procedure described in (Kaudal et al., 2018). In this process, organic materials (~1.7 kg of raw food waste per batch and in a total of 9 batches and ~3 kg of biosolid per batch and a total of 6 batches) were placed into a tray. About 5% sawdust (*Eucalyptus Regnans)* biochar was added as microwave susceptor (in first batch only and then used the produced own biochar in subsequent batches) and intimately mixed before placing in a 6kW microwave chamber to trap the heat and initiate the reaction. After completion of the heating cycle, product was considered as food waste biochar (FWB) and biosolid biochar (BSB) (Figure 4.1C).


Sample preparation for pyrolysis
Mixing of saw dust biochar
Microwave pyrolysis chamber
Pyrolysis process: sample putting into the chamber and cooling down process at the end of each run
Food waste biochar (FWB)
Biosolid biochar (BSB)

Figure 4.1 C: Steps of preparation of biochar using a microwave pyrolysis setting.

Compost: Compost was produced from a different feedstock to that used for FWR and BSR and therefore FWC and BSC cannot be considered as a production sequence. This was a deliberate strategy owing to the constraints of producing a compost at a small scale with acceptable certainty.

The food waste compost and biosolid compost were collected from commercial operations: Geelong compost, Geelong, Victoria, Australia for food waste and; Gippsland water, Gippsland, Victoria, Australia, for biosolid. At Geelong, food waste compost (FWC) was prepared in a windrow composter and consisted of 80% recycled green organics, 5% fruit waste (pulped fruit from a fruit juice manufacturer), 10% sugar mud (a bi-product of the sugar processing industry) and 5% poultry manure (with rice hulls bedding). At Gippsland, biosolid compost (BSC) was prepared in a combination of in vessel and open windrow composting setting and consisted of green waste and other organic waste. The precise makeup of this product was not disclosed for commercial reasons.

4.2.3 Chemical characterization procedure of organic amendments

The oven-dried OA (≤ 2 mm) was chemically characterized by determining pH (H_2O), electrical conductivity (EC) and Olsen P following methods 4A1, 3A2 and 9C2a, as described in (Rayment and Lyons, 2011), respectively. Total C and N (≤ 0.5 mm in size) were determined by a high-frequency induction furnace LECO (Trumac CN analyzer). Total elemental concentration was determined following an Aqua Regia digestion method: about 0.25± 0.01 g samples (≤ 0.5mm) were placed into a 50 mL Greiner Polypropylene centrifuge tubes. 1.9 mL of concentrated nitric acid, 0.65 mL concentrated hydrochloric, followed by 0.5 mL 30% hydrogen peroxide was added, and the tubes were capped and vortexed for 10 seconds and then left overnight for pre-digestion. The tubes were heated on a digestion block at 80° C for 30 minutes and the built-up pressure was released by removing the cap slowly. The cap was then firmly reseated and the temperature was increased to 122° C until the samples were completely bleached. Once the digestion was completed the tubes were cooled down to room temperature and diluted to 25 mL using Milli Q water. The digested extract was analyzed for the total elements (P, Al, Fe, Zn, Mn, Ca, Mg, Na, K and S) using an ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) (Perkin Elmer Optima 8300 DV-radial view).

The quality of the chemical analysis was controlled either by using external reference materials (both soil and plant samples) from the Australian Soil and Plant Analysis Council (ASPAC) or by using internal standards. The extraction efficiency and recovery rate were taken into consideration during data processing.

4.2.4 Nuclear Magnetic Resonance (NMR) characterization of organic amendments

Solution-state ^{31}P NMR

To prepare the sample for solution-state ^{31}P NMR, all the OA (≤ 0.5 mm in size) were extracted using 0.25 M NaOH and 0.05 M EDTA solution at 1:20 sample to solution ratio following the method described in Turner (2004) and Mackay et al. (2017). The extract was centrifuged at 4500 rpm for 20 minutes and filtered through Whatman no. 42 filter paper to collect the supernatant. About 30 ml of aliquot was immediately frozen using liquid nitrogen and freeze-dried. After freeze-drying, 150 mg of sub-sample was ground and re-dissolved in 1.5 ml of deionized water in a 2 ml Eppendorf tube. This was then centrifuged at 1300 g for 20 min. Precisely 0.7 ml of aliquot of the supernatant was placed in a 5 mm NMR tube with 80 µL of deuterium oxide for analysis in the NMR. Methylene diphosphonic acid solution was added as an external standard at the rate of 6 g L^{-1}. The spectra were acquired at 25 °C on an Agilent 500 MHz Solution-state ^{31}P NMR spectrometer at a ^{31}P frequency of 202.34 MHz with a recovery delay of 26 seconds. A 90° pulse of 23 µs was used with an acquisition time of 1 s and broadband ^{1}H decoupling. 50,000 scans were acquired for each sample. The spectra were processed with a 5 Hz line broadening. The instrument (solution-state ^{31}P NMR spectrometer) was based at the Bio21, The University of Melbourne, Parkville campus.

Solid-state ^{13}C NMR study

Finely ground (≤ 0.5 mm) materials were used for solid-state ^{13}C NMR study following the method described in Mackay et al. (2017). Solid-state ^{13}C cross-polarization (CP) NMR spectra were acquired with magic angle spinning (MAS) at a ^{13}C frequency of 150.33 MHz on an Agilent 600 MHz spectrometer. Samples were packed in a 4.2 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 10 kHz. Spectra were acquired using a cross-polarization pulse sequence (tancpx). 1 ms contact time and 1 second of recycling delay were used and 100,000 transients were collected for each spectrum. All spectra were processed with a 50 Hz Lorentzian line broadening. Chemical shifts were externally referenced to the methyl resonance of Adamantane (Morcombe and Zilm, 2003). All spectral processing was completed using Bruker TopSpin 3.6 software.

The following chemical shifts were used to provide estimates of broad carbon types: 0-45 ppm (alkyl C), 45-60 ppm (Methoxyl and N-alkyl C), 60-110 ppm (O-alkyl C), 110-145 ppm (aryl C), 145-165 ppm (O-aryl-C), and 165-215 ppm (carbonyl C). Signal intensity found in spinning sidebands was allocated back to their parent resonances according to the calculations presented by Baldock and Smernik (2002). The instrument (solid-state ^{13}C NMR spectrometer) was based at Bio21, The University of Melbourne, Parkville campus.

4.3 Results

4.3.1 Chemical characterization of organic amendments

The chemical characterization of OA (on an oven-dry basis) are presented in Table 4.1. The pyrolysis had a relatively greater impact on food waste substrate compared to the biosolid substrate. Pyrolysis increased the pH, total C and total P in FWB relative to FWR, whereas BSB showed very little to no effect compared to BSR. Similarly, pyrolysis markedly decreased the Olsen P concentration in FWB compared to FWR and slightly in BSB than BSR. In case of FWC and BSC, the greatest difference was observed in total Al, Fe and Mg content compared to FWR, FWB, BSR and BSB due to having different feedstock materials. FWC had a higher Al, Fe, Ca and Mg content compared to FWR and FWB, whereas was lower in case of BSC compared to BSR and BSB.

Table 4.1: Selected chemical characterization of organic amendments (oven dried mass basis).

Parameters	Units	Food waste			Biosolid		
		FWR^1	FWB^1	FWC	BSR^2	BSB^2	BSC
pH (H_2O)		4.33	9.95	6.67	6.34	6.37	6.81
EC	dS/m	5.96	5.85	7.80	2.34	2.18	6.66
Olsen P	mg/kg	1729	455	695	433	409	463
Total C	%	42.6	67.8	17.9	9.0	9.1	25.0
Total N	%	1.36	2.38	2.13	1.48	1.38	2.40
Total P	mg/kg	1975	6204	5507	19053	20490	6056
Total Al	mg/kg	72	275	8416	43586	50215	5888
Total Fe	mg/kg	46	242	13897	19991	25848	7266
Total Zn	mg/kg	14	102	246	274	275	228
Total Mn	mg/kg	18	59	242	399	402	201
Total Ca	mg/kg	3922	14547	27619	10759	12356	19580
Total Mg	mg/kg	1157	3115	5693	5117	5614	4013
Total Na	mg/kg	1368	4194	2216	725	977	3155
Total K	mg/kg	17033	44511	11708	4393	5624	10338
Total S	mg/kg	898	1452	2865	3008	3074	4916

^{1} (Food waste) and ^{2} (Biosolid) processed from similar feedstock materials.

4.3.2 Identification of forms of P in the organic amendments

The solution-state ^{31}P NMR spectrometer identified orthophosphate, orthophosphate monoesters, pyrophosphate and phospholipid compounds from OA in this study (Figure 4.2).

In FWR, the dominant forms of P compound were orthophosphate monoesters P (89.25%) followed by orthophosphate (10 %), phospholipid (0.34%) and pyrophosphate (0.28%) (Table 4.2). Pyrolysis of food waste substrate converted all the P monoesters compounds of FWR (89%) to orthophosphate (93 %) in FWB, which was the dominant form P. It was also interesting to note that biochar materials contained a higher amount of pyrophosphate (6.73% in FWB) compared to other processed forms of organic materials used in this experiment (Table 4.2).

There was little to no effect of pyrolysis on biosolid materials observed. In biosolid materials, orthophosphate and orthophosphate monoesters peaks were overlapped with each other (Figure 4.2) due to having a high metal concentration in the biosolid materials, which affected the NMR signals. The presence of Fe and other metal species at higher concentrations might exert a paramagnetic effect in NMR signals by affecting instrument relaxation and surface relaxivity (Keating and Knight, 2010). In FWC and BSC, the dominant forms of P compounds were orthophosphate, followed by orthophosphate monoesters and pyrophosphate.

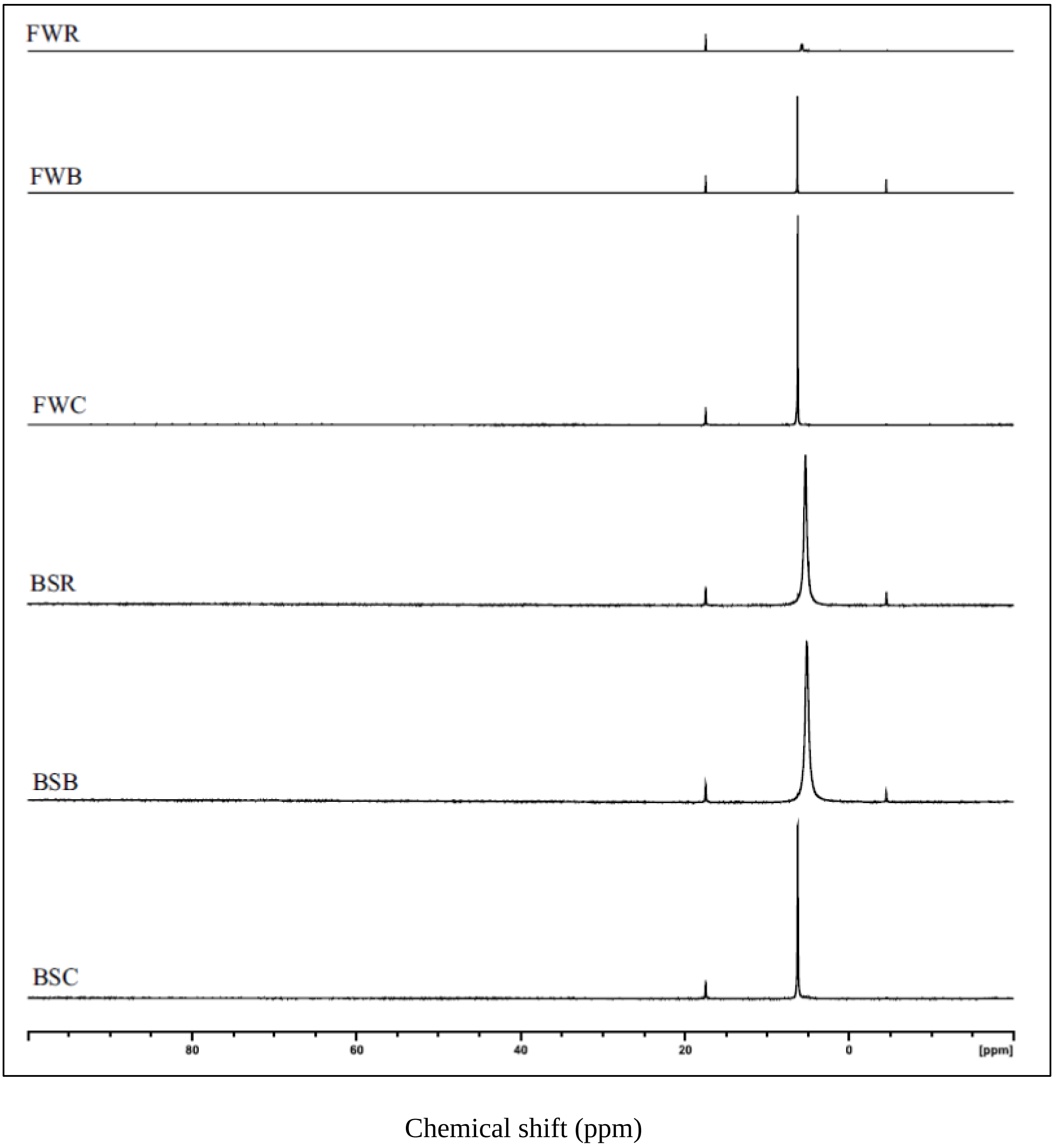


Figure 4.2: Solution-state ^{31}P NMR spectra of the organic amendments used for identifying different forms of P compounds following the chemical shift assigned for Orthophosphate at 6.2 ppm, orthophosphate monoesters at of 5.5 to 4.8 ppm, phospholipid at 0.5 to 1.9 ppm and pyrophosphate was at -4.5 to -4.7 ppm as described in Turner (2004). The height of the peak was not standardized among different materials.

Table 4.2: The abundance of the identified P compounds in organic amendments using solution-state ^{31}P NMR. The abundance of P compounds was calculated in percentage from the total P determined by NMR spectroscopy.

OA	Food waste			Biosolid		
P compounds	FWR	FWB	FWC	BSR	BSB	BSC
Orthophosphate (%)	10.13	93.12	99.63	99.24[b]	99.43[b]	94.64
Monoester (%)	89.25	0.15	0.24			5.16
Pyrophosphate (%)	0.28	6.73	0.12	0.76	0.57	0.20
Phospholipid (%)	0.34	-	-	-	-	-
Total P (mg/kg)[a]	1975	6204	5507	19053	20490	6056
P Extraction Efficiency (%)[c]	97	44	90	101	95	94

[a] Total P extracted by NaOH-EDTA and determined using an ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) (Perkin Elmer Optima 8300 DV-radial view).

[b] In BSR and BSB, the spectra of orthophosphate and monoester were overlapped and presented together here.

[c] P Extraction efficiency by NaOH-EDTA was calculated by comparing with total P of OA extracted by aqua regia digestion.

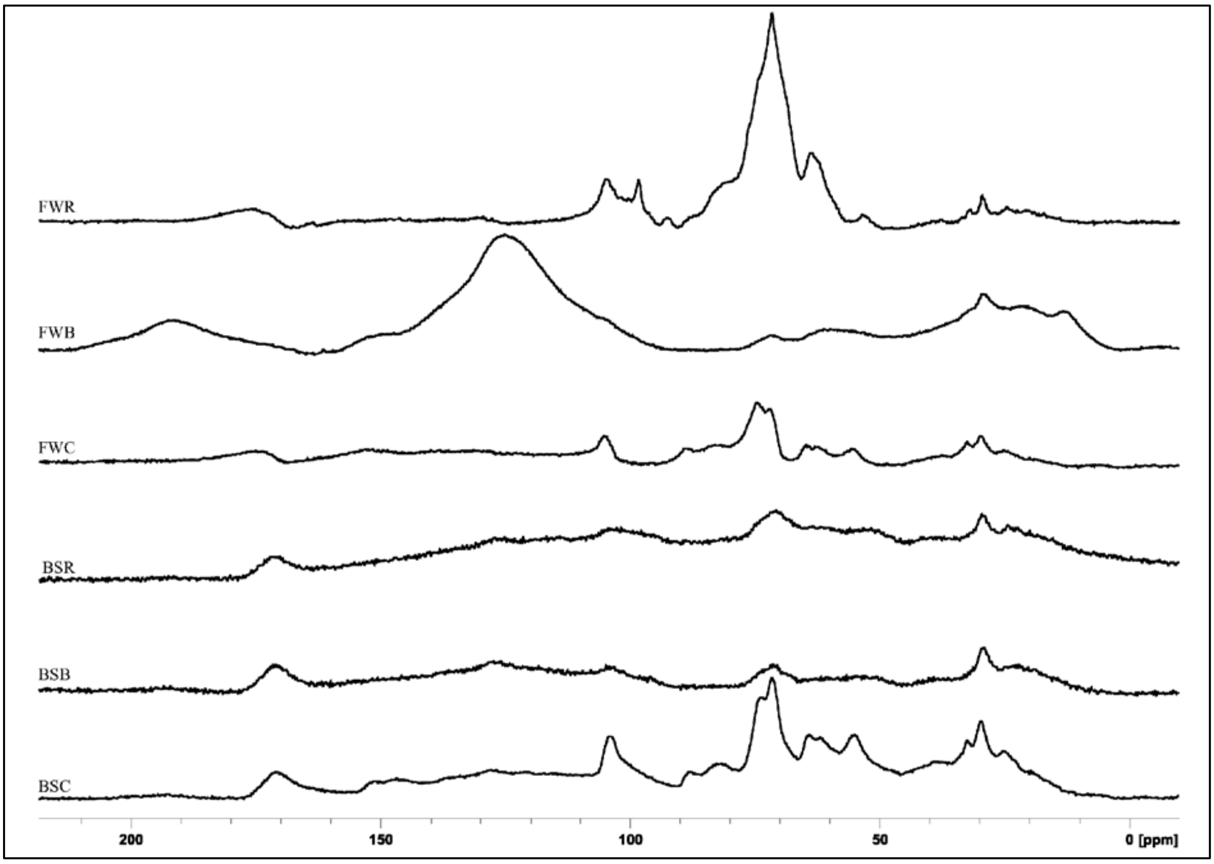
4.3.3 Identifying the forms of C of organic amendments

The solid-state ^{13}C NMR identified alkyl C (represents aliphatic lipids, fatty acids and waxes), methoxyl and N-alkyl C (methoxyl function of lignin components, amino acids and amino sugars), O-alkyl C (oxygenated C in carbohydrate which includes sugars and polysaccharides), aryl C (alkyl-substituted aromatic compounds), O-aryl C (phenolic compounds), carbonyl C (carboxylic, amide and ketone compounds) (Spaccini et al., 2012, Albrecht et al., 2008, Baldock and Smernik, 2002) in all the OA (Figure 4.3).

The O-alkyl C (sugars and polysaccharides) (88.1%) was the major C form in FWR with the alkyl C to O-alkyl C ratio of 0.1 (Table 4.3). Pyrolysis of FWR decreased the abundance of O-alkyl C and increased the abundance of alkyl C, N-alkyl C, aryl-C (aromatic), O-aryl C (phenolic) and carbonyl C forms in FWB (Table 4.3). In FWB, the major form of C was aryl C (aromatic) (46.3%) followed by alkyl C (24.3%), N-alkyl C (4.7%), phenolic (2.7%) and carbonyl C (11.3%), with phenolic to carbonyl C ratio of 2.3 and alkyl C to O-alkyl C ratio of 0.9.

Similar to FWR, the abundant C form was O-alkyl C (sugars and polysaccharides) (38.9%) in the BSR with the alkyl to O-alkyl C ratio 0.6. Pyrolysis of the BSR reduced the alkyl C, N-alkyl C and O-alkyl C and increased the aryl C (aromatic) (27.8%), O-aryl C (7.8) and carbonyl C (10.3) content in BSB (Table 4.3). In FWC and BSC, the major form of C was O-alkyl C (sugars and polysaccharides) 4 with the alkyl C to O-alkyl C ratio of 0.2 and 0.6, respectively (Table 4.3).

Amongst all the OA, the highest abundance of carbonyl C was observed in BSB (10.3%) and the highest abundance of phenolic C was observed in FWC (10.5%). Together phenolic C and carbonyl C abundance were highest in the FWC (18.7%) followed by BSB (18.1%), FWB (14%), BSC (9.4%) and FWR (4.1%) (Table 4.3).



Chemical shift (ppm)

Figure 4.3: Solid-state ^{13}C NMR spectra of the organic amendments used for identifying different forms of C following the chemical shift to provide estimates of broad carbon types: 0-45 ppm (alkyl C), 45-60 ppm (N-alkyl C), 60-110 ppm (O-alkyl C), 110-145 ppm (aromatic C), 145-165 ppm phenolic C), and 165-215 ppm (carbonyl C). The height of the peak was not standardized among different materials.

Table 4.3: The abundance of the forms of C in organic amendments identified using solid-state ^{13}C NMR spectroscopy. The abundance of each C form was calculated as a percentage from the total C detected in the ^{13}C NMR spectroscopy.

Organic amendments (OA)	alkyl-C (%)	Methoxyl and N-alkyl C (%)	O-alkyl C (%)	aryl C (%)	O-aryl C (%)	Carbonyl C (%)	Total Phenolic and Carbonyl C (%)[a]	Ratio of Phenolic to Carbonyl C	Ratio of alkyl to O-alkyl C[b]
Chemical shift (ppm)	0-45	45-60	60-110	110-145	145-165	165-215			
FWR	5.9	0.4	88.1	1.6	0.1	4.0	4.1	0.03	0.1
FWB	24.3	4.7	10.7	46.3	2.7	11.3	14.0	0.24	2.3
FWC	9.8	2.5	48.3	20.8	10.5	8.2	18.7	1.28	0.2
BSR	22.9	10.4	38.9	21.7	2.6	3.6	6.2	0.72	0.6
BSB	21.2	8.7	24.3	27.8	7.8	10.3	18.1	0.76	0.9
BSC	23.1	11.9	40.1	15.5	4.5	4.9	9.4	0.92	0.6

[a] Summation of phenolic and carbonyl C content of the OA identified from solid-state ^{13}C NMR.

[b] the ratio of alkyl to O-alkyl C was calculated from the C abundance presented in 0-45 ppm and 60-110 ppm, respectively following the method described in Baldock and Smernik (2002).

4.4 Discussion

4.4.1 The effect of processing of OA on the selected chemical properties

A direct comparison was only made between raw and biochar materials due to having similar feedstock materials compared to composted materials in this study. The pyrolysis of food waste and biosolid materials increased the pH, total C, P and other elemental concentrations and decreased Olsen P concentration (Table 4.1). The total N increased in FWB and decreased in BSB compared to FWR and BSR, respectively. Similar effect of the pyrolysis on organic materials (plant residues, animal manure and biosolid) was also observed in previous characterization studies (Li et al., 2018, Robinson et al., 2018, Yang et al., 2018).

The increase in pH was attributed to the decrease in acidic functional groups during the thermal treatment of organic materials (Dai et al., 2017, Song and Guo, 2012). The increase in the concentration of C, P and other elements was attributed to the loss of mass of the materials during pyrolysis in the form of volatile hydrocarbons, hydrogen ($H_{2)}$, carbon monoxides (CO) and carbon dioxide (CO_2) (Robinson et al., 2018). The increase in the C concentration was also attributed to the formation of stable C compounds especially aromatic C (Baldock and Smernik, 2002, Demirbas, 2004) which was further confirmed from the solid-state ^{13}C NMR analysis of the biochar materials (aryl and O-aryl C content) (Table 3.3). The increase in N concentration after pyrolysis in plant-derived materials and decreased in biosolid materials was may be due to the high labile form of N in biosolid. Similar results also observed in a previous study by (Robinson et al., 2018). Labile N content of OA vaporizes at a relatively low temperature with a peak at 200 (Surampalli et al., 2015) to 300° C (Baldock and Smernik, 2002) compared to other nutrients such as P at around 1000° C (Zhang et al., 2012). In this study, the biochar was produced at a temperature ranging from 550 to 600° C.

The decrease in the Olsen P was attributed to the formation of hydroxyapatite and oxyapatite during the pyrolysis process of the organic materials at a high temperature above 450° C (Li et al., 2018, Hunger et al., 2008). Hydroxyapatite and oxyapatite are usually absent in raw feedstock materials (Hunger et al., 2004) and likely to form during the pyrolysis process which is considered as non-labile in the sequential extraction of the P from organic materials (Li et al., 2018).

4.4.2 Changes in abundance of P compounds during different forms of processing of OA

The P extraction efficiency is an important factor to identify different forms of P in the OA using solution-state ^{31}P NMR. The P extraction efficiency of NaOH and EDTA was more than 90% for all the amendments in this study except for FWB (44%) (Table 4.2). A similar P extraction efficiency of NaOH-EDTA ranging from 46-86% was observed by Chen et al. (2004) and low extraction efficiency in the case of biochar (25%) by Stutter (2015) compared to other processed forms of OA such as compost, manure and anaerobic digest.

The lowest orthophosphate content and highest monoesters content was observed in FWR compared to all other materials used in this study (Table 4.2). A similar higher abundance of phospho-esters was reported in a study by Idowu et al. (2017) for having high lipid content in food waste materials.

A greater abundance of orthophosphate content after the pyrolysis ranging from 10% in FWR to 93% in FWB (Table 4.2) was identified in this study. The pyrolysis of food waste reported to convert phosphoesters to orthophosphate in a previous study by (Idowu et al., 2017).The conversion of organic P to inorganic P (orthophosphate) ranging from from 67 to 99% during the pyrolysis of organic materials has also been reported in previous studies (Li et al., 2018, Huang et al., 2017). The pyrolysis of the organic materials also increased the abundance of pyrophosphate compound in this study. The polymerization of orthophosphate to form pyrophosphate during the pyrolysis process has also been reported (Xu et al., 2016).

It was interesting to observe that, the abundance of the orthophosphate increased in the biochar processed forms of organic materials compared to their raw form, but the Olsen P content decreased. As discussed earlier, this was maybe due to the formation of less bioavailable metal orthophosphate compounds such as Al, Fe, Ca and Mg phosphate during the pyrolysis of organic materials at elevated temperature (Rose et al., 2019, Li et al., 2018). In some recent studies, the use of X-ray absorption near edge structure (XANES) spectroscopy identified the formation of less water-soluble P compounds in biochar such as octacalcium phosphate (Hunger et al., 2008), variscite (Al-phosphate) (Rose et al., 2019), hydroxyapatite (Robinson et al., 2018) as new dominant forms of P.

The composted product of the food waste and biosolid used in this study was rich in orthophosphate content. A similar higher abundance of orthophosphate was found in food waste compost by Stutter (2015) and in sewage sludge compost by Galvez-Sola et al. (2010).

4.4.3 Changes in abundance of the forms of C during different processing of OA

In this study, the pyrolysis of the OA changed the abundance of the different forms of C compared to their raw materials as identified by solid-state ^{13}C NMR spectroscopy (Figure 4.3 and Table 4.3). Similar to the chemical characterization of the OA, pyrolysis had a greater impact on food waste substrate to change the abundance of forms of C compared to the biosolid substrate (Table 4.3).

The greater decrease in the abundance of O-alkyl C from 88% to 10.7% and increase in alkyl C (from 5.9 to 24.3 %), aryl C (1.6 to 46.3%), O-aryl C (0.1 to 2.7%) and carbonyl C (4 to 11.3%) was observed in FWB compared to FWR (Table 4.3). A similar trend of decrease in O-alkyl C and increase in the alkyl, N-alkyl, aryl, O-aryl and carbonyl C was observed in some recent studies after the pyrolysis of the olive mill waste (Marra et al., 2018) and food waste (Lee et al., 2017). The O-alkyl C (61-110 ppm) usually represents the sugars and polysaccharides compounds in the OA which are the labile forms of C compounds that can quickly convert to the more stable C forms (aromatic C) during the heating process of biochar production (Almendros et al., 2003). An augmentation in the alkyl C region was observed when olive mill waste was heated at 300° C and a gradual increase in the aromatic region (aryl C and O-aryl C) was observed when heated to 500° C to 1000° C (Marra et al., 2018). This may explain the reason for decrease in O-alkyl C (sugars and polysaccharides) abundance in FWB and increase in alkyl and aromatic C (aryl C and O-aryl C) region after pyrolysis at 550-600° C compared to FWR in this study.

In the composted materials, FWC and BSC, the abundance of O-alkyl, N-alkyl and alkyl C was greater compared to aryl and O-aryl C. A recent study by Mayans et al. (2019) has also shown the higher abundance of this aliphatic C (O-alkyl, N-alkyl and alkyl C) forms compared to the aromatic C (aryl and O-aryl C) forms in pruning waste compost, pine bark compost, vermicompost and sheep and horse manure compost. Furthermore, during the composting process the conversion of the aliphatic compounds (O-alkyl, N-alkyl and alkyl C) to aromatic (aryl C), phenolic (O-aryl C) and carboxylic (carbonyl) compounds have been reported (Tapia et al., 2010, Spaccini and Piccolo, 2008, Chefetz et al., 1996). This may be the reason for having higher aryl (from 1.6 to 20.8%) and O-aryl C (from 0.1 to 10.5%) and lower O-alkyl C (from 88.1 to 48.3%) compounds in FWC compared to FWR (Table 4.3). However, it is important to note that, FWC and BSC had a different feedstock compared to FWR and BSR, respectively and therefore the comparison may not be valid and also this is may be why, BSC did not follow the decreasing trend in the abundance of O-alkyl and increasing trend in aryl C abundance while comparing with BSR.

The carbonyl C range (165 to 215 ppm) includes the carboxylic, amide, aldehyde and ketone compounds. However, in this study, the presented ranges for carbonyl C (165 to 215 ppm) compounds will be considered as carboxylic compounds. Because the absence of amide, aldehyde and ketone compounds in organic materials (Al-Faiyz, 2017) has been reported. No signal of amide, aldehyde and ketone compounds were also found in olive mill waste and olive mill waste biochar (Marra et al., 2018). A very recent study also demonstrated a complete absence of amide, aldehyde and ketone compounds in the pruning waste compost, vermicompost, and sheep and horse manure compost and a negligible amount (1.6%) in pine bark compost (Mayans et al., 2019). GCMS (gas chromatography and mass spectroscopy) analysis of the selected FWR, FWB, BSR and BSB also could not detect any aldehyde or ketone compounds in this study (appendix 1).

4.5 Conclusions

The primary aim of this work was to produce materials from two different feedstocks with differing combinations of organic functional groups. This was not achieved due to having different feedstock materials between biochar and compost. The comparison was made only between raw and biochar materials due to the use of similar feedstock materials.

The nutrient concentrations and forms of C and P compounds changed with the origin (Food waste vs Biosolid) and processing (raw vs biochar vs compost) of the organic amendment. The nutrient and total metal concentrations were higher in the biosolid materials compared to the food waste materials. The aromatic C compounds (aryl and O-aryl C) were abundant in the biochar materials (FWB and BSB) and the aliphatic C compounds (O-alkyl, N-alkyl and alkyl C) were abundant in the raw and composted materials (FWR, FWC, BSR and BSC). The processing of raw materials to biochar and compost increased the inorganic forms of P (orthophosphate). However, the bioavailability would be dependent on the actual P species present.

The abundance of organic anion producing C compounds (phenolic and carbonyl) was changed with the processing of organic materials to biochar and compost. The effect of these different organic materials with different abundance of phenolic and carbonyl on P availability in a P limiting soil will be studied in the next Chapter 5 and also their effect on plant P uptake in Chapter 7.

Chapter 5: Phenolic and carbonyl C contents of organic amendments might predict P availability in an acidic soil

5.1 Introduction

Plant availability of P is very limited in acidic soils due to the formation of insoluble phosphate complexes with soil cations (especially Fe and Al) (Price, 2006, Juo and Franzluebbers, 2003, Glendinning, 2000, White, 1981). This is a global concern because around 50% of the world's agricultural lands are acidic (Von Uexküll and Mutert, 1995) and many of these lands exist in developing countries. Organic acids (both carboxylic and phenolic) have been reported to increase soil P availability (Chapter 2). Organic anions, the dissociation product of the organic acids have been reported to take part in the ligand exchange reactions to substitute cation fixed P and also to bind with P sorption sites by forming complexes with soil cations (Al and Fe) (Hu et al., 2005b, Bolan et al., 1994, Hue, 1991, Violante et al., 1991, Hue et al., 1986).

Organic amendments (OA) have been reported as one of the sources of organic acids in soil (Piškur et al., 2009) and a large body of literature supports the positive effect of OA addition to increase P availability in acid soil (meta-analysis in Chapter 3) by substituting previously fixed P, blocking of P sorption sites through complexation of metal ions by the action of organic anions (Huang, 2004, Hansen and Strawn, 2003, Siddique and Robinson, 2003, Bolan et al., 1994, Martinez et al., 1984,).

Both phenolic and carbonyl C represent a major source of organic acids in OA. Lignin, lignin-cellulose complexes, flavonoid and tannins represent the main phenolic compounds in organic materials (Berg and McClaugherty, 2008, Siqueira et al., 1991), and these go through a series of slow degradation processes to produce phenolic acids as an end product (Siqueira et al., 1991). Carbonyl C includes carboxylic and amide compounds in OA. Carboxylic compounds are composed of high and low molecular weight aliphatic organic acids (Adeleke et al., 2017).

To date, many studies have been conducted and demonstrated the positive effect of OA on P availability upon addition to soil (meta-analysis, Chapter 3), but no studies have attempted to relate organic anion producing C content of OA (phenolic and carbonyl) to soil P availability. This chapter aims to investigate the effect of OA on soil P availability and to understand if the phenolic and carbonyl C content have any relation with soil P availability. I hypothesize that the addition of the OA in acidic soil would increase soil P availability by both releasing native soil P, substituting previously fixed P and reducing soil P sorption through the formation of organometallic complexes and the phenolic and carbonyl C content of OA might be used to predict this behaviour.

In this study, I conducted a laboratory-based soil incubation study with a range of differently processed OA such as raw food waste (FWR), food waste biochar (FWB), food waste compost (FWC), raw biosolid (BSR), biosolid biochar (BSB) and biosolid compost (BSC) and determined their effect on soil pH, P availability (Olsen P), cation concentration (Mehlich 3 extractable Al and Fe) and soil P buffering capacity (PBC). Finally, to understand the relation between phenolic and carbonyl C content of OA on soil P availability, the changes in the soil Olsen P availability (ΔOlsen P, expected vs observed) and soil PBC (ΔPBC, treatment-control) were correlated with the phenolic and carbonyl C content of the OA.

5.2 Materials and Methods

5.2.1 Collection and processing of soil

A highly P fixing acidic cropping soil, Red Chromosol (Isbell, 2016) was collected from near Rutherglen, North East Victoria, Australia. This is the dominant acidic soil type within the agricultural zone of Victoria (Isbell et al., 1997) and also extensively used in previous P availability studies (Schefe and Tymms, 2013, Schefe et al., 2011, Schefe et al., 2009, Schefe et al., 2008).

The soil was collected from the top 0 to10 cm. The collected soil was then air-dried and sieved to < 2 mm using a cylinder grinder before further use. The soil electrical conductivity (EC), pH (H_2O), pH ($CaCl_2$), Olsen P, $CaCl_2$ extractable P and cation exchange capacity (CEC) were determined following the methods 3A2, 4A1, 4B2, 9C2a, 9F1 and 15D3 as described in (Rayment and Lyons, 2011), respectively. Total C and N ($\leq$ 0.5 mm in size) and other elemental concentrations (P, Al, Fe, Zn, Mn, Ca, Mg, Na, K and S) were determined following the method described in Chapter 4 under the subsection of 4.2.3. The results from the chemical characterization of the soil presented in Table 5.1.

5.2.2 Collection and characterization of organic amendments

The different processed forms of food waste and biosolid (raw, biochar and compost) were used as sources of OA in this study. The collection, processing and characterization procedure of raw food waste (FWR), food waste biochar (FWB), food waste compost (FWC), raw biosolid (BSR), Biosolid biochar (BSB) and biosolid compost (BSC) were presented in Chapter 4 under the subsections 4.2. The characterization results of OA were presented in Chapter 4 under subsection 4.3.

Table 5.1: Selected chemical properties of Rutherglen soil.

Parameters	Values
pH (H_2O)	4.60
pH ($CaCl_2$)	3.80
EC (dS/m)	0.04
CEC (cmol(+)/kg)	3.93
Olsen P (mg/kg)	14.30
$CaCl_2$ P (mg/kg)	0.17
Total C (g/kg)	14.80
Total N (g/kg)	1.30
Total P (g/kg)	0.23
Total Al (g/kg)	7.84
Total Fe (g/kg)	12.91
Total Zn (mg/kg)	30
Total Mn (mg/kg)	480
Total Ca (mg/kg)	134
Total Mg (mg/kg)	386
Total Na (mg/kg)	17
Total K (mg/kg)	992
Total S (mg/kg)	100

5.2.3 Incubation experiment with organic amendments

In this study, about 100 g of soil was incubated in a 250 mL plastic vial for 110 days with (FWR, FWB, FWC, BSR, BSB and BSC) or without the addition of OA (control) at the rate of 0.5 g C, which resulted in the addition of different amounts of N and P in the soil (Table 5.2). The rate of OA addition in this study was selected from the preliminary experiment in Appendix 2, where the maximum increase in soil P availability was observed with the addition of 0.5 g C to the soil from compost, biochar and biosolid (Figure A2.1 and Figure A2.3).

Vials were incubated at 20° C with moisture content at 70% of soil water holding capacity (WHC). In order to stabilize microbial activity, all vials were pre-incubated with only miliQ water for 7 days prior to adding treatments (a total of 112 incubation vials). After the pre-incubation, all the treatments were added and mixed well before capping the vials and placing them into the incubator. Vials were destructively sampled at 7, 30, 60 and 110 days. Each sample collection date had a separate control treatment and all the treatments had 4 replications. All the vials were aerated and watered regularly to maintain a similar aerobic condition throughout the experiment (Figure 5.1). At each time point of sample collection, the soil was oven-dried (40° C) overnight before chemical analyses. A subsample of the dried soil was used to determine the effect of OA addition on soil pH ($CaCl_2$), plant-available P (Olsen P) and Mehlich-3 (M3) extractable soil Al and Fe concentration following the methods described under subsection 4.2.1. The M3 extractable Al and Fe were determined following the method 18F1 described in (Rayment and Lyons, 2011).

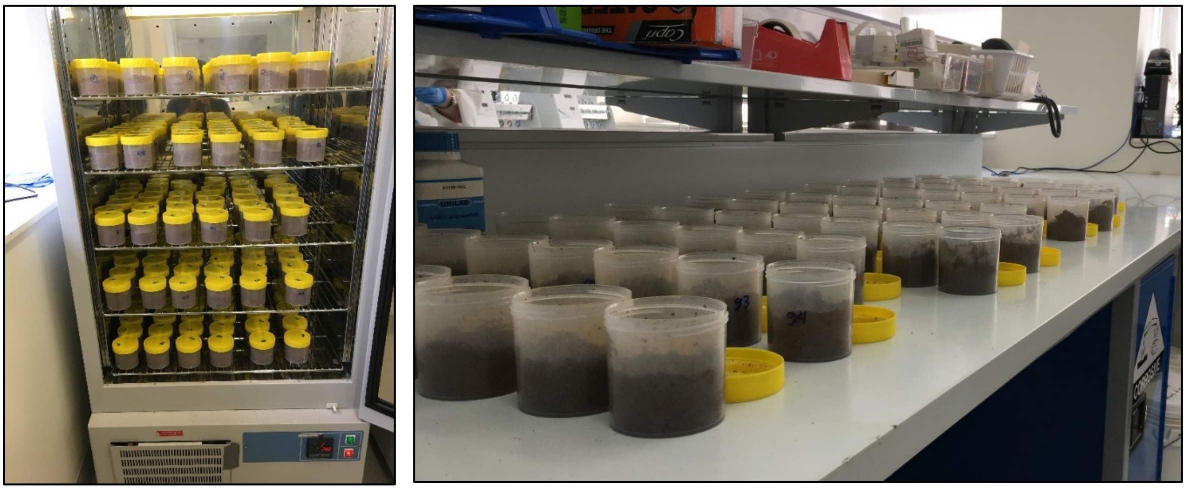


Figure 5.1: Incubation experiment setup (left) and regular watering and airing steps (right).

Table 5.2: Amount of organic amendments added per incubation vial and the resultant addition of C, N and P.

Organic amendments (OA)*	Total OA added (g)	Total C added (mg)	Total N added (mg)	Total P added (mg)	C:N	C:P
FWR	1.2	498	15.9	2.3	31.3	216.2
FWB	0.7	495	17.4	4.5	28.5	109.4
FWC	2.8	500	59.4	15.3	8.4	32.6
BSR	5.6	500	82.4	106.4	6.1	4.7
BSB	5.5	501	75.9	112.8	6.6	4.4
BSC	2	500	48.0	12.2	10.4	41.0

*FWR: Raw food waste, FWB: Food waste biochar, FWC: Food waste compost, BSR: Raw biosolid, BSB: Biosolid biochar, BSC: Biosolid compost

5.2.4 Determination of soil phosphorus buffering capacity (PBC)

Soil PBC was determined following the modified method of 9J2 described in Rayment and Lyons (2011). About 2.5 g of oven-dried incubated soil (all treatments) was placed into a 50 mL centrifuge tube and 25 ml of 0.01 M $CaCl_2$ solution containing differing concentrations of P (KH_2PO_4) ranging from 0, 10, 20, 40 and 80 mg/L was added. Two drops of chloroform were added to suppress microbial growth. Then it was shaken for 17 h using an end-over-end shaker, centrifuged and filtered (Whatman no 5 filter paper) to collect the supernatant. The phosphate concentration in the supernatant was determined colorimetrically following Murphey and Riley (1962) method using a segmented flow analyzer (SFA) (Skalar SAN++). P sorption was calculated according to Equation 5.1.

$$\text{P adsorbed (mg/kg)} = (C_0 - C_e) \times \text{V/M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

Where, C_0 and C_e were the initial phosphate concentration and phosphate concentration in the supernatant (mg L^{-1}), respectively. V represents the volume of solution (mL) and M is the mass of the soil taken (g).

Soil Phosphorus Buffering Capacity (PBC) was calculated by plotting P adsorbed (mg/kg) on Y-axis against $\log_{10}C_0$ (initial P concentration) and fitted with a linear equation. The slope of the linear fitting was presented as PBC in mg/kg/$\log_{10}$mg/L, as described in (Rayment and Lyons, 2011).

5.2.5 Statistical analysis

Data were statistically analyzed by analysis of variance (ANOVA) following a general linear model using the software package Minitab 18 (Akers, 2018). Treatment means were separated using the least significant difference (LSD) value at a 5% level of probability at a specific sample collection point. Pearson’s correlation coefficient was used in correlation studies.

5.3 Results

5.3.1 Effect of organic amendments on soil pH

The addition of all the organic amendments significantly ($P \leq 0.05$) increased soil pH (3.9 to 4.7) relative to the control (3.7 to 3.8) across all the points of sample collection (Figure 5.2). No significant difference was observed in soil pH between raw and biochar of both food waste and biosolid substrates most of the time. In composted materials, FWC and BSC significantly increased the soil pH compared to control at each point of sample collection. The peak pH increase was observed at 30 days of incubation by all the OA treatments.

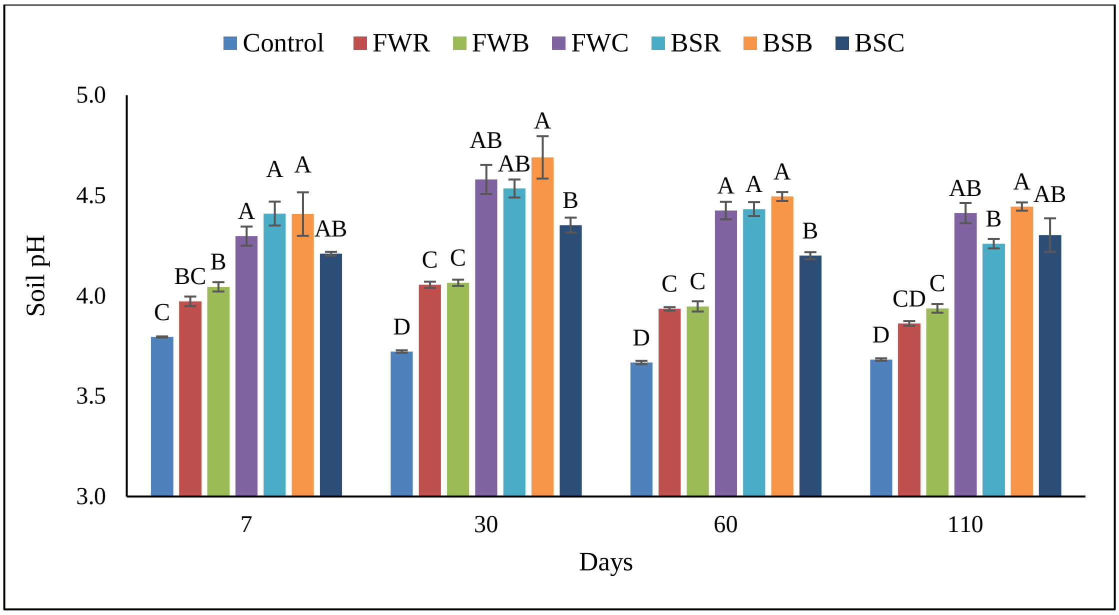


Figure 5.2: Effect of organic amendments on soil pH across all the points of sample collection. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

5.3.2 Effect of organic amendments addition on soil Olsen P

The addition of all the organic materials significantly ($P \leq 0.05$) increased soil Olsen P at all times relative to the control except for FWR and FWB (Figure 5.3). The FWR and FWB did not show any significant difference on soil Olsen P compared to control at any time. FWC had a significant ($P \leq 0.05$) increase of soil Olsen P at all the time points among all the food waste processed materials. In case of biosolid materials, among BSR, BSB and BSC no significant difference was observed initially (7 days) and later the highest Olsen P increase was observed by BSB at 30 and 110 days and by BSR at 60 days. BSC always had the least effect on soil Olsen P among all the biosolid processed materials in 30, 60 and 110 days. It is interesting to observe that no significant difference was observed initially among FWC, BSR, BSB and BSC in most of the cases at 7 and 30 days. In 60 and 110 days, the soil Olsen P was significantly increased by the BSR and BSB compared to FWC and BSC. In most of the cases, no significant difference was also observed between FWR and FWB; BSR and BSB (except 60 days) and FWC and BSC at any time.

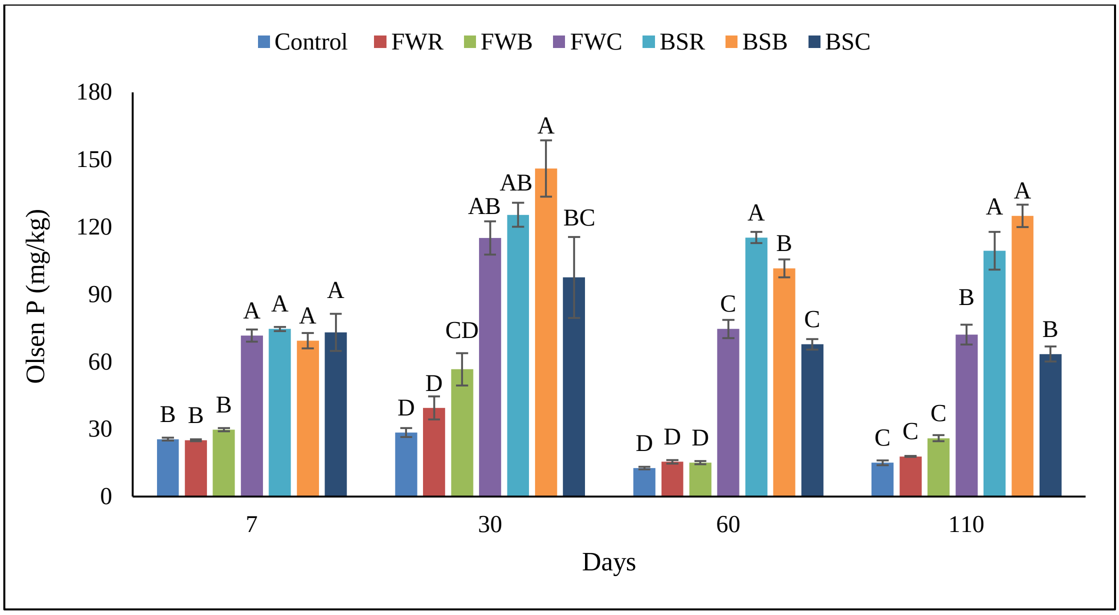


Figure 5.3: Effect of organic amendments on soil Olsen P across all the points of sample collection. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

5.3.3 Effect of OA on soil Mehlich-3 extractable cations (Al and Fe)

Compared with control all the OA significantly ($P \leq 0.05$) decreased M3 extractable Al concentration in soil at 7 days except BSR. The BSR had no significant ($P \leq 0.05$) difference in soil M3 extractable Al concentration at 7, 30 and 60 days compared with control. The soil M3 extractable Al was significantly ($P \leq 0.05$) decreased as observed by the FWR and FWC compared with control at all the time except by FWC at 110 days. The FWC showed no significant ($P \leq 0.05$) difference in M3 extractable Al concentration at 110 days compared to control. In 30, 60 and 110 days, compared to control, no significant ($P \leq 0.05$) difference on soil M3 extractable Al concentration by FWB, BSR, BSB and BSC was observed except at 110 days. At 110 days, BSR and BSB significantly increased ($P \leq 0.05$) M3 extractable Al concentration compared with all the treatments.

Similar to soil M3 extractable Al concentration, the addition of OA significantly decreased the soil M3 extractable Fe concentration at 7 days. The FWR had a significant effect on decreasing soil M3 extractable Fe concentration at all the time compared to control and all other treatments. Compared to control, at 30 and 60 days, no significant difference was observed among any of the treatments except FWR. At 110 days BSR and BSB significantly increased the M3 extractable Fe concentration compared to all other treatments, whereas no significant difference was observed among control FWB, FWC and BSC.

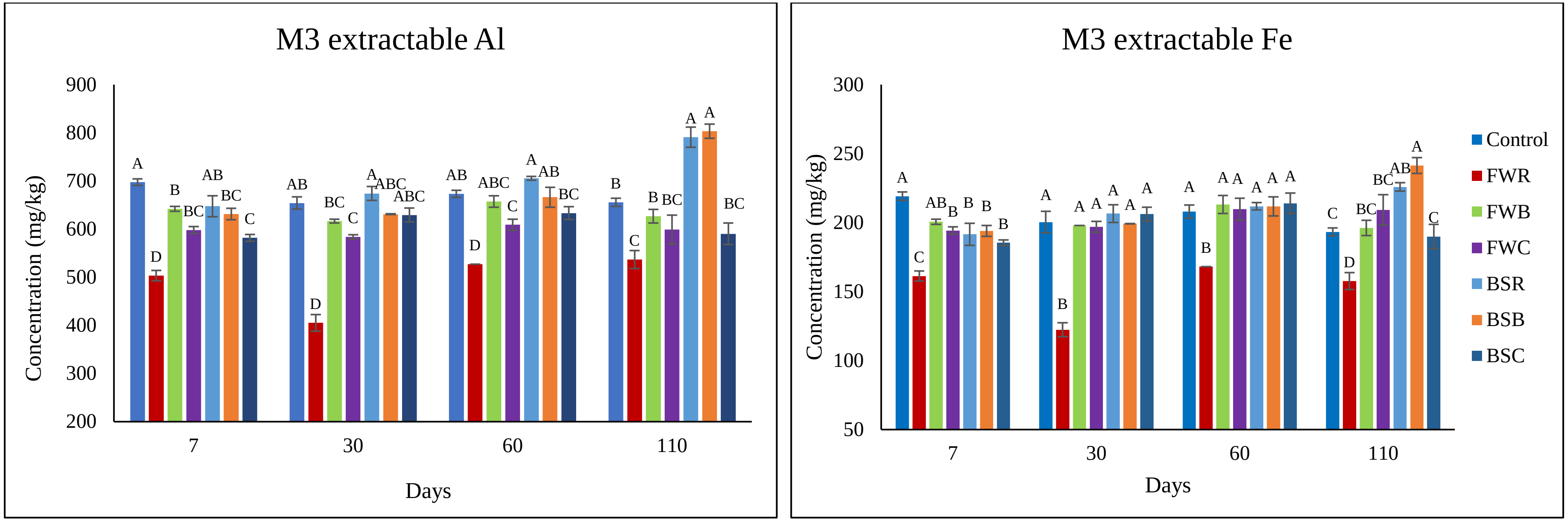


Figure 5.4: Effect of organic amendments on soil Mehlich-3 (M3) extractable Al and Fe concentration across all the points of sample collection. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

5.3.4 Effect of organic amendments on soil phosphorus buffering capacity

The addition of OA significantly decreased ($P \leq 0.05$) soil PBC at each time compared to control (Figure 5.5). Compared with all the processed forms of OA, the composted materials of both food waste (FWC) and biosolid (BSC) had the highest decrease in soil PBC. Between FWC and BSC, FWC significantly ($P \leq 0.05$) decreased soil PBC at all the time compared to BSC except 7 and 30 days. There was no significant ($P \leq 0.05$) difference was observed among FWR, FWB, BSR and BSB at any time except by BSB at 30 and 110 days. The BSB significantly decreased soil PBC at 30 and 110 days compared to FWR, FWB and BSR. It is also interesting to observe that the soil PBC showed a decreasing trend of varying degrees by all the treatment as incubation time progressed.

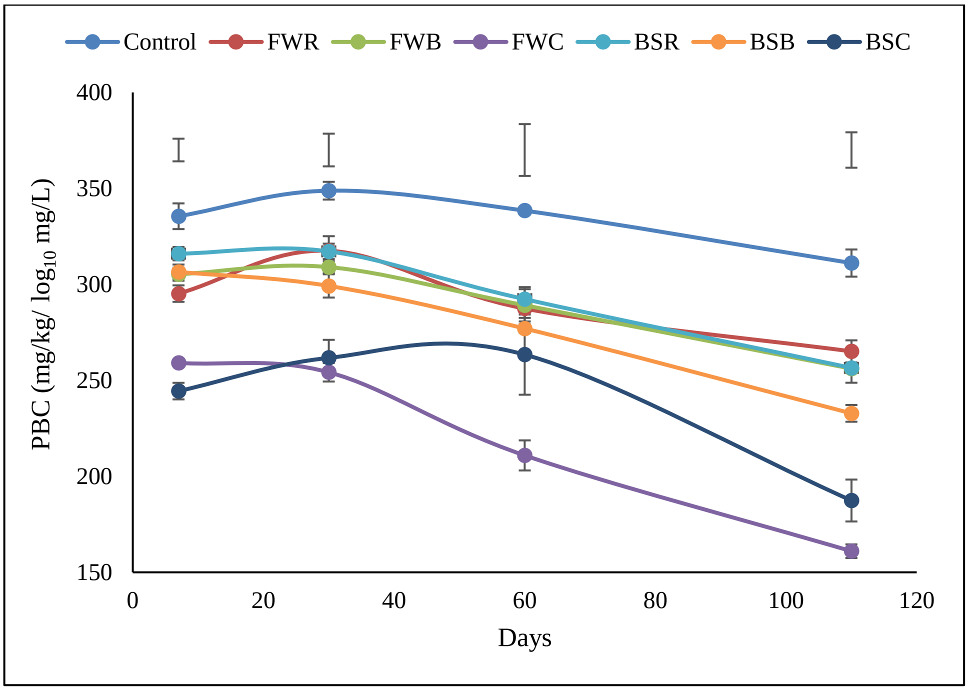


Figure 5.5: Effect of organic amendments on soil Phosphorus Buffering Capacity (PBC) at each time. The bar on each trend line representing standard error (n=4) and the bar on the top representing l.s.d at $P \leq 0.05$ at a point of sample collection.

5.4 Discussion

5.4.1 Effect of organic amendments on soil P availability

The addition of OA have been reported to increase soil pH (up to pH 6.5 to 7) with a concomitant increase in soil P availability in previous studies (Yan et al., 1996, Hue, 1992, Haynes and Swift, 1989, Ritchie and Dolling, 1985). In this study, the observed soil pH ranged from 3.7 to 4.7 throughout the experiment (Figure 5.2) which is still a zone for soil P fixation by the soil cations such as Al^{3+} and Fe^{3+} (Figure 5.6) (Penn and Camberato, 2019). Therefore, the change in native soil pH from 3.7 to 4.7 by the OA is unlikely to be the reason for increased soil P availability in this study.

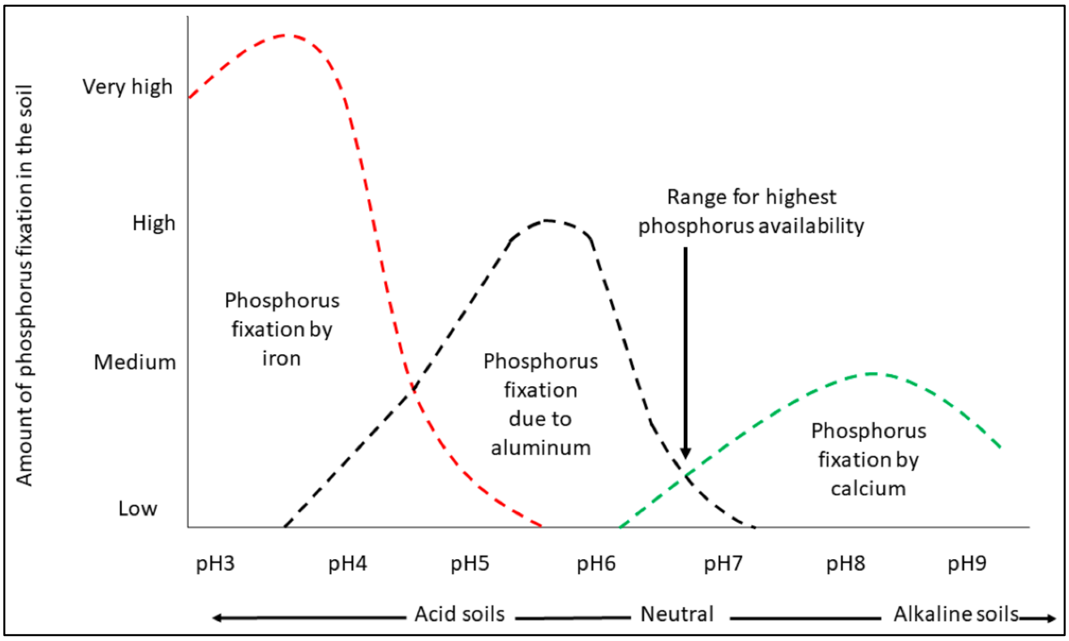


Figure 5.6: Effect of change of pH and P availability in the soil, adopted from (Price, 2006) and (Penn and Camberato, 2019).

The addition of OA significantly increased soil Olsen P to a varying degree in this study (Figure 5.3). A similar increase in the soil Olsen P was also observed in the preliminary study after the addition of OA (Appendix 2). The addition of different amounts of P from different OA (Table

5.2) can explain the varying degree of increase of soil Olsen P. The obtained lower soil Olsen P at all times by FWR and FWB and higher by BSR and BSB compared to control may further support the effect of the addition of different amounts of P ranging from 2.3 mg (FWR) to 112.8 mg (BSB) of total P from OA (Table 5.2) and an increase of varying degrees of soil Olsen P.

OA contain both organic and inorganic P (orthophosphates). Inorganic orthophosphate P is considered as readily available and organic P is needed to be mineralized to inorganic orthophosphate P before become available. The organic P content of the OA used in this experiment ranged from 1 to 7% except for FWR (~90%) (Table 4.2) as identified using solution-state ^{31}P NMR spectroscopy (Chapter 4). Among different forms of organic P present in OA, the major form of organic P was orthophosphate monoesters which are considered as less bioavailable due to its slow mineralization in the soil and also due to its high charge density and formation of stable complexes with cations, clay and organic matter in the soils (Leytem and Maguire, 2007, Turner et al., 2005, Celi et al., 1999). Moreover, in this study, the concentration of soil Olsen P in the control treatment was fairly constant throughout the experiment (Figure 5.3) Therefore, the mineralization of organic P (from both in soil and OA) was considered as a non-dominant phenomenon in this experiment for increasing soil Olsen P.

To determine the contribution of inorganic P content from OA on increasing soil P availability, the expected Olsen P was calculated using both the orthophosphate (NMR recoveries) and Olsen P content added from OA (Figure 5.7). The calculation showed that none of the predicted Olsen P was better fitted with the observed Olsen P (Figure 5.7). The expected Olsen P (when calculated considering orthophosphate content of OA) exceeded observed Olsen P in most of the cases except for FWR. It has been reported that NMR overestimates the bioavailable P concentration (orthophosphate) if orthophosphate is present in the form of orthophosphate-metal complexes in the samples (Turner et al., 2003a). In some recent studies, the use of X-ray absorption near edge structure (XANES) spectroscopy also identified less bioavailable orthophosphate compounds such as calcium phosphate (Hunger et al., 2008), variscite (Al-phosphate) (Rose et al., 2019), hydroxyapatite (Robinson et al., 2018) as dominant forms of P in OA, especially in biochar. These compounds were also likely to present in the organic materials used in this experiment (especially in the biochar and compost) and may have caused the overestimation of the bioavailable orthophosphate content when identified using solution-state ^{31}P NMR in Chapter 4.

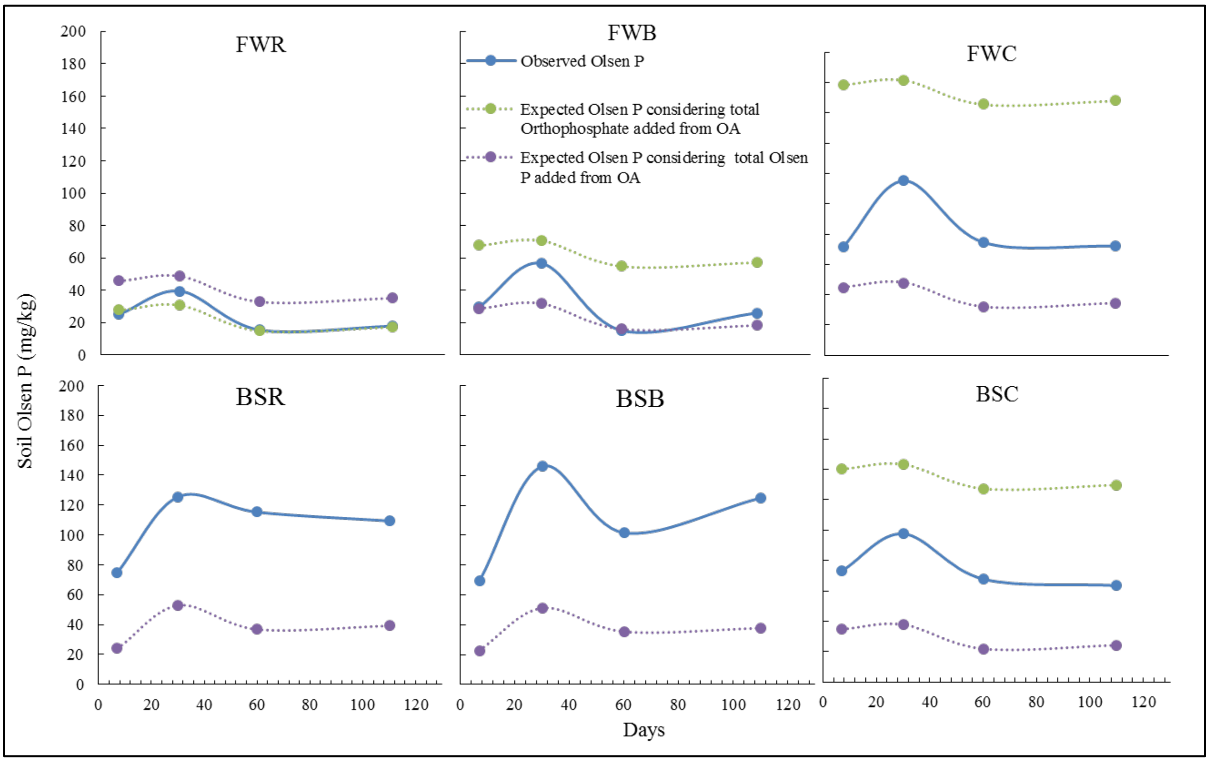


Figure 5.7: The observed and expected Olsen P concentration in this study. The expected Olsen P was calculated by combining obtained control soil Olsen P + P added from OA in the form of orthophosphate (NMR recoveries) (green dotted line) and Olsen P (purple dotted line) at each time. The blue line represents observed Olsen P in this study. In case of BSR and BSB, orthophosphate content was not available due to high Fe content which exerts paramagnetic effect during NMR detection (Table 4.2).

The observed Olsen P showed an additional increase for FWC, BSR, BSB and BSC at all times compared to P added from OA in the form of Olsen P (Figure 5.7). The FWR showed a lower observed Olsen P at all the time compared to the expected Olsen P. The expected Olsen P fitted well the observed Olsen P in case of FWB at all the time except at 30 days. The mechanisms for obtaining this additional Olsen P increase are hypothesized to be due to the substitution of the previously fixed P by the organic anions and the formation of the organometallic complexes in the soil (Hansen and Strawn, 2003, Siddique and Robinson, 2003). The process of substitution of previous fixed P by the action of organic anions produced from organic acid compounds presented in Figure 5.8.

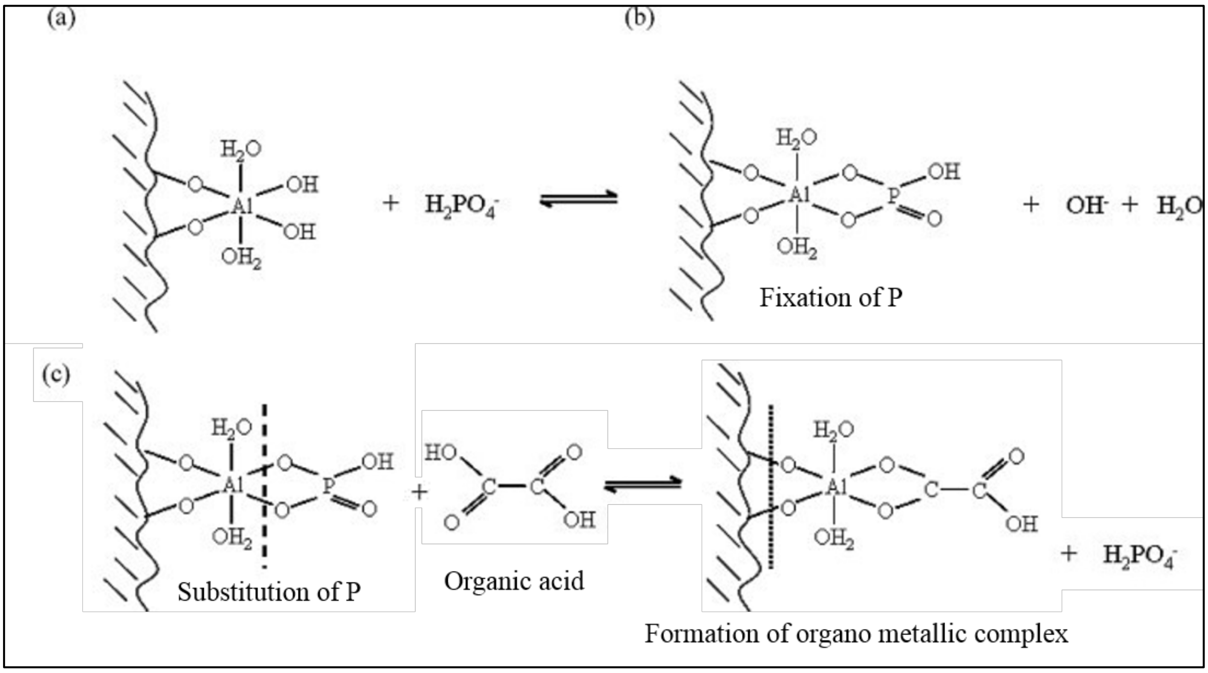


Figure 5.8: (a and b) Process of fixation of P by the Al-hydroxide compound and (c) substitution of P by the organic acid and formation of organometallic complex. This figure was adopted from (Schefe et al., 2009).

The representative organic acid-producing compounds in the OA are phenolic and carbonyl C (Eldridge et al., 2013, Spaccini et al., 2012, Albrecht et al., 2008) and are expected to show a correlation with the additional increase of soil Olsen P (ΔOlsen P, the difference between observed and expected Olsen P). In this current study, a correlation study between the ΔOlsen P and phenolic and carbonyl C content of the OA (Table 4.3, Chapter 4) was conducted (Table 5.3). The ΔOlsen P was correlated with the individual, total and the ratio of the phenolic to carbonyl C content of the OA. The correlation coefficient (r) value showed a strong positive significant ($P<0.01$) correlation (ranging r value from 0.60 to 0.83) with the ratio of the phenolic to carbonyl C content of the OA compared to their individual and total abundance (Table 5.3). The correlation study did not show any significant relationship with the carbonyl C content of the OA whereas it showed a very strong correlation with the phenolic C content of the OA (Table 5.3).

In general, carbonyl compounds dissociate more readily and are capable of forming stable organo-metal complexes in the soil (Lindegren and Persson, 2009, Hu et al., 2005a, Hu et al., 2005b, Ron-koul et al., 2004). However, the microbial degradation of the carbonyl compounds (due to aliphatic structure) is much quicker relative to the phenolic compounds in the soil ranging from 3 hr to several days (Ström et al., 2001) and this may explain why the carbonyl C of OA did not show any significant correlation with ΔOlsen P. The presence of a ring structure in phenolic compounds, make them resistant to microbial degradation, which means they have a longer residence time in the soil and may provide organic anions for a longer period (Schefe and Tymms, 2013). During the degradation process, phenolic compounds go through a series of slow degradation steps with the production of simple organic acids as an end product (Kassim et al., 1982, Shindo and Kuwatsuka, 1976, Haider et al., 1975, Dagley, 1967) which may supply organic anions for a longer period in soil and also explains the reason for showing significant correlation with the ΔOlsen P.

The complementary effect between phenolic and carbonyl C content of the OA may further explain the reason for obtaining strong correlation between ∆Olsen P and the ratio of phenolic to carbonyl C. For instance, some phenolic compounds are known to be toxic to the soil microbes (Wu et al., 2016, Hu et al., 2005b), which may delay the degradation of carbonyl compounds and prolong their effect on soil P availability.

Table 5.3: Pearson's correlation study between the change in soil Olsen P (mg/kg) (∆Olsen P, the difference between observed and expected Olsen P, considering Olsen P contribution from OA) and phenolic and carbonyl C content of the OA at each sampling time. The values representing Pearson's correlation coefficient (r) (n= 24).

Days	Phenolic C content of the OA (%)	Carbonyl C content of the OA (%)	Total abundance of phenolic and carbonyl C content (%)	Ratio of phenolic to carbonyl C of OA
7	0.62***	-0.03^{ns}	0.36*	0.83***
30	0.67***	0.16^{ns}	0.50***	0.69***
60	0.57***	-0.14^{ns}	0.26^{ns}	0.71***
110	0.58***	0.08^{ns}	0.40*	0.60***

***indicating significant at $P < 0.01$, ** significant at $P < 0.05$, * significant at $P < 0.1$ and ns- non-significant.

As time progressed in this current study, the Olsen P decreased at 60 days and remained stable until 110 days for most of the treatments (Figure 5.3). The decrease of Olsen P may be due to the degradation of the organic anions as time progressed, which released the Al or Fe from organometallic complexes and caused re-adsorption of the P in the soil (Schefe and Tymms, 2013). The weaker correlation between the ratio of phenolic and carbonyl C content of OA and ∆Olsen P as time progressed may also support the degradation of organic anions and re-adsorption of P and reasons for decreasing soil Olsen P.

As the organometallic complexes formed at the beginning of the OA addition, less Al and Fe were expected to be extracted. The addition of OA initially at 7 days significantly decreased the soil M3 extractable Al and Fe concentrations with the highest decrease by FWR at all times and increased back as time progressed (Figure 5.4). Although the highest decrease in the soil M3 extractable Al and Fe concentration was obtained by FWR, no increase in soil Olsen P was observed. FWR was low in organic acid compounds (phenolic and carbonyl) and was also rich in orthophosphate monoesters compounds. As mentioned earlier, the Al and Fe were likely to form strong complexes with the orthophosphate monoesters compounds when FWR was added to the soil and recorded the lowest M3 extractable Al and Fe.

5.4.2 Effect of organic amendments on soil PBC

The results showed that soil PBC decreased with the addition of all the OA (Figure 5.5) and kept decreasing as time progressed. As discussed earlier, the mechanisms proposed for decreasing PBC after the OA addition were the blocking of the soil P sorption sites by forming organometallic metal complexes with organic anions (Hansen and Strawn, 2003, Siddique and Robinson, 2003) or competition between organic anions with phosphate ions to be fixed (Cheng et al., 2008, Hu et al., 2005b, Kwabiah et al., 2003, Geckeis et al., 2002, Iyamuremye et al., 1996, Sibanda and Young, 1986, Hue et al., 1986, Mnkeni and MacKenzie, 1985, Borie and Zunino, 1983, Levesque and Schnitzer, 1967).

Like soil ΔOlsen P, a similar correlation between the ΔPBC, (difference between $PBC_{treatment}$ - $PBC_{Control}$) and the phenolic and carbonyl C of OA was expected. A significant strong negative correlation between ΔPBC and the phenolic and carbonyl compounds of OA at each time was observed (Table 5.4). The correlation was stronger with the ratio of phenolic to carbonyl C content of the OA with the ΔPBC at each time point compared to individual and total abundance of the phenolic and carbonyl C content of the OA (Table 5.4). However, unlike Olsen P as time progressed from 7 to 110 days the correlation between ΔPBC and phenolic and carbonyl C content of the OA became stronger with a range of correlation coefficient values from 0.50 to 0.80 (Table 4.5). This prolonged effect of OA on decreasing soil PBC may be due to the sequential and slow degradation of phenolic compounds, which were supplying organic anions for a longer period in the soil. The M3 extractable Al and Fe concentration was expected to decrease as the time progressed in this current study but observed otherwise (Figure 5.4). This was likely due to the large amounts of Al and Fe that were added to the soil from the OA themselves, which increased the M3 Al and Fe concentration in this study. Furthermore, the degradation of organic anions that are firmly held by soil cations (an organometallic complex) is still controversial (Adeleke et al., 2017, Jones, 1998). Both fast (if held loosely) (Adeleke et al., 2017, Jones and Edwards, 1998) and slow (Andrade et al., 2013, Fischer et al., 2010, Ström et al., 2001) bio-degradation of organometallic complexes by soil microbes have been reported. As the continuous decrease of the soil PBC was observed, a slower degradation of the organic metallic complexes is likely to be happening in this study as time progressed. Therefore, the decrease in soil Olsen P at 60 and 110 days was not likely due to the degradation of organometallic complexes and re-adsorption of P by Al and Fe as discussed earlier. Another hypothesis would be the immobilization of P from the soil, which possibly explains the decrease in soil Olsen P at 60 and 110 days. Because the addition of OA with a low O-alkyl to alkyl C ratio is likely to inspire microbial activity due to the availability of mineralizable C in the soil (Bernal et al., 1998, Baldock et al., 1997, Skene et al., 1996). The range of O-alkyl to alkyl C ratio of the OA used in this study was 0.1 to 2.3 (Table 4.3 in Chapter 4) and this was likely to increase microbial activity and immobilize P from soil.

Furthermore, in this study, the OA with the lower ratio of phenolic to carbonyl C content (FWR and FWB) have shown little effect on increasing Olsen P and decreasing soil PBC compared to the OA with a higher ratio of phenolic to carbonyl C content. It is also interesting to note that, the OA with the equal abundance of phenolic and carbonyl C content (FWC and BSC) had maximum effect on decreasing soil PBC may be due to the complementary effect between phenolic and carbonyl compounds as discussed earlier.

Table 5.4: Pearson's correlation study between the change in soil PBC (ΔPBC, difference between $PBC_{treatment} - PBC_{control}$)) and phenolic and carbonyl C content of the OA at each time. The values representing Pearson's correlation coefficient (r) (n= 24).

Days	Phenolic C content of the OA (%)	Carbonyl C content of the OA (%)	Total abundance of phenolic and carbonyl C content (%)	Ratio of phenolic to carbonyl C of OA
7	- 0.33 ^{ns}	- 0.08 ^{ns}	- 0.15 ^{ns}	- 0.50**
30	- 0.64 ***	- 0.13 ^{ns}	- 0.46 **	- 0.74***
60	- 0.67 ***	- 0.16 ^{ns}	- 0.50 **	- 0.65***
110	- 0.71 ***	- 0.12 ^{ns}	- 0.50 **	- 0.80***

***indicating significant at P <0.01, **significant at P < 0.05 and ns- non-significant.

5.5 Conclusions

The addition of organic amendments in this acidic soil increased soil P availability by supplying both organic and inorganic P, also by a series of other mechanisms such as substituting previously fixed P and reducing P sorption through forming organometallic complexes.

The orthophosphate content identified by solution-state ^{31}P NMR may not be able to predict the P fertilization value of the organic materials due to the overestimation of the bioavailable orthophosphate content. The Olsen P content of the OA might be a good indicator of the bioavailable P content in the soil. However, for obtaining a more accurate prediction of the contribution of bioavailable orthophosphate content from OA, other spectroscopic techniques such as XANES needed to be combined with the NMR analysis.

The phenolic and carbonyl C content represents organic acid compounds of the OA and could be used to predict their role in reducing P sorption in the soil. The OA with a higher or equal abundance of phenolic C compounds relative to carbonyl C compounds had a superior effect on soil P availability compared to the lower abundance.

Therefore, I recommend that the phenolic and carbonyl C content of OA could be used to understand the effectiveness of an OA on soil P availability. The ratio of phenolic to carbonyl C content would better predict the role of OA in increasing soil P availability compared to their total abundance.

Chapter 6: The combined addition of aliphatic and aromatic organic acid to an acidic soil prolonged phosphorus availability

6.1 Introduction

Organic acids (both aliphatic and aromatic) are abundant in nature. The major sources of organic acids in the soil are plant root exudates, microbial secretion/degradation and externally from OA addition such as manure, compost, biochar and other waste materials (Mimmo et al., 2008, Nwoke et al., 2008, Jones et al., 2003, Dakora and Phillips, 2002). Naturally occurring organic acids have been shown to increase P availability by mobilizing fixed P in soil (Yang et al., 2013b, Harrold and Tabatabai, 2006, Hu et al., 2005a, Bolan et al., 1994, Fox et al., 1990) and by reducing P sorption sites (Lindegren and Persson, 2009, Hue, 1991). The key mechanisms proposed are that the organic acids dissociate in the soil and provide organic ligands (carboxyl and hydroxyl ions), which compete with phosphate ions to be fixed or form stable metal complexes to reduce P sorption (Hue, 1991, Violante et al., 1991, Traina et al., 1986).

Many studies have been conducted to understand the effect of naturally abundant low molecular organic acids (both aliphatic and aromatic) on soil P solubilization, release, mobilization and availability (Yang et al., 2013b, Harrold and Tabatabai, 2006, Hu et al., 2005a, Bolan et al., 1994, Fox et al., 1990), P sorption (Lindegren and Persson, 2009, Hue, 1991) fertilizer dissolution (Ron-koul et al., 2004), fertilizer efficiency (Schefe and Tymms, 2013, Hue, 1991) and plant growth and plant P availability (Chatterjee et al., 2015, Kpomblekou-A and Tabatabai, 2003). To date, studies on the effect of combined addition of both aliphatic and aromatic acids are very limited. Knowledge of the effect of aliphatic and aromatic compounds contained in OA on P availability would be useful in screening novel/newly formulated OA for enhancing P availability. In Chapter 5, the phenolic (representing aromatic organic acids) and carbonyl C content (representing aliphatic organic acids) of the OA (FWR, FWB, FWC, BSR, BSB and BSC) showed a strong correlation in increasing soil P availability where a nearly equal abundance of phenolic and carbonyl compounds in OA (FWC and BSC) increased the soil P availability the most. In this chapter, I tested if some of those naturally occurring organic acids (which were identified from FWR, FWB, FWC, BSR, BSB and BSC, appendix 1, Table A 1.7) could increase soil P availability when applied both individually and in combination. This study hypothesized that the combined addition of aliphatic and aromatic organic acid may have a prolonged effect in increasing soil P availability due to the complementary effect on each other compared to their individual addition. In general, the microbial degradation of aliphatic compounds is quicker compared to the aromatic compounds due to their simple structure ranging from 3 hours (malate) (Ström et al., 2001) to around 12 hours (citrate) (Jones and Darrah, 1994). On the other hand, aromatic compounds possess longer residence time in soil (< 10 days) as suggested by Shindo and Kuwatsuka (1975) involving a series of microbial and enzymatic steps before entering into the TCA (tricarboxylic acid) cycle for final breakdown to CO_2 (Nair et al., 2008). Some aromatic compounds have also been reported to be toxic to soil microbes (Hu et al., 2005b) which may also favor the delayed degradation and prolonged contribution of aromatic organic anions to the soil (Schefe and Tymms, 2013).

Similar to Chapter 5, in this current study, I conducted a laboratory-based soil incubation experiment with some selected aliphatic and aromatic organic acids and determined their effect on soil pH, P availability (Olsen P), cation concentration (Mehlich 3 extractable Al and Fe) and soil P buffering capacity (PBC).

6.2 Materials and Methods

6.2.1 Collection and processing of soil

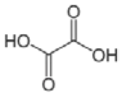
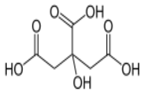
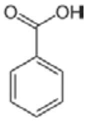
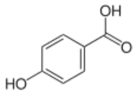
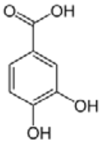
The soil used in this experiment was as same as used in Chapter 5. The collection, processing and characterization procedure of the soil used in this experiment was described in Chapter 5 under subsection 5.2.1. The soil characterization result was presented in Table 5.1.

6.2.2 Selection of organic acids

The aliphatic and aromatic organic acids which were identified in OA (FWR, FWB, FWC, BSR, BSB and BSC, appendix 1, Table A 1.7) and also used in a previous P availability study by Schefe and Tymms (2013) was selected for the test in this study.

Analytical grades of both aliphatic and aromatic organic acids were purchased from Chemsupply (oxalic, citric, benzoic and protocatechuic acid) and Sigma Aldridge (4-dihydroxybenzoic acid). Aliphatic organic acids containing di and tricarboxylic functional groups were selected (oxalic acid citric acid, respectively). Monocarboxylic compounds, eg acetic acid, were not selected, as the literature suggests they have little effect on soil P availability (Harrold and Tabatabai, 2006). From the aromatic organic acids, benzoic, 4-dihydroxybenzoic and protocatechuic acids were selected containing one carboxylic (-COOH) functional group in each and hydroxyl functional (-OH) groups following the order of 0, 1 and 2, respectively (Table 6.1). Some basic properties of selected organic acids are presented in Table 6.1.

Table 6.1: Some basic properties of the selected organic acids.

IUPAC name	Chemical formula	Structure	Molecular weight (g/mol)	Dissociation constant		
				pK$_{a1}$	pK$_{a2}$	pK$_{a3}$
Oxalic acid	$C_2H_2O_4$ $.2H_2O$		126.07	1.23	4.14	
Citric acid	$C_6H_8O_7.$ H_2O		210.14	3.13	4.76	6.40
Benzoic acid	$C_7H_6O_2$		122.12	4.2		
4-hydroxybenzoic acid	$C_7H_6O_3$		138.12	4.54		
Protocatechuic (3,4 dihydroxy benzoic) acid	$C_7H_6O_4$		154.12	4.48		

6.2.3 Incubation experiment with organic acids

100 g of soil was incubated in a 250 ml plastic vial, with and without (control) addition of organic acid at 20° C with a moisture content of 70% water holding capacity. The rate of organic acid addition was 0.4 g C/100g soil (w/w) based on a preliminary experiment, where the addition of 0.4g/100g soil was the lowest rate of addition that (in a range of 0 to 1g C/100g soil) demonstrated a significant increase in soil P availability (appendix 3, Figure A 3.1). The aliphatic and aromatic organic acids were added either individually or in combination with 4 replications. Combined treatments included the addition of citric acid with benzoic, 4-

dihydroxybenzoic and protocatechuic acids at the ratio of 1:1(w/w), respectively (Table 6.2). In order to stabilize microbial activity, the soil was pre-incubated with only Mili Q water for 7 days before adding treatments. The incubation experiment was conducted for 110 days and sufficient samples were prepared to allow destructive sampling at 7, 15, 30, 60 and 110 days (a total of 180 incubation vials). Each sample collection time had its own control treatment. All the vials were aerated and watered regularly to maintain a similar aerobic condition throughout the experiment. At each sample collection point, samples were collected, oven-dried (40° C) overnight. A subsample of the dried soil was used to determine pH ($CaCl_2$), Olsen P and Mehlich-3 (M3) extractable cations (Fe and Al) following the method described in Chapter 5 under subsection 5.2.3. In this study, the M3 extractable Fe and Al were determined only at 7, 60 and 110 days of sample collection.

Table 6.2: The treatment combinations and organic acids utilized in the incubation experiment.

Treatments	Amount added (g) @ 0.4% C	Concentration of acid (mM) (calculated based on the amount added)
Control	0	0
Oxalic	2.10	16.65
Citric	1.17	5.57
Benzoic	0.58	4.75
4-hydroxybenzoic	0.66	4.78
Protocatechuic acid	0.73	4.74
Citric+ Benzoic*	0.58 + 0.29	5.13 (2.76 + 2.37)
Citric+ 4-hydroxybenzoic*	0.58 + 0.33	5.15 (2.76 + 2.39)
Citric+ Protocatechuic*	0.58 + 0.37	5.16 (2.76 + 2.40)

*Added half amount compared to their individual rates to achieve final 0.4% C rate of addition.

6.2.4 Determination of soil phosphorus buffering capacity (PBC)

In this study, the effect of the organic acids on soil P buffering capacity (PBC) was determined only at the first and last point of the sample collection (7 and 110 days). The procedure for determining soil PBC was presented in Chapter 5 under subsection 5.2.4.

6.2.5 Statistical analysis

Data were statistically analyzed by analysis of variance (ANOVA) following a general linear model using the software package Minitab 18 (Akers, 2018). Treatment means were separated using the least significant differences (LSD) value at the 5% level of probability at a specific time of sample collection.

6.3 Results

6.3.1 Effect of organic acids on soil pH

The addition of aliphatic organic acids significantly ($P \leq 0.05$) decreased the soil pH at 7 and 15 days compared with control and then significantly ($P \leq 0.05$) increased at 30, 60 and 110 days (Figure 6.1). In comparison between oxalic and citric acid, the oxalic acid resulted in significantly ($P \leq 0.05$) lower pH (2.7 and 2.9) at 7 and 15 days and significantly ($P \leq 0.05$) higher pH (ranging from 4.5 to 4.8) in 30, 60 and 110 days. The pH value of the citric acid ranged from 3.3 to 4.3.

Addition of all the aromatic organic acid showed a similar trend like control and the pH values remained relatively constant at all times (Figure 6.1). The protocatechuic acid resulted in a significant ($P \leq 0.05$) increase in soil pH at all times compared to the control with pH values ranging from 3.9 to 4.0. The addition of 4-hydroxybenzoic acid had a significantly ($P \leq 0.05$) higher soil pH at all times except at 15 days compared to the control. The pH value ranged from 3.4 to 3.9 for benzoic acid treatment with an initially significant ($P \leq 0.05$) decrease at 7 and 15 days compared to the control and no significant difference at 30, 60 and 110 days was observed. The benzoic acid was recorded as the lowest pH among all other aromatic acids at each time with a significant ($P \leq 0.05$) difference at 7 and 15 days only (Figure 6.1).

Similar to the aliphatic acid, the combined addition of both aliphatic and aromatic organic acids decreased the soil pH at 7 and 15 days and increased at 30, 60 and 110 days compared to control except for citric+ benzoic acid treatment. The citric+ benzoic acid significantly ($P \leq 0.05$) decreased soil pH compared to all other treatments ranging from 3 to 3.2 throughout the experiment (Figure 6.1). The pH ranged from 3.2 to 4.2 for both citric+ 4-hydroxybenzoic and citric + protocatechuic acid treatment.

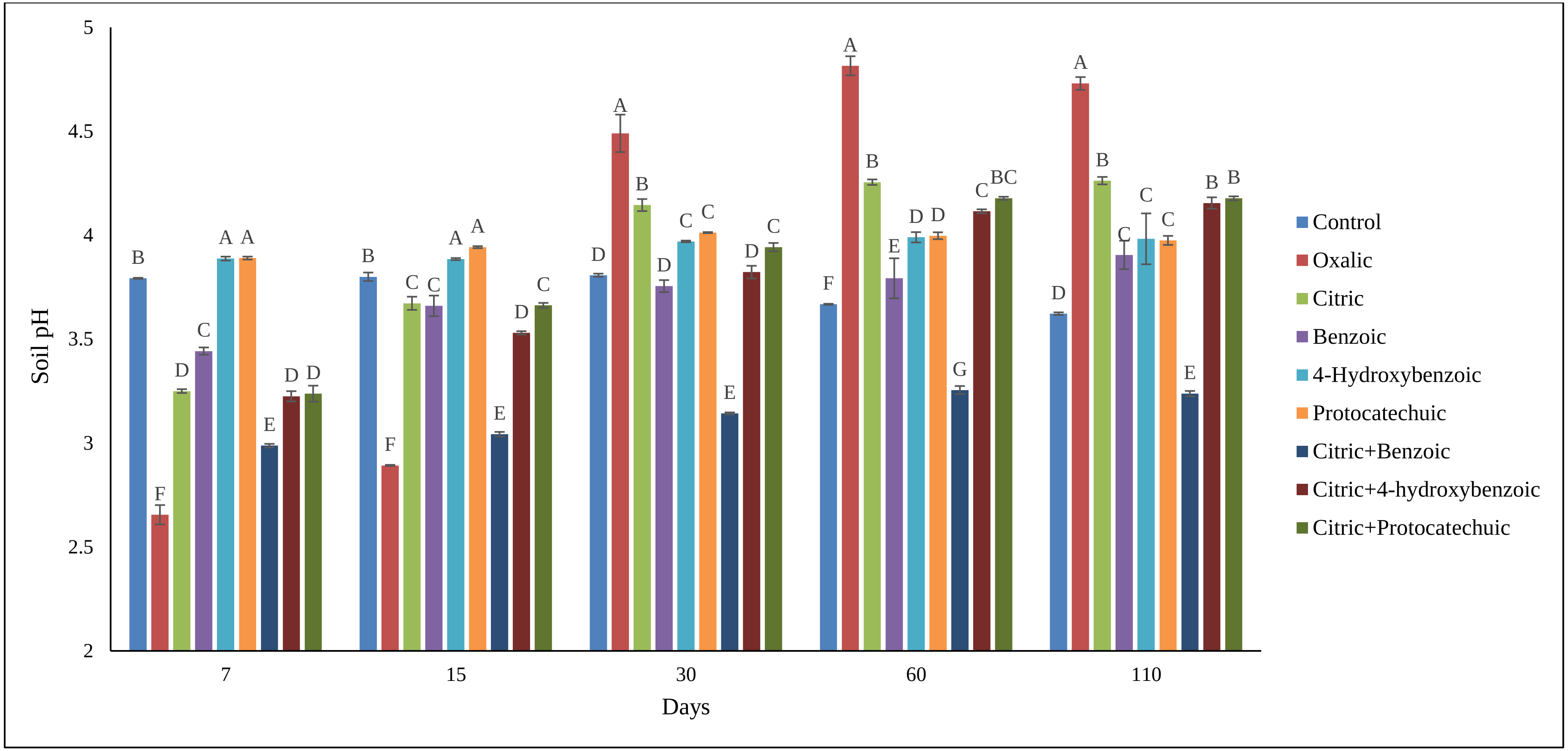


Figure 6.1: Effect of aliphatic and aromatic organic acids on soil pH across all points of sample collection. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

6.3.2 Effect of organic acids on soil Olsen P

The addition of oxalic acid decreased the soil Olsen P most of the time except for 15 days compared to control, whereas citric acid significantly ($P \leq 0.05$) increased soil Olsen P until 60 days. In 110 days, citric acid significantly ($P \leq 0.05$) decreased soil Olsen P compared to control (Figure 6.2). Between oxalic and citric acid treatment, citric acid was recorded as the higher soil Olsen P at each time with a range of 15.4 to 27.6 mg/kg compared to oxalic acid.

The addition of aromatic organic acid showed either a non-significant effect or a negative effect on soil Olsen P compared to control (Figure 6.2). The Olsen P was not statistically significant between benzoic acid and control in most of the cases except 30 and 110 days. The addition of 4-hydroxybenzoic acid resulted in a significantly lower Olsen P compared to the control throughout the experiment. The protocatechuic acid treatment showed no significant difference at 7 and 110 days on soil Olsen P compared to control.

Among the combined addition of aliphatic and aromatic acid treatments, the citric and benzoic acid significantly ($P \leq 0.05$) increased soil Olsen P compared to the control at all times with a value ranged from 28.6 to 42.6 mg/kg (Figure 6.2). The citric+ 4-hydroxybenzoic and citric+ protocatechuic acid treatment significantly ($P \leq 0.05$) increased soil Olsen P availability until 30 days compared to control, whereas no significant difference was observed at 60 and 110 days. In addition to that, the combined addition of citric+ 4-hydroxybenzoic and citric+ protocatechuic acid treatment showed a relatively constant Olsen P throughout the experiment.

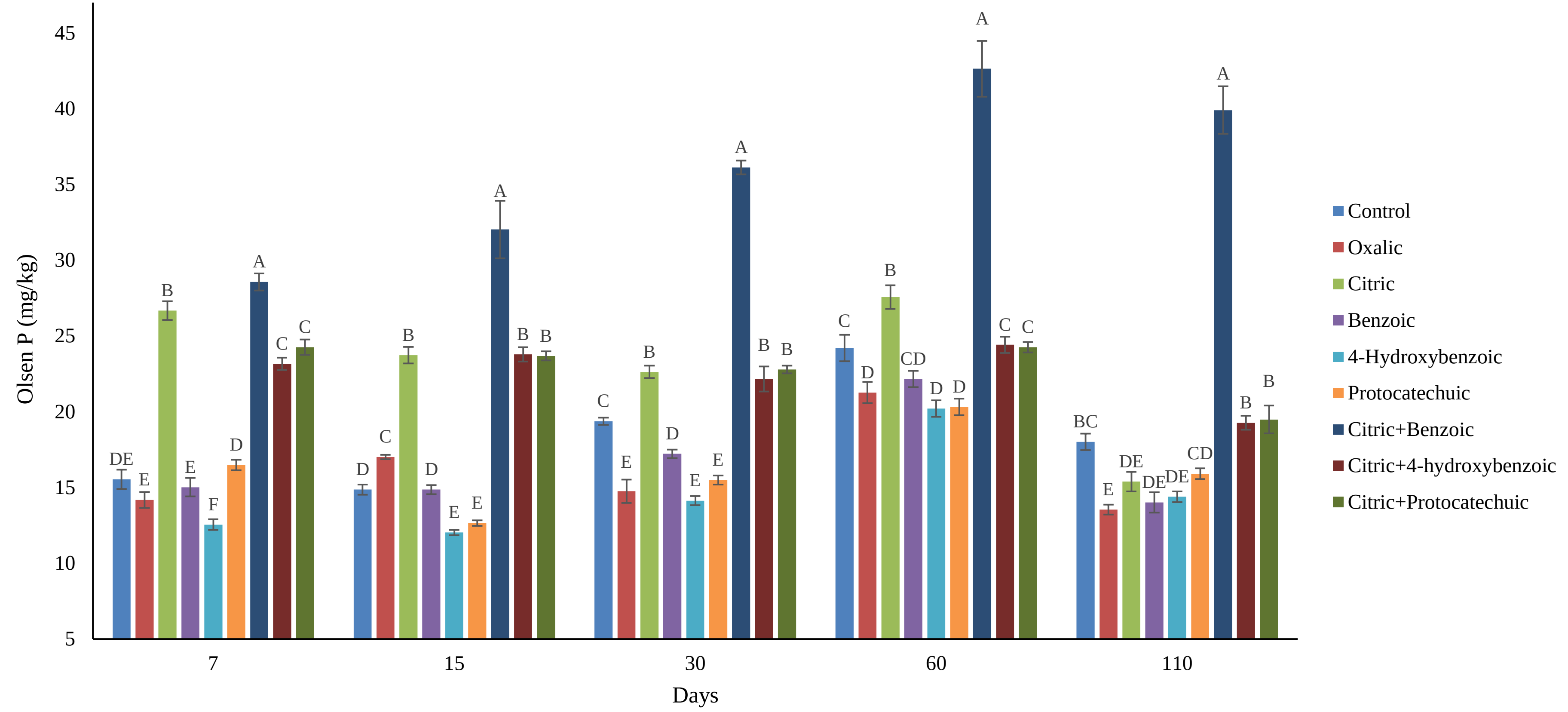


Figure 6.2: Effect of aliphatic and aromatic organic acids on soil Olsen P across all points of sample collection. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

6.3.3 Effect of organic acids on soil Mehlich-3 (M3) extractable cations (Al and Fe)

Among all the organic acid treatments, the highest and significant ($P \leq 0.05$) M3 extractable Al and Fe concentration was observed with the oxalic acid at all times except for Fe concentration at 60 and 110 days (Figure 6.3). The oxalic acid showed a distinct decrease for M3 extractable Al and Fe concentration as time progressed from 7 to 60 days and then remain constant till 110 days. The citric acid significantly ($P \leq 0.05$) increased Fe concentration compared to control at each time and showed either non-significant difference (7 days) or low Al concentration in 60 and 110 days.

The aromatic acids showed the lowest M3 extractable Al and Fe concentration compared to all other organic acid treatments throughout the experiment (Figure 6.3). Compared with the control, the addition of aromatic organic acids showed either a decrease (in case of M3 extractable Al concentration) or non-significant ($P \leq 0.05$) differences (in case of M3 extractable Fe concentration) at all times.

The combined addition of aliphatic and aromatic organic acids significantly ($P \leq 0.05$) increased the M3 extractable Al concentration compared to the control and their individual addition at 7 days (Figure 6.3). In 60 and 110 days, the combined addition showed a decrease and a non-significant difference in Al concentration except for citric+benzoic acid treatment. The Al concentration remained relatively constant by citric+benzoic acid treatment throughout the experiment. In the case of M3 extractable Fe, all the combined addition of aliphatic and aromatic organic acids significantly ($P \leq 0.05$) increased the concentration compared to control and their individual aromatic acid addition in the soil at each time.

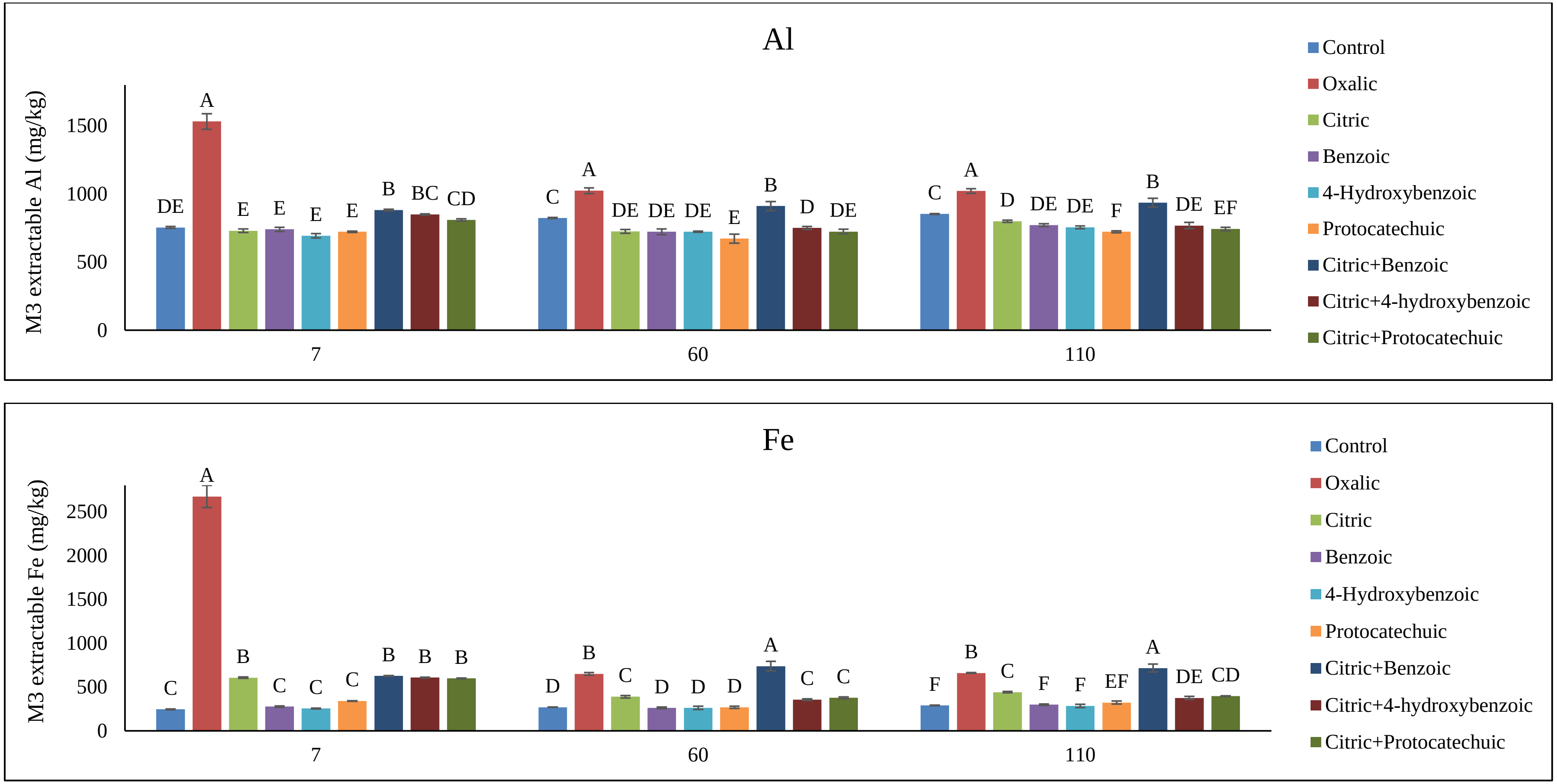


Figure 6.3: Effect of organic acids on soil Mehlich-3 (M3) extractable Al and Fe at 7, 60 and 110 days. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

6.3.4 Effect of organic acids on soil P buffering capacity

Compared to the control, the addition of aliphatic organic acids significantly ($P \leq 0.05$) decreased the soil P buffering capacity (PBC) at 7 days and significantly ($P \leq 0.05$) increased at 110 days (Figure 6.4). Between aliphatic organic acid treatments, the citric acid recorded significantly ($P \leq 0.05$) lower soil PBC in both 7 and 110 days compared to oxalic acid.

The aromatic organic acids initially at 7 days showed no statistically significant difference in soil PBC compared to control except hydroxybenzoic acid. The hydroxybenzoic acid significantly ($P \leq 0.05$) decreased the soil PBC at 7 days compared to control. In 110 days, compared to control, all the aromatic acid significantly ($P \leq 0.05$) increased soil PBC (Figure 6.4).

Similar to aliphatic acids, all the combined addition of aliphatic and aromatic organic acids significantly ($P \leq 0.05$) decreased the soil PBC in 7 days compared to control. At 110 days, the addition of all the combined aliphatic and aromatic acids significantly ($P \leq 0.05$) increased soil PBC except for citric+ benzoic acid. The citric+ benzoic acid was recorded significantly ($P \leq 0.05$) lower soil PBC at 110 days compared to control and all other treatments (Figure 6.4).

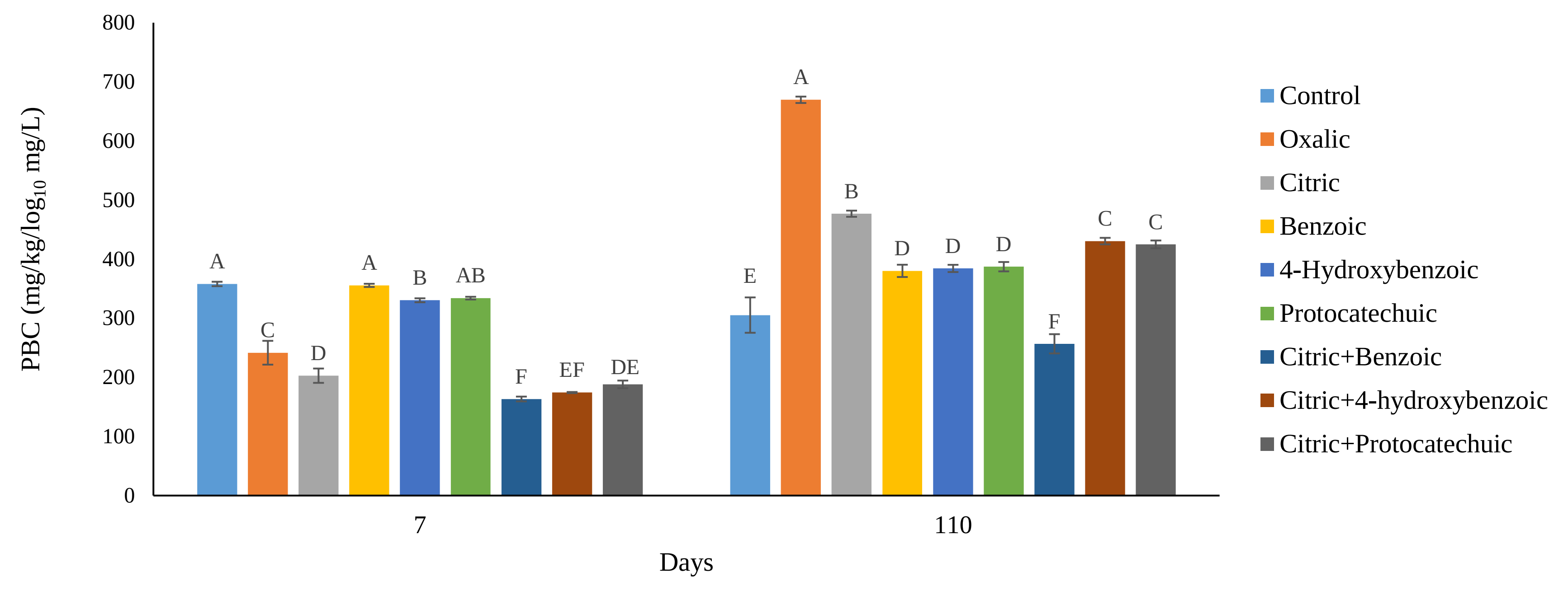


Figure 6.4: Effect of organic acids on soil phosphorus buffering capacity (PBC) at the beginning (7 days) and the end (110 days) of the incubation experiment. The line on the top of the bar indicates standard error (n=4) and different letters indicate difference among the treatments statistically significant at $P \leq 0.05$ at a specific point of sample collection.

6.4 Discussion

6.4.1 Effect of individual addition of organic acids

The original pH of the soil was 3.8 ($CaCl_2$) and the addition of organic acids initially decreased the soil pH as low as 2.7 by oxalic acid and then increased back later on (Figure 6.1) which was unlike the soil pH observed with the addition of OA in the previous study in Chapter 5. The addition of OA significantly increased the soil pH at all times (Figure 5.2). However, in this study, the initial contribution of protons during the dissociation of organic acids and later microbial degradation accounts for the observed decrease in soil pH. The first dissociation constant (pK_{a1} value) of an organic acid is inversely related to the proton contribution; the lower the dissociation constant value, the higher the proton contribution (Harrold and Tabatabai, 2006), which explains why the lowest soil pH was obtained by the Oxalic acid (lowest pK_{a1} value of 1.23) among all the organic acid treatments at 7 days. A positive correlation (r^2= 0.92) was also observed between the first dissociation constant of the organic acids (pK_{a1}) (Table 6.1) and the initial soil pH at 7 days (Figure 6.1) in this study.

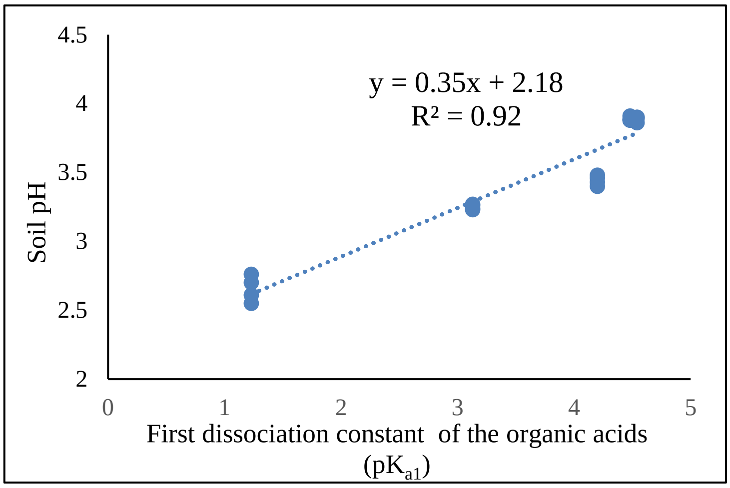


Figure 6.5: The relationship between soil pH at 7 days obtained from oxalic, citric, benzoic, 4-hydroxybenzoic acid and protocatechuic acid (n=20) and their first dissociation constant (pk_{a1} value) (Table 6.1)

Proton contribution from organic acids is a very important factor to consider in this study. In the type of acidic soil used in this study, the presence of oxides and hydroxide compounds of Al and Fe was expected, which may dissociate into Al^{3+} and Fe^{3+} ions by reacting with protons (Equation 6.1 and 6.2) which would further act as P sorption sites in the soil (Penn et al., 2018).

$$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O \dots\dots (6.1)$$

$$Fe(OH)_3 + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O \dots\dots (6.2)$$

The addition of the organic acids increased the soil Olsen P in the current study and also reported in previous studies conducted by (Yang et al., 2013b, Harrold and Tabatabai, 2006, Hu et al., 2005a, Bolan et al., 1994, Fox et al., 1990). This increase may be due to dissolution of the previously fixed P such as aluminum-phosphate or iron-phosphate as soil pH decreased (Equation 6.3 and 6.4) in the current study.

$$AlPO_4.\ 2H_2O + 2H^+ \Leftrightarrow Al^{3+} + H_2PO_4^- + 2H_2O \dots\dots (6.3)$$

$$FePO_4.\ 2H_2O + 2H^+ \Leftrightarrow Fe^{3+} + H_2PO_4^- + 2H_2O \dots\dots (6.4)$$

However, this might not be the only hypothesis that explains the increase in soil Olsen P in this study. Because a significant increase of soil Olsen P compared to control was expected with a decrease in soil pH (Figure 6.1) and increase in soil Al and Fe concentration (Figure 6.3), but an opposite result was observed especially in case of oxalic acid at 7 days, which showed no significant changes in soil Olsen P compared to control (Figure 6.2). Other hypotheses suggest that organic acids dissociate in the soil and provide organic ligands (carboxyl and hydroxyl ions), which could substitute previously fixed P or compete with phosphate ions to be fixed or form stable organometallic complexes to reduce P sorption in soil (Hue, 1991, Violante et al., 1991, Traina et al., 1986). Therefore, the substitution of previously fixed P and formation of organometallic complexes in this current study may explain the reason for increase in soil Olsen P availability (as also explained in the previous study in Chapter 5, Figure 5.8).

In this current study, citric acid was more effective in increasing soil Olsen P compared to oxalic acid at all times. Similar higher activity of citric acid for increasing P availability in acidic soil was observed by (Harrold and Tabatabai, 2006) and (Kpomblekou-A and Tabatabai, 2003). In general, the higher the number of carboxylic functional groups, the more soil P availability is expected to increase due to having higher competitive ability (Hu et al., 2001, Parfitt, 1979). In addition to that, the presence of a hydroxyl (-OH) group at β position in an aliphatic organic acid has been reported to form very stable organometallic complexes due to their ability to chelate metals in a six-membered ring structure (Pohlman and Mc Coll, 1986). In this current study, compared to oxalic acid, the citric acid contained three carboxyl (-COOH) functional groups and a hydroxyl (-OH) functional group at β position (structure presented in Table 6.1) and resulted in the highest P availability at all the time.

The effect of aromatic organic acids that were used in this study either had a significantly negative (4-hydroxybenzoic acid) or a non-significant effect (benzoic acid at 7, 15 and 110 days and protocatechuic acid at 7 and 110 days) on soil Olsen P compared to the control (Figure 6.2). Harrold and Tabatabai (2006) observed a similar result for para-hydroxybenzoic and protocatechuic acid on soil P availability. The low dissociation capacity of aromatic organic acids (due to having high dissociation constant) may be responsible for the less impact on soil Olsen P in this study (Hu et al., 2005a). In addition to that, the aromatic organic acids with a hydroxyl functional group at the ortho position have been reported as being highly effective in increasing soil P availability (Pohlman and Mc Coll, 1986). None of the aromatic organic acids used in this study had a hydroxyl group at ortho position (structure presented in Table 6.1).

Unlike the previous study in Chapter 5, due to no external addition of Al and Fe to the soil, it was expected to observe the effect of organic acid on the soil Al and Fe concentration in this study. It was expected to observe a high concentration of the Fe and Al initially due to the decrease in soil pH. As also expected the addition of aliphatic organic acids had more effect on the soil M3 extractable Al and Fe concentration compared to the aromatic organic acid due to their low dissociation capacity in the soil. The effect of aliphatic organic acid on M3 extractable Fe was more distinct compared to the M3 extractable Al due to the low pH obtained which ranged from 2.7 to 3.3, where Fe concentration expected to be higher (Penn and Camberato, 2019, Price, 2006). It is also interesting to note that the effect of the addition of oxalic acid was much higher in extracting M3 extractable Fe and Al compared to citric acid in this current study. This was either due to the addition of oxalic acid at around three times higher concentration (~17 mM) compared to the citric acid (~ 5.5 mM) (Table 6.2) or due to the strong affinity of the oxalic acid to extract Al and Fe from soil (Rayment and Lyons, 2011).

As time progressed in this study, the soil pH increased again, however, the soil Olsen P remained stable until 60 days and then decreased again at 110 days. The decrease in the soil Olsen P at 110 days was may be due to the degradation of the organic anions and re-adsorption of the P (Schefe and Tymms, 2013). Therefore a higher concentration of the M3 extractable Al and Fe concentration was also expected compared to their initial concentration (Figure 6.3)

Similar to the soil Olsen P, with the addition of organic acids, the soil PBC decreased initially at 7 days and increased back at 110 days (Figure 6.4). It was hypothesized that the complexation of the Al and Fe with organic anions would reduce the P adsorption in soil initially and result in lower PBC. The microbial mineralization of the organic anions may later release Al and Fe back and causes re-adsorption of the P in the soil (Schefe and Tymms, 2013). However, the mineralization of organic anions that are firmly held by soil cations (an organometallic complex) is still controversial (Adeleke et al., 2017, Jones, 1998). Both fast (if held loosely) (Adeleke et al., 2017, Jones and Edwards, 1998) and slow (Andrade et al., 2013, Fischer et al., 2010, Ström et al., 2001) bio-degradation of organometallic complexes by soil microbes have been reported.

The soil PBC observed in this study at 110 days did not follow what was observed in Chapter 5. A decrease in soil PBC as time progressed was observed with the OA addition to the soil in Chapter 5 (Figure 5.5). It is speculated that the use of simple organic acids in this study compared to the types of aliphatic and aromatic organic acid compounds present in the OA may be responsible for this dissimilarity in soil PBC over time in Chapter 5 and 6. The aliphatic and aromatic organic acid compounds in OA are expected to be more complex and could possess a longer residence in the soil compared to the simple organic acids used in this study. The half-life of the aliphatic and aromatic organic acid used in this study has been reported to range from few hours to few weeks in the soil (Daniel et al., 2007, Ström et al., 2001, Jones, 1998, Jones and Darrah, 1994, Shindo and Kuwatsuka, 1975). The mineralization rates of the oxalic and citric acids have been measured as 22-29 and 9-39 nano-mol/h/g, respectively (Van Hees et al., 2003) and the benzoic and 4-hydroxybenzoic acids have been measured as 1.6-2.0 and 1.9-4.4 nano-mol/h/g soil, respectively (Ning et al., 2010) and thus organic acid used in this study was expected to be degraded as time progressed.

6.4.2 Effect of combined addition of aliphatic and aromatic organic acids

The combined addition of aliphatic and aromatic organic acid had a prolonged effect in this study compared to their individual addition. For instance, the individual addition of citric acid maintained the low soil pH for only about 15 days and then increased back at 30, 60 and 110 days compared to control, whereas the addition of only aromatic compounds had very minimal effect (Figure 6.1). The combined addition of citric acid with aromatic acid held the soil pH for about 30 days by the citric+ hydroxybenzoic and 110 days by the citric + benzoic acid treatments.

Furthermore, the individual addition of citric acid significantly ($P \leq 0.05$) decreased the soil Olsen P at 110 days compared to control. Whereas the soil Olsen P at 110 days by combined addition of citric acid and aromatic organic acids was either significantly ($P \leq 0.05$) higher or no difference was observed compared to control (Figure 6.2).

Moreover, the combined addition of aliphatic and aromatic (citric+ benzoic acid) organic acids had the highest effect on decreasing soil PBC at 110 days compared to control and individual addition. All the individual addition of aliphatic and aromatic organic acid significantly ($P \leq 0.05$) increased soil P adsorption and soil PBC at 110 days (Figure 6.4).

All the beneficial effects of the combined addition of aliphatic and aromatic acids on soil P availability over individual addition is likely due to their contrasting nature. As also discussed earlier in Chapter 5, aliphatic organic acids are degraded quickly by the microbial action through entering the TCA cycle (due to their aliphatic nature) compared to aromatic compounds. During the degradation process, aromatic compounds go through a series of degradation steps involving enzymatic activities by microbes (Kassim et al., 1982, Haider et al., 1975, Dagley, 1967). The degradation steps include the formation of catechol (the introduction of a hydroxyl group at the ortho-position of phenolic compounds. Catechol is degraded via enzymatic activities (such as 1, 2 dioxygenases, or 2, 3 dioxygenases) (Pradhan and Ingle, 2007) to produce relatively simple and intermediate compounds (oxopent 4- enoate, oxaloacetate, β-oxo-adipate etc) before entering the TCA cycle after breaking down of the ring structure (Cerniglia, 1984). The degradation steps of relatively simple aromatic compounds such as coumaric acid were described by (Shindo and Kuwatsuka, 1975) to hydroxybenzoic acid and then rapidly to protocatechuic acid. Therefore, the aromatic acid may continue to supply proton and organic anions for an extended period due to their delayed degradation, also proposed by Schefe and Tymms (2013).

In addition to that, the aromatic organic acids have also been reported as toxic to the soil microbes (Wu et al., 2016, Hu et al., 2005b, Blum, 1996), which may delay the degradation and prolong the chemical effect of aliphatic carboxylic compounds, while added in combination.

6.5 Conclusions

The addition of organic acids increased P availability and decreased P sorption in acidic soil to a different extent based on their chemical structure, solubility and degradation profile (rate of degradation and intermediate compounds produced). The aliphatic organic acids were more effective compared to the aromatic organic acids, most likely due to their higher dissociation capacity and formation of stable metal complexes. The primary mechanism of increasing soil P availability was likely either due to the dissolution of cation fixed P due to a decrease in the soil pH by proton contribution from organic acids or by the substitution of previously cation fixed P and formation of organo-metal complexes by organic anions in this study.

The longevity and effectiveness of aliphatic organic acid (citric) increased when applied in combination with aromatic organic acids.

The findings from this experiment may help to understand the role of organic acids on increasing P availability and reducing P sorption in acidic soil when originating from natural resources such as organic waste materials. If the organic materials contain more aliphatic organic acid compounds (carbonyl compounds), the effect on soil P availability would be more effective compared to organic materials containing a higher abundance of aromatic organic acid compounds (phenolic compounds). However, the effect of organic amendments would be prolonged on soil P availability if the organic materials contain an equal abundance of aliphatic and aromatic organic acid producing compounds.

Chapter 7: Investigation of the effect of organic amendments and selected organic acids on plant P uptake

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7.1 Introduction

Chapter 5 demonstrated that the addition of organic amendments (OA) increased P availability and decreased P sorption in the soil and the ratio of phenolic to carbonyl C content of the OA (identified in Chapter 4) was highly correlated with the P availability and P sorption in the soil. The incubation study in Chapter 6 with organic acids further demonstrated that the combined addition of aliphatic (representative of carbonyl compounds) and aromatic (representative of phenolic compounds) organic acids (at 1:1 ratio) were more effective in increasing soil P availability compared to their individual addition.

Chapters 5 and 6 did not however investigate the effect of addition OA or organic acids on plant P uptake. Therefore, in this current study, I conducted a plant bioassay experiment, where the effect of OA and organic acid with or without P addition on soil P availability and plant P uptake was evaluated. The current study aimed to investigate (i) the effect of addition of OA and organic acids (both individual and combined) without any external P addition on soil P availability and plant P uptake and (ii) the effect of addition of OA and organic acids (both individual and combined) on soil P availability and plant P uptake from an external P source. This study hypothesized that the addition of OA and organic acid without any external P would increase soil P availability and plant P uptake by substituting previously fixed P in the soil and would also form organometallic complexes to decrease sorption of added P and increase plant P uptake. OA with equal abundance of phenolic and carbonyl C content would be more effective in increasing soil P availability and plant P uptake. The combined addition of the aliphatic and aromatic organic acid would perform better in increasing soil P availability and plant P uptake compared to their individual addition by providing organic anions for a longer period in the soil.

Similar to Chapters 5 and 6, in this current study, the effect of OA and aliphatic and aromatic organic acids (added both in combination and individually) on soil pH, P availability (Olsen P) and cation concentration (Mehlich 3 extractable Al and Fe) were determined. In addition to that, in this study, the effect of addition of OA and aliphatic and aromatic organic acids on plant P uptake were also determined.

7.2 Materials and methods

7.2.1 Soil characterization

The soil that was used for incubation studies in chapters 5 and 6 was collected again for conducting plant bioassay experiment in March 2019. The soil sample was collected from 0 to 0.10 m depth and passed through a 4 mm mesh sieve for using in the pot for growing plants and a 2 mm mesh sieve for chemical analysis. The soil was characterized by determining pH (H_2O), pH ($CaCl_2$), electrical conductivity (EC), Olsen P, cation exchange capacity (CEC), total C, N and other elemental concentration (P, Al, Fe, Zn, Mn, Ca, Mg, Na, K and S) following the methods described in Chapter 5 under the subsection 5.2.1. The characterization of the soil is presented in Table 7.1.

Table 7.1: Selected chemical properties of Rutherglen soil.

Parameters	Values
pH (H_2O)	4.97
pH ($CaCl_2$)	3.80
EC (dS/m)	0.07
CEC (cmol(+)/kg)	4.10
Olsen P (mg/kg)	16
Total C (g/kg)	13.77
Total N (g/kg)	1.25
Total P (g/kg)	0.25
Total Al (g/kg)	9.57
Total Fe (g/kg)	13.20
Total Zn (mg/kg)	19
Total Mn (mg/kg)	443
Total Mg (mg/kg)	474
Total Na (mg/kg)	34
Total K (mg/kg)	1300
Total Ca (mg/kg)	327
Total S (mg/kg)	168

7.2.2 Collection and characterization of organic amendments and organic acids

The same OA from the previous incubation experiment (Chapter 5) was used in this experiment. The different processed forms of food waste and biosolid (raw, biochar and compost) were used as a source of OA. The collection, processing and characterization procedure of raw food waste (FWR), food waste biochar (FWB), food waste compost (FWC), raw biosolid (BSR), biosolid biochar (BSB) and biosolid compost (BSC) are presented in Chapter 4 under the subsections 4.2. The characterization results were presented in Chapter 4 under subsection 4.3.

Only the citric and benzoic acids were added both individually and in combination (1:1) in this experiment as a source of aliphatic and aromatic organic acids, respectively. The properties of both citric and benzoic acid were presented in Chapter 6 under subsection 6.2.2 in Table 6.1.

7.2.3 Experimental approaches

The plant experiment was conducted for 8 weeks from April to June 2019 in a temperature-controlled glasshouse (maintained within 20 to 25° C) at the University of Melbourne, Parkville campus. The experimental approach included the collection and germination of seeds, pot preparation and growth of plant, harvesting and chemical analysis.

7.2.3.1 Collection and germination of seed

The seeds of Triticale (cv Astute) (genus *Triticosecale*) were collected from Baker Seed Co located at Rutherglen, north east of Victoria, Australia. Seeds were pretreated with Rancona (fungicide) and Gaucho (insecticide) as per industry standard rates. The cultivar Astute was selected for its tolerance of high levels of Al and resistance to stem, leaf and stripe rust (Baker seed co web page http://bakerseedco.com.au/). Seeds were pre-germinated on petri dishes in an incubator (25° C) before transplanting to the pot.

7.2.3.2 Pot preparation

During pot preparation, the soil was mixed with both the OA and organic acid treatments separately. OA were added at the rate of 0.5% C (w/w basis) and organic acids were added at the rate of 0.05% C (w/w basis). Then nutrient solutions containing ammonium nitrate, potassium sulfate, calcium chloride and magnesium chloride at the rate of 100, 57, 35 and 30 kg/ha were added as a source of N, K, Ca and Mg to the soil, respectively for all the treatments. Then both the soil mixed with OA and organic acids, respectively divided into three different portions where one portion received zero P (P_0) and other two portions received P at the rate of 50 kg/ha (P_1) and 100 kg/ha (P_2), respectively from a solution containing KH_2PO_4 and considered as three different P addition treatments. The control soil did not receive any OA or organic acid treatments but received all the nutrients doses and P treatments. All the treatments had three replications. The layout of the experimental design is presented in Figure S 6.1 of the supplementary information.

Exactly 1.8 kg of soil mixed with all the treatments were transferred to plastic pots of 0.14 m diameter and 0.13 m depth containing drainage holes at the bottom. Each pot was watered with distilled water at 90% water holding capacity. Then three seedlings were transplanted to each pot. All the pots were placed in the glasshouse and divided into three different blocks based on P addition rates and then pots were placed randomly within the block with rotation once per week. All the pots received regular watering with distilled water throughout the experiment.

7.2.3.3 Harvesting and chemical analysis of the plant samples

All plants from each pot were harvested by cutting off the shoot at the base after 8 weeks of transplantation and placed into paper bags.

Shoot samples were put into an oven at 60° C for 48 h for drying. The dry shoot weight was recorded and then ground to fine powder using a ball mill. The total P concentration was analyzed by nitric acid, hydrochloric acid and peroxide digestion and determined through ICP-OES (Perkin Elmer Optima 8300 DV-radial view) (methodology described in Chapter 4 under subsection 4.2.3). The nutrient uptake of the plant was calculated from the plant dry weight and nutrient concentration and reported on a per pot basis.

7.2.4 Soil characteristics at the end of the experiment

About 300 g of soil was collected from each pot at the end of the experiment. After removing the roots by hand from soil, the soil was oven-dried at 40° C and ground less than 2 mm before further analysis. Soil pH ($CaCl_2$), soil Olsen P and Mehlich-3 (M3) extractable Al and Fe were determined following the method described in Chapter 5 under subsection 5.2.3.

7.2.5 Statistical analysis

Data were statistically analyzed by analysis of variance (ANOVA) following a general linear model using the software package Minitab 18 (Akers, 2018). Treatment means were separated using the least significant differences (LSD) value at the 5% level of probability and compared among all the treatments. Pearson’s correlation coefficient was used in correlation studies.

7.3 Results

7.3.1 Effect of organic amendments addition on soil pH

The addition of OA to soil with P_0 significantly ($P \leq 0.05$) increased soil pH ranging from 4.2 to 4.54 compared to control (Figure 7.1). The most significant effect was obtained by BSB (4.54) treatment followed by FWC> FWR> FWB ≥ BSC. The addition of P_1 and P_2 to the soil with OA had no significant difference in soil pH compared to their P_0 treatments except for FWR, FWB and BSR. In case of FWR and BSR the addition of P_2 significantly ($P \leq 0.05$) increased soil pH compared to its P_0 (Figure 7.1) whereas, the addition of P_2 with FWB significantly ($P \leq 0.05$) decreased the soil pH compared to its P_0 and P_1.

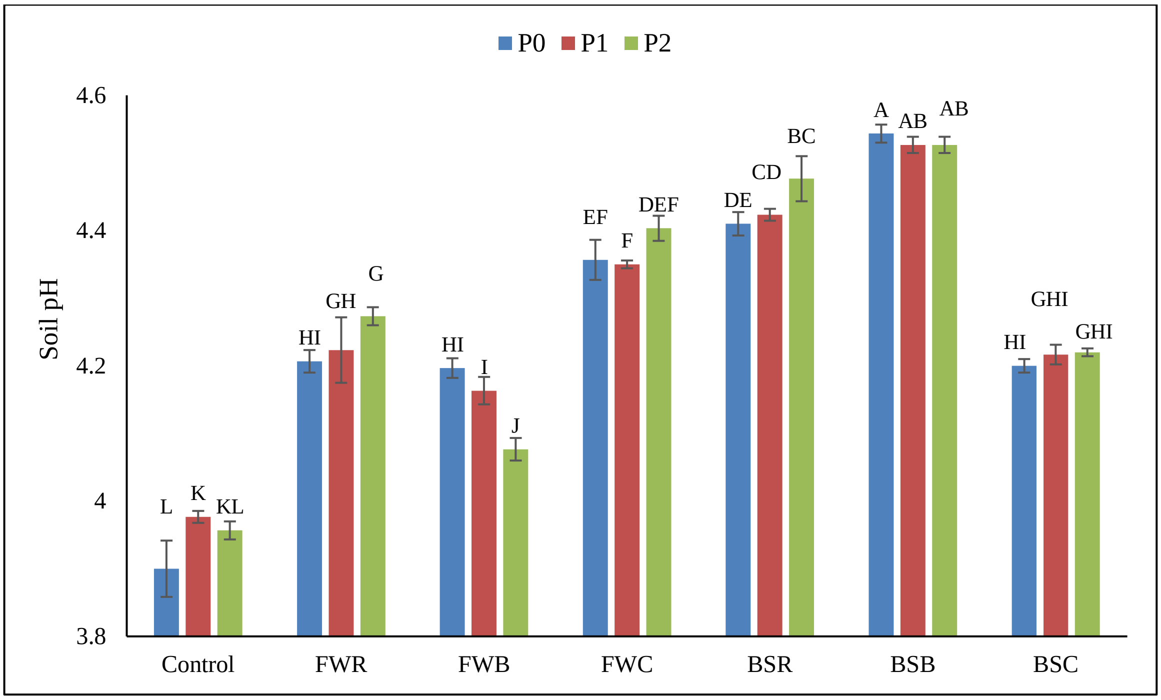

Figure 7.1: Effect of organic amendments on soil pH after 8 weeks of plant growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.2 Effect of organic amendments on soil Olsen P

The OA with (P_1 and P_2) or without P (P_0) addition significantly ($P \leq 0.05$) increased Olsen P compared to control except for FWR and FWB (Figure 7.2). The FWR and FWB addition showed no significant difference in soil Olsen P compared to control. A significant ($P \leq 0.05$) increase of soil Olsen P was observed as the P addition rate increased for all the treatments compared to their low P addition rates (Figure 7.2). However, no significant difference in soil Olsen P was observed between FWR and FWB; BSR and BSB and FWC and BSC both with (P_1 and P_2) or without P (P_0) addition except for few cases. The addition of P_2 with FWB significantly increased soil Olsen P compared to FWR and similarly by BSB compared to BSR.

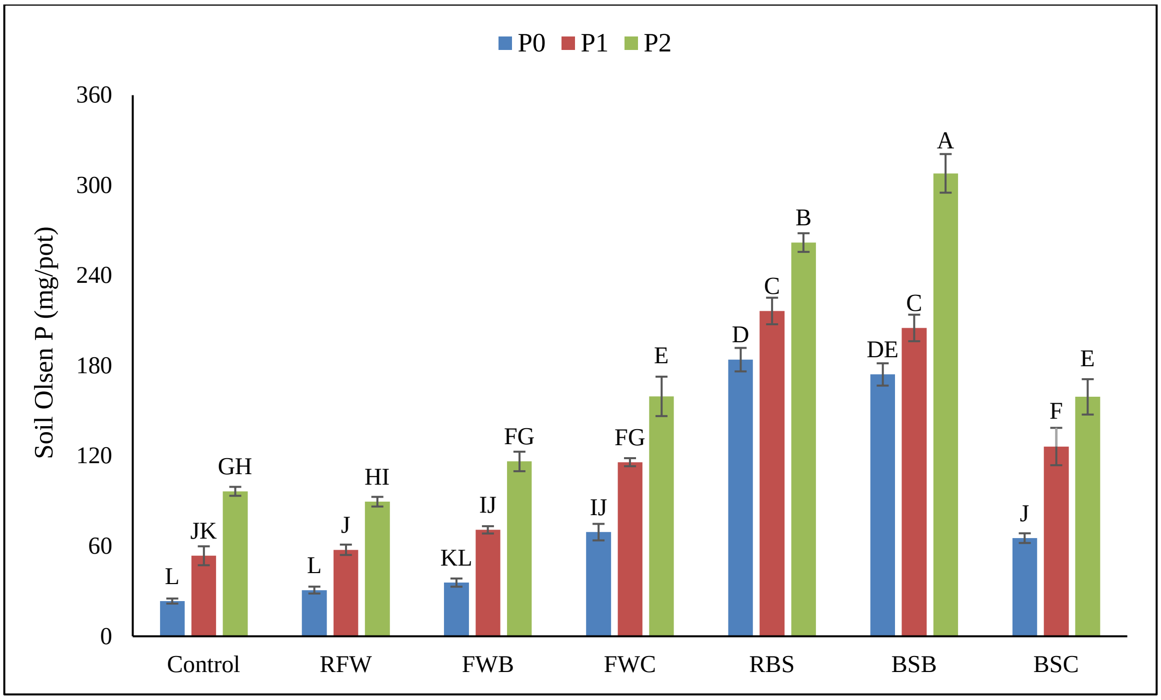

Figure 7.2: Effect of organic amendments on soil Olsen P after 8 weeks of plant growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.3 Effect of organic amendments on soil extractable cations (Al and Fe)

Compared to the control, when no P (P_0) was added, a significant ($P \leq 0.05$) decrease in soil M3 extractable Al concentration was observed by the addition of FWR and FWB, whereas a significant ($P \leq 0.05$) increase was observed by BSR and BSB (Figure 7.3). The addition of FWC and BSC did not show any significant ($P \leq 0.05$) difference compared to control in soil M3 Al concentration. The addition of P_1 and P_2 significantly ($P \leq 0.05$) decreased the M3 extractable soil Al concentration by FWR compared to control and significantly increased by BSR and BSB and showed no significant difference by FWB, FWC and BSC.

Similar to M3 extractable Al, the addition of BSR, BSB and BSC with P_0 significantly ($P \leq 0.05$) increased the soil M3 extractable Fe concentration compared to control whereas the addition of FWR, FWB and FWC showed no significant difference (Figure 7.3). The addition of P_1 did not have any significant ($P \leq 0.05$) difference on soil M3 extractable Fe compared to control except FWR. The addition of P_2 significantly increased the M3 extractable Fe by BSR, BSB and BSC and significantly decreased by FWR compared to control, whereas FWB and FWC showed no significant difference.

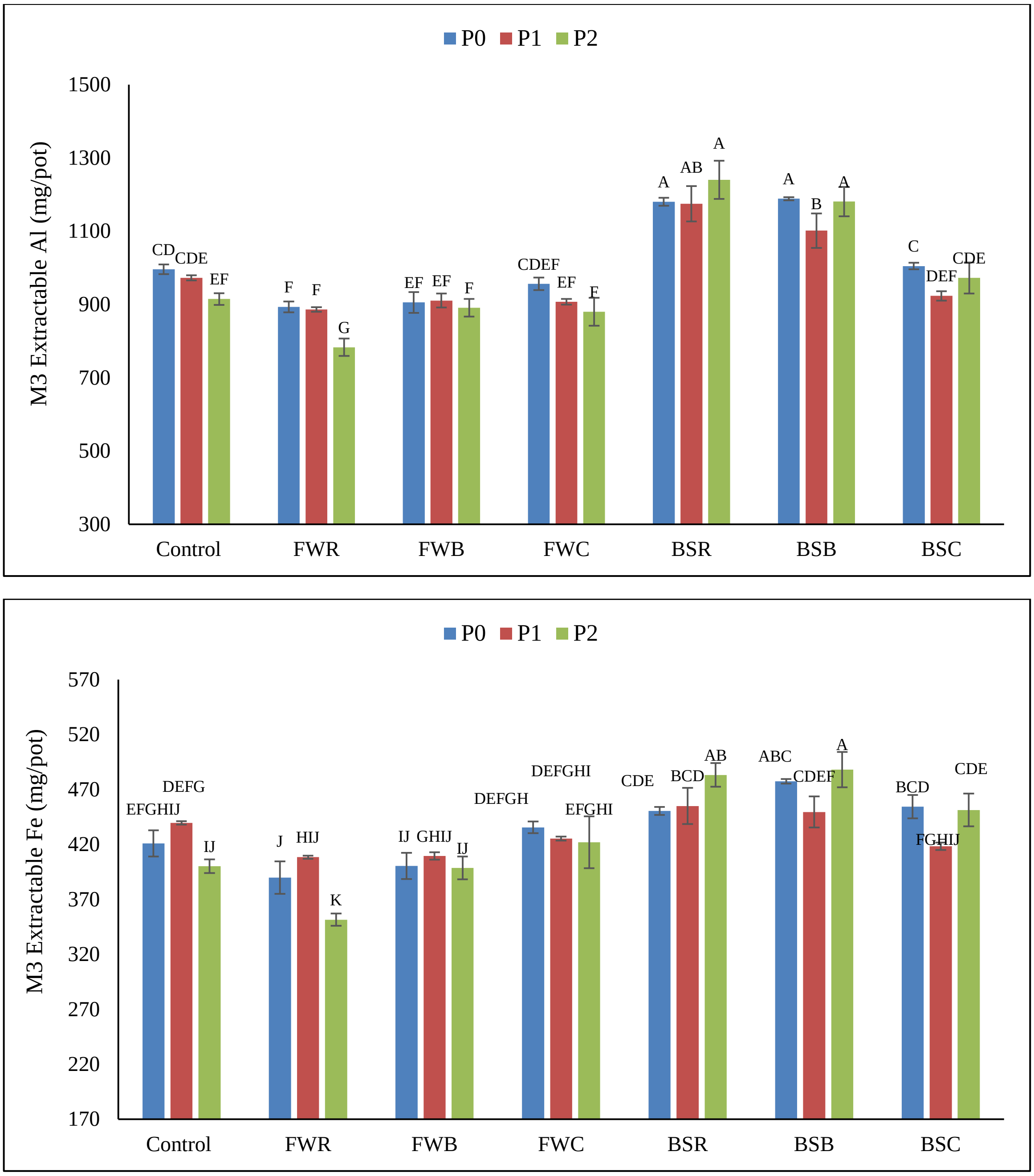

Figure 7.3: Effect of organic amendments on soil Mehlich 3 extractable cations (Al and Fe) after 8 weeks of plant growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.4 Effect of organic amendments on plant biomass (dry weight)

The control treatment recorded the lowest plant dry weight ranging from 0.6 to 1.4 g/pot with all three P addition rates (Figure 7.4). The addition of OA with P_0 and P_1 significantly ($P \leq 0.05$) increased plant dry weight compared to control except FWR (Figure 7.4). The addition of P_2 significantly ($P \leq 0.05$) increased plant dry weight by all the treatments compared to control (Figure 7.4). The addition of P_1 and P_2 did not show any significant difference in plant dry weight with FWC (ranging from 2.1 to 2.2 g/pot) and BSR (1.9 to 2.1 g/pot) compared to their P_0 treatment, whereas FWR (ranged from 0.8 to 1.7 g/pot) and FWB (ranged from 1.1 to 1.9 g/pot) showed a significant increase with increased P addition. The addition of P_1 with BSB did not show any significant effect on plant dry weight compared to P_0 but showed a significant increase when added with P_2. The highest dry weight was obtained by FWC mostly with the P_0 and P_1 addition. The increase in plant dry weight was not significant among FWC, BSR, BSB and BSC when added with P_2. A photo of the effect of addition of different OA along with 3 different rates of P addition (such as P_0, P_1 and P_2) on plant growth presented in Figure S6.2 of the supplementary information.

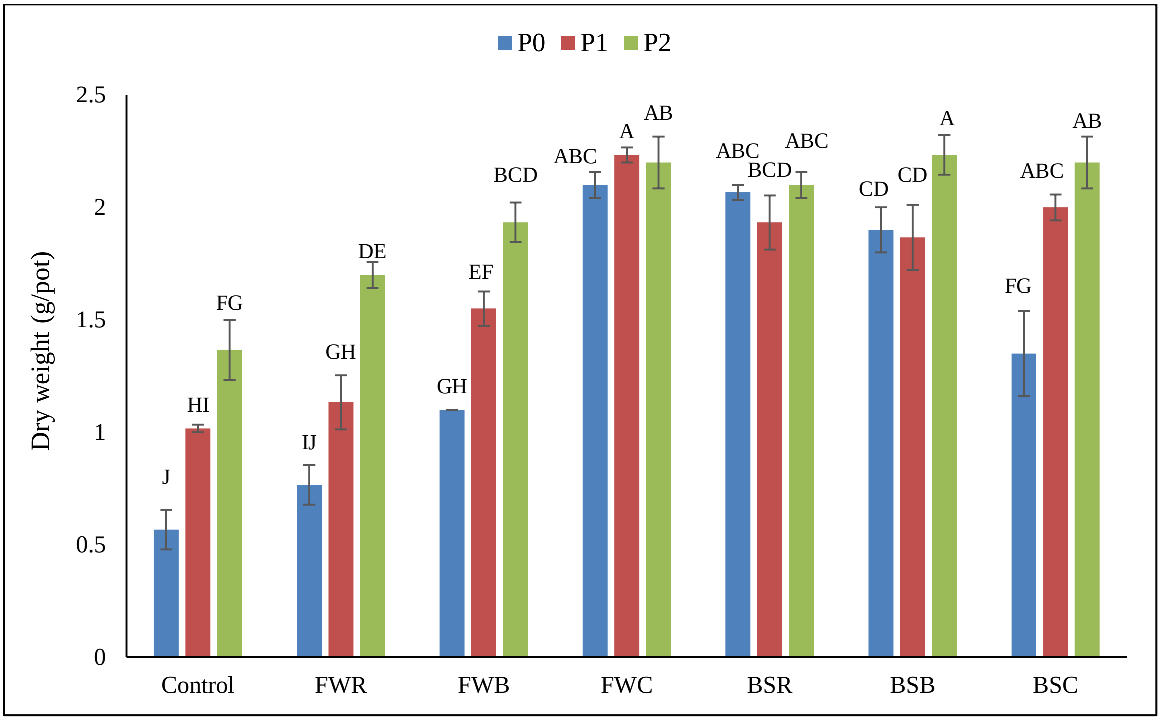

Figure 7.4: Effect of organic amendments on plant biomass (dry weight) after 8 weeks of growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.5 Effect of organic amendments on plant P uptake

The addition of OA to soil with P_0, P_1 and P_2 significantly ($P \leq 0.05$) increased plant P uptake except for FWR with P_0 and P_1 compared to control (ranging from 2 mg/pot to 10.7 mg/pot) (Figure 7.5). The most significant increase of plant P uptake was observed by BSR with P_0 (8.8 mg/pot) and by BSB with both P_1 (9.2 mg/pot) and P_2 (10.7 mg/pot). The addition of FWB, FWC, BSB and BSC with P_1 significantly ($P \leq 0.05$) increased plant P uptake compared to their P_0. The addition of P_2 did not show any significant ($P \leq 0.05$) increase on plant P uptake by FWC, BSR and BSC compared to their P_1, whereas P_2 with FWR, FWB and BSB significantly increased compared to their P_1. The FWR, FWB, BSB and BSC showed a significant increase in plant P uptake as the rate of P addition was increased in this study.

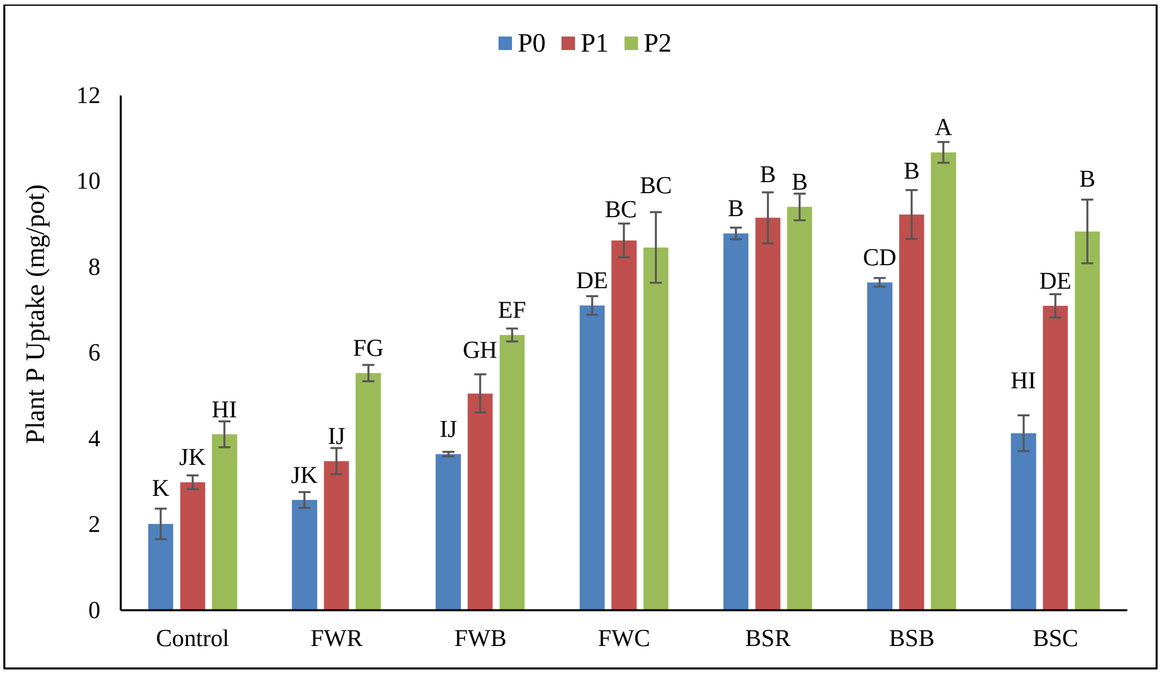

Figure 7.5: Effect of organic amendments on plant P uptake after 8 weeks of growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.6 Effect of organic acids addition on soil pH

The addition of organic acids significantly ($P \leq 0.05$) increased soil pH compared to the control (Figure 7.6). The addition of P_1 and P_2 with organic acids did not have any significant effect in soil pH compared to their P_0 treatments except citric acid with P_2. No significant effect was observed between citric and citric+ benzoic acid treatment, whereas soil pH was significantly ($P \leq 0.05$) increased in citric acid treatment compared to benzoic acid treatment when added with P_1 and P_2. The addition of P_1 and P_2 significantly ($P \leq 0.05$) increased the soil pH in control compared to its P_0 treatment.

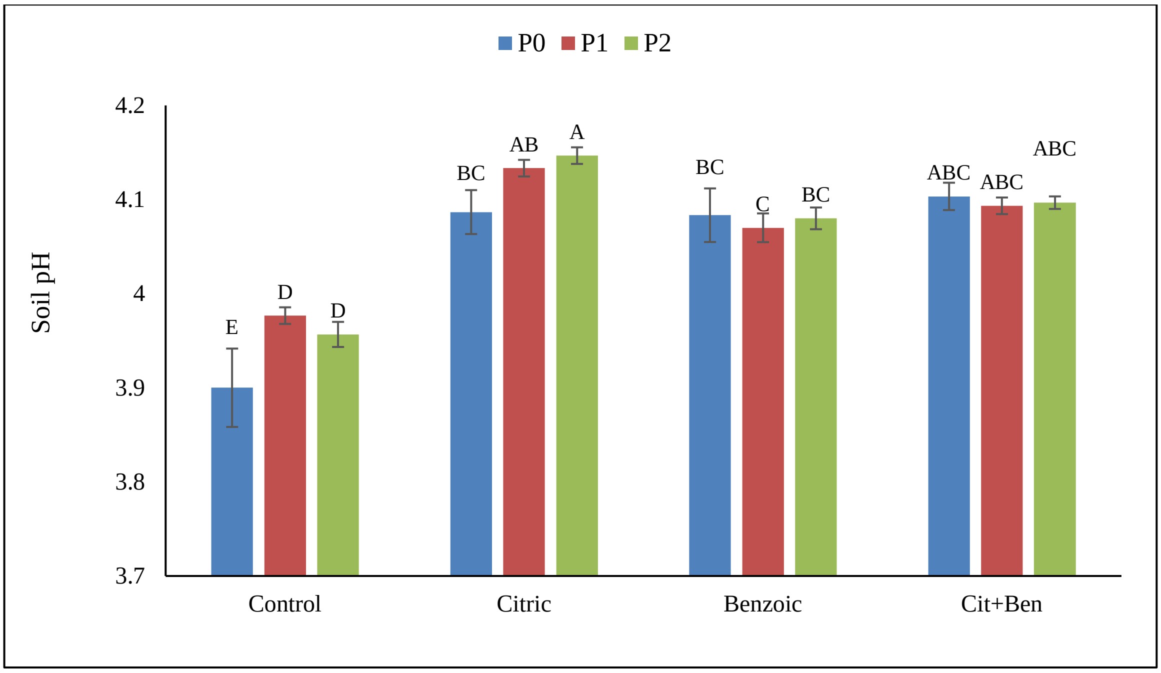

Figure 7.6: Effect of organic acids addition on soil pH after 8 weeks of plant growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. Cit and Ben represent citric and benzoic acid, respectively. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.7 Effect of organic acids on soil Olsen P

The addition of organic acids with P_0 did not show any significant effect on soil Olsen P compared to control (Figure 7.7). The combined addition of citric+ benzoic acid with P_1 and P_2 significantly ($P \leq 0.05$) increased soil Olsen P compared to control, whereas the effect was non-significant compared with their individual addition except citric acid with P_2. The individual addition of citric and benzoic acid did not show a significant difference compared to control except the addition of benzoic acid with P_2 which increased soil Olsen P significantly. All the treatments significantly ($P \leq 0.05$) increased soil Olsen P as the P addition rates were increased compared to their low addition rates.

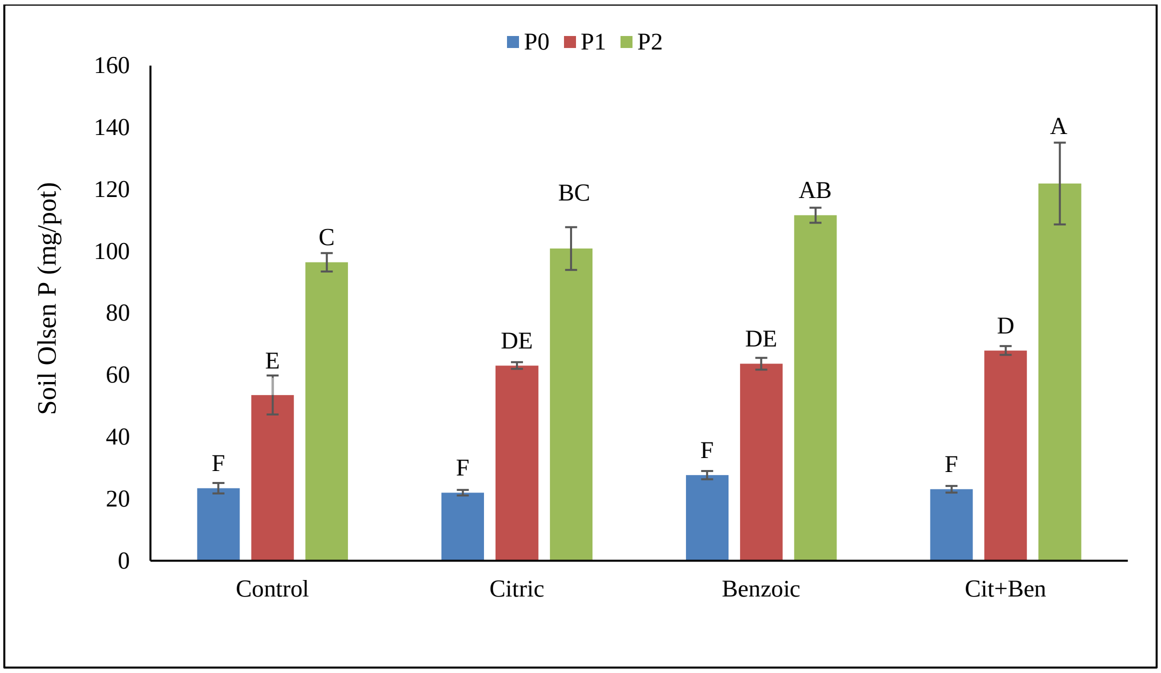

Figure 7.7: Effect of organic acids addition on soil Olsen P after 8 weeks of plant growth. The line on the top of the bar represents standard error. Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. Cit and Ben represent citric and benzoic acid, respectively. P0, P1 and P2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.3.8 Effect of organic acids on soil Mehlich-3 (M3) extractable cations (Al and Fe)

The addition of organic acids did not have any significant ($P \leq 0.05$) effect over control in most of the cases in soil M3 extractable Al and Fe concentrations (Figure 7.8). The addition of P_1 decreased the M3 extractable Al and Fe concentrations by all the organic acids compared to control, whereas the concentration increased when P_2 was added. In the control treatment, the increase in P rates such as P_1 and P_2 showed a decrease in M3 extractable Al and Fe concentrations compared to P_0 treatment.

7.3.9 Effect of organic acids on plant biomass (dry weight)

The addition of organic acid did not have any significant increase in plant dry weight compared to control. The higher P addition showed a significant ($P \leq 0.05$) increase in plant dry weight in all the treatments compared with lower P addition rates (Figure 7.9).

7.3.10 Effect of organic acids on plant P uptake

The addition of both individual and combined organic acids with P_0 and P_1 did not show any significant ($P \leq 0.05$) effect on plant P uptake compared to control (Figure 7.10). The combined addition of citric + benzoic acid with P_2 significantly ($P \leq 0.05$) increased plant P uptake compared to control, whereas no significant ($P \leq 0.05$) difference was observed with their individual addition. Furthermore, the addition of P_1 had no significant ($P \leq 0.05$) difference in plant P uptake compared to P_0, whereas the addition of P_2 significantly ($P \leq 0.05$) increased plant P uptake compared to P_0 and P_1 treatments.

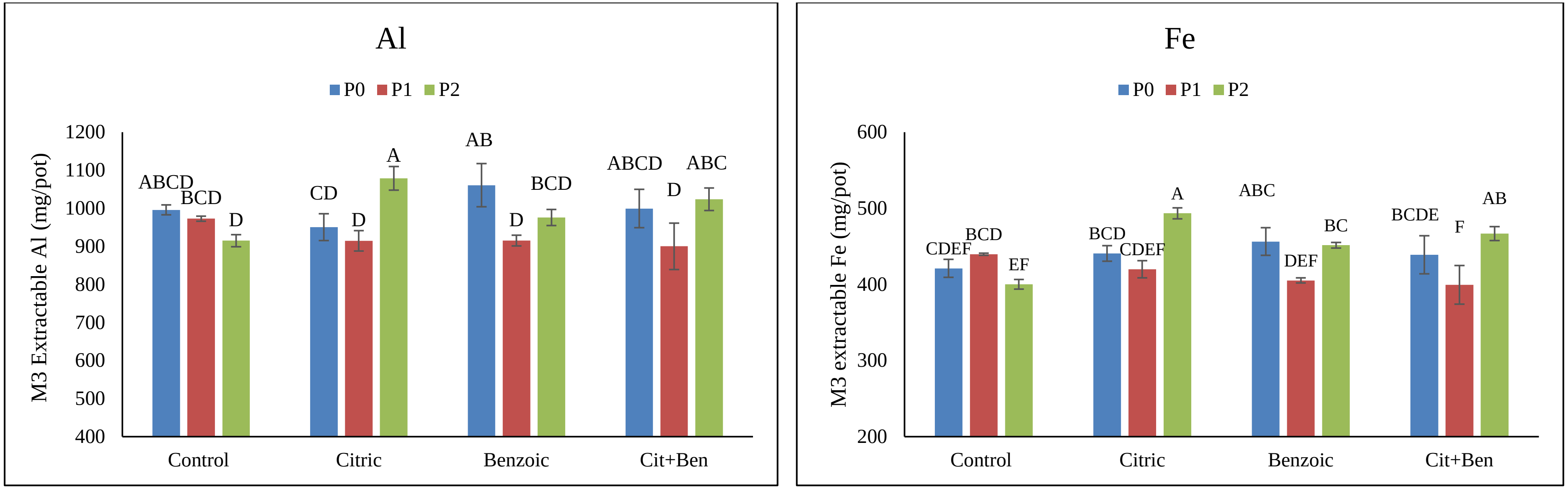

Figure 7.8: Effect of organic acids addition on soil Mehlich-3 (M3) extractable Al and Fe after 8 weeks of plant growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. Cit and Ben represents citric and benzoic acid, respectively. P0, P1 and P2 represents 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

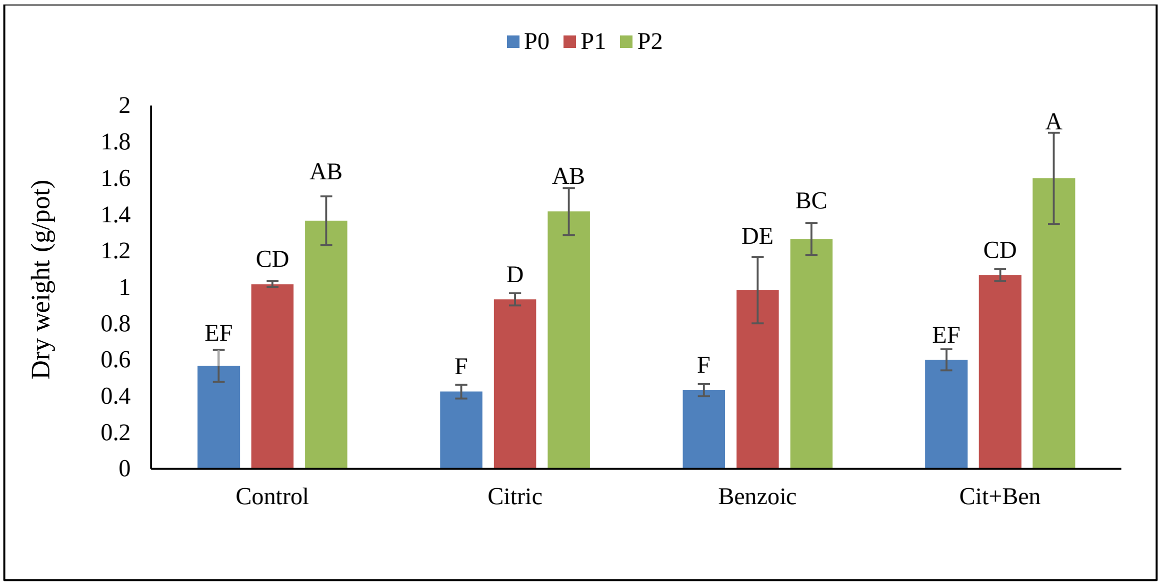

Figure 7.9: Effect of organic acids addition on plant biomass (dry weight) after 8 weeks of growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. Cit and Ben represents citric and benzoic acid, respectively. P0, P1 and P2 represents 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

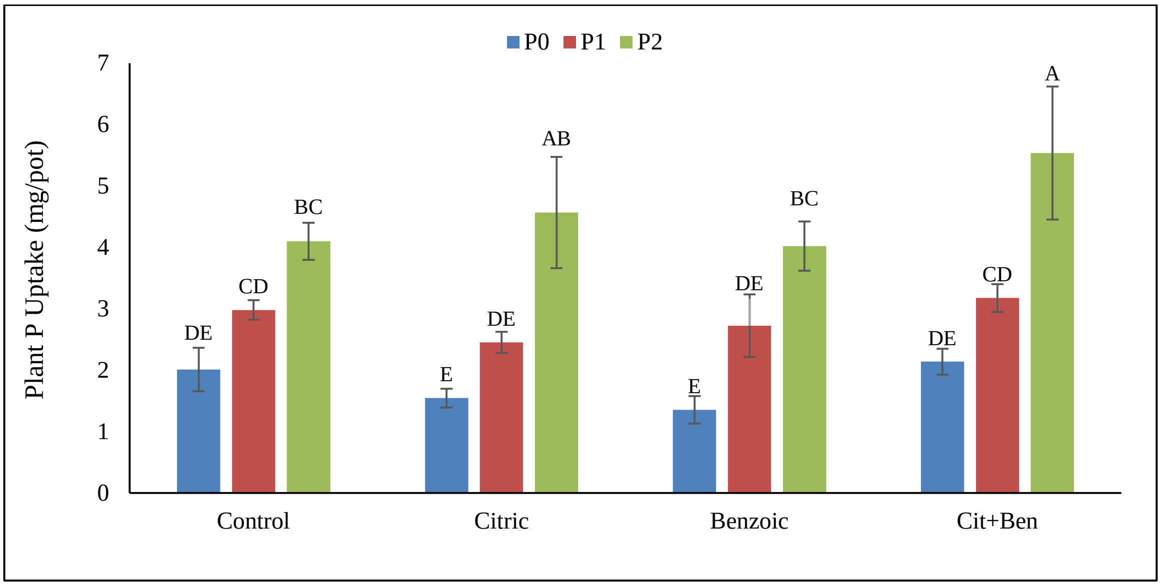

Figure 7.10: Effect of organic acids addition on plant P uptake after 8 weeks of growth. The line on the top of the bar represents standard error (n=3). Different letters indicate difference among the treatments statistically significant at $P \leq 0.05$. Cit and Ben represents citric and benzoic acid, respectively. P0, P1 and P2 represents 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

7.4 Discussion

7.4.1 Effect of organic amendments on soil pH and Olsen P availability

As discussed earlier in Chapter 5 and 6, the change in soil pH would change soil P availability either through the dissolution of the mineral P and previously fixed soil native P if the soil pH decreased below 2.5; or by reducing P adsorption sites in the soil by forming hydroxides of Al and Fe compounds if the soil pH increased up to 6.5 to 7 (Penn and Camberato, 2019, Price, 2006). In this study, the observed soil pH ranged from 3.9 (control) to 4.5 (BSB) (Figure 7.1), which is also similar to the soil pH obtained in Chapter 5 (Figure 5.2). This soil pH is within the range for high soil P fixation by the soil cations such as Fe and Al (Figure 5.6) (Penn and Camberato, 2019). Therefore, this change in soil pH from 3.9 to 4.5 was unlikely to increase soil Olsen P neither through the dissolution of mineral P or previously fixed P in soil in this current study.

The increase of the soil Olsen P was reported to a varying degree due to the addition of different amounts of P from OA in the previous incubation experiment in Chapter 5. This experiment also followed a similar trend as like as in Chapter 5 due to the use of the same soil and similar addition rates of OA in both studies. For instance, the FWR and FWB recorded as the lowest Olsen P and BSR and BSB recorded the highest soil Olsen P in this current study (Figure 7.2) as also observed in Chapter 5 (Figure 5.3).

In addition to the P contribution from OA (Olsen P), an additive effect in increasing soil Olsen P was observed by FWC, BSR, BSB and BSC in Chapter 5 (Figure 5.7). The substitution of previously fixed P and formation of stable organometallic complexes in soil by the phenolic and carbonyl C compounds of OA was reported as the main mechanism for obtaining that additive effect in Olsen P in Chapter 5 (Figure 5.8) and showed a positive correlation (Table

5.3) between ∆Olsen P (the difference between observed and expected Olsen P) and ratio of phenolic to carbonyl C content of the OA (identified in Chapter 4). In this current study a similar additive effect of the addition of FWC, BSR, BSB and BSC with P_0 on soil Olsen P was observed (Figure 6. 11) and dissimilar to Chapter 5 the additive increase of soil Olsen P, ΔP_0 (the difference between observed and expected Olsen P with P_0) showed a non-significant correlation with ratio of phenolic to carbonyl C content of the OA (Table 6. 2). The differences in experiment type in Chapter 5 (laboratory incubation) and Chapter 7 (plant bioassay experiment) was speculated as responsible for this dissimilar correlation between those studies. In this study, samples were collected at a single point by the end of the experiment only. Furthermore, plant experiments are expected to be more complex compared to laboratory incubation studies due to the introduction of several new factors such as plant and plant root interaction with the soil which may inspire microbial activity and immobilization of P for instance.

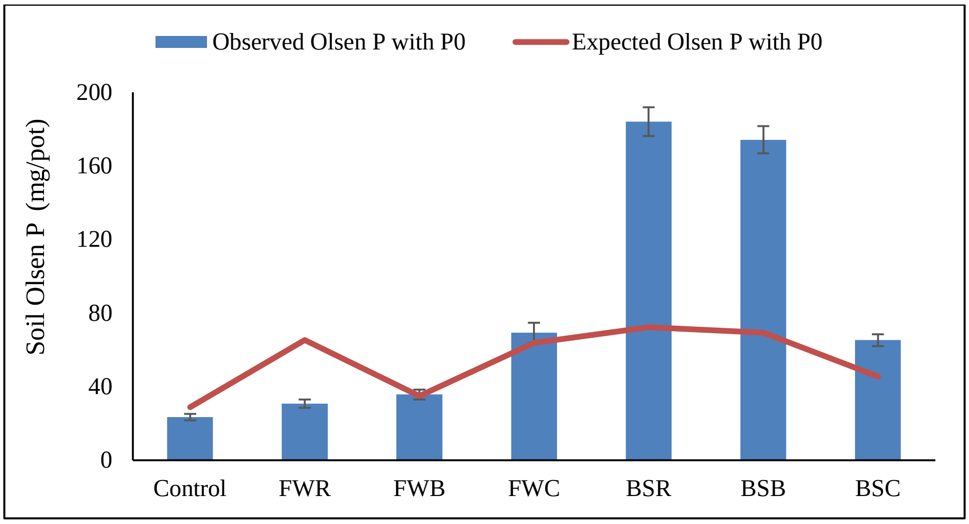

Figure 7.11: The expected and observed Olsen P (ΔP_0) (mg/pot) when OA were added to the soil with P_0 after 8 weeks of plant growth. The expected Olsen P was calculated from the contribution of Olsen P from soil + contribution of Olsen P from OA. The line on the top of the bar represents standard error (n=3).

Table 7.2: Pearson's correlation study between ΔP_0, ΔP_1, ΔP_2 and phenolic and carbonyl C content of the OA. The values representing Pearson's correlation coefficient (r) (n= 18).

Days	Phenolic C content of the OA (%)	Carbonyl C content of the OA (%)	Total abundance of phenolic and carbonyl C content (%)	Ratio of phenolic to carbonyl C of OA
ΔP_0	0.31^{ns}	-0.05^{ns}	0.16^{ns}	0.35^{ns}
ΔP_1	0.22^{ns}	-0.04^{ns}	0.11^{ns}	0.40^{ns}
ΔP_2	0.55^{**}	0.45^{*}	0.60^{***}	0.41^{*}

***indicating significant at $P < 0.01$, ** significant at $P < 0.05$, * significant at $P < 0.1$ and ns-non-significant.

Dissimilar to the Chapter 5, in this study, P from an external source (KH_2PO_4) was added to the soil at two different rates such as P_1 (50 kg/ha) and P_2 (100 kg/ha) to understand the effect of addition of OA on soil P availability from added P. The difference between P_1 and P_0 (ΔP_1) and P_2 and P_0 (ΔP_2) (Table 7.3) from observed Olsen P was calculated to understand the effect of addition of different types of OA on soil P availability from added P. Varying degree of soil P availability (ΔP_1 and ΔP_2) with different types of OA addition was observed and it was hypothesized that the phenolic (represents aromatic organic acids) and carbonyl C (represents aliphatic organic acids) content of the OA would correlate with ΔP_1 and ΔP_2. Two mechanisms were proposed, firstly, the organic anions (the dissociation product of organic acids) would form organometallic complexes to reduce P sorption sites in soil and secondly, they would compete with P to be adsorbed to reduce added P sorption (Hansen and Strawn, 2003, Siddique and Robinson, 2003).

The phenolic and carbonyl C content of the OA showed a non-significant correlation with ΔP_1 and a moderate correlation with the ΔP_2 (Table 7.2). In this study, OA and P were added simultaneously to the soil. Therefore, a competition between organic anions (which was coming from the dissociation of organic acid compounds of OA) and P to be adsorbed and was expected to increase P availability in the soil. However, preferential sorption of P by Al and Fe compared to the formation of organometallic complexes has been reported in a previous study (Agbenin and Igbokwe, 2006). This may explain why the ΔP_2 showed a moderate correlation with the phenolic and carbonyl C content of the OA. The phenolic and carbonyl C content of OA would correlate strongly with the soil P availability if OA were added first (which will reduce P sorption by forming organometallic complexes) and then P to the soil. This hypothesis supported the obtained result from the previous study in Chapter 5, where the soil was incubated with OA for a certain period and then P was added to the soil and P availability showed a high correlation with the phenolic and carbonyl C content of the OA (Table 5.4). A study by (Schefe and Tymms, 2013) also demonstrated that the co-addition of the P and organic acid was less effective in increasing soil P availability compared to their phased addition (which was the addition of OA and then P). Therefore, the phenolic and carbonyl C content of the OA would predict soil P availability better if OA were added first and then P added to the soil compared to their simultaneous addition.

Furthermore, the soil used in this experiment has a high P sorption capacity. The addition of P_1 and P_2 resulted in the addition of about 241 and 482 mg P (in the form of phosphate, $H_2PO_4^-$), respectively per pot. The soil phosphorus buffering capacity (PBC) with or without OA addition ranged from 244 to 345 (mg/kg/$\log_{10}$mg/L) as determined in Chapter 5 (Figure 5.5). Therefore, the soil is expected to adsorb most of the P added from P_1 and may explain the reason for obtaining a non-significant correlation between ΔP_1 and phenolic and carbonyl C content of OA (Table 7.2).

In this study, the ΔP_1 and ΔP_2 were non-significant compared to the control for most of the treatments except for BSC (in case of ΔP_1) and BSB (in case of ΔP_2) (Table 7.3). The non-significant effect may be due to the contribution of Al and Fe from OA, which added additional

P sorption sites in the soil which was further evident by the decrease in M3 extractable Al and Fe concentration when P_1 and P_2 were added to the soil (Figure 7.3).

Table 7.3: Effect of organic amendments on ΔP_1 and ΔP_2 (calculated from soil Olsen P). Different letters are indicating statistically significant at $P \leq 0.05$.

Treatments	ΔP_1 (P_1-P_0) (mg/pot)	ΔP_2 (P_2-P_0) (mg/pot)
Control	30 ± 7 (b)	73 ± 4 (bc)
FWR	27 ± 5 (b)	59 ± 5 (c)
FWB	35 ± 4 (ab)	81 ± 4 (bc)
FWC	47 ± 5 (ab)	90 ± 17 (b)
BSR	32 ± 12 (ab)	78 ± 13 (bc)
BSB	31 ± 15 (ab)	134 ± 8 (a)
BSC	61 ± 14 (a)	94 ± 12(b)

7.4.2 Effect of organic amendments on plant biomass and P uptake

The addition of OA increased the plant dry biomass and plant P uptake. The addition of both P_1 and P_2 with OA increased plant dry biomass compared to their P_0 treatment except for FWC and BSR. The plant growth seemed to plateau as reached its maximum growth of around 2.2 g biomass/pot (Figure 7.4), which may explain the reason for no additional growth of the plant biomass with the addition of P in case of FWC and BSR.

Plant uptake of P was increased when OA were added with (P_1 and P_2) or without P (P_0) from KH_2PO_4. This increase of plant uptake of P showed a strong positive correlation (r^2=0.87) with the soil Olsen P content (Figure 7.12). However, the plant P uptake plateaued at a certain point in case of FWC and BSR also evident in Figure 7.7. This may indicate that at the period of 8 weeks growth, the plant reaches a P limited yield where no more than 50 kg P/ha needed to be added if applied with FWC and no P needed to be adding if applied with BSR. The addition of FWR and FWB would still be needed to add more P either from organic or inorganic sources to reach the peak plant P uptake. (Figure 7.5).

The lowest Plant P uptake was observed by FWR and FWB with all the P addition rates P_0, P_1 and P_2. Both the FWR and FWB had a lower ratio of phenolic to carbonyl C content and a lower abundance of phenolic and carbonyl C content compared to FWC, BSR, BSB and BSC (Table 4.3). Therefore, a low ratio and abundance of phenolic and carbonyl C of FWR and FWB were less effective in increasing soil P availability concomitant with plant P uptake.

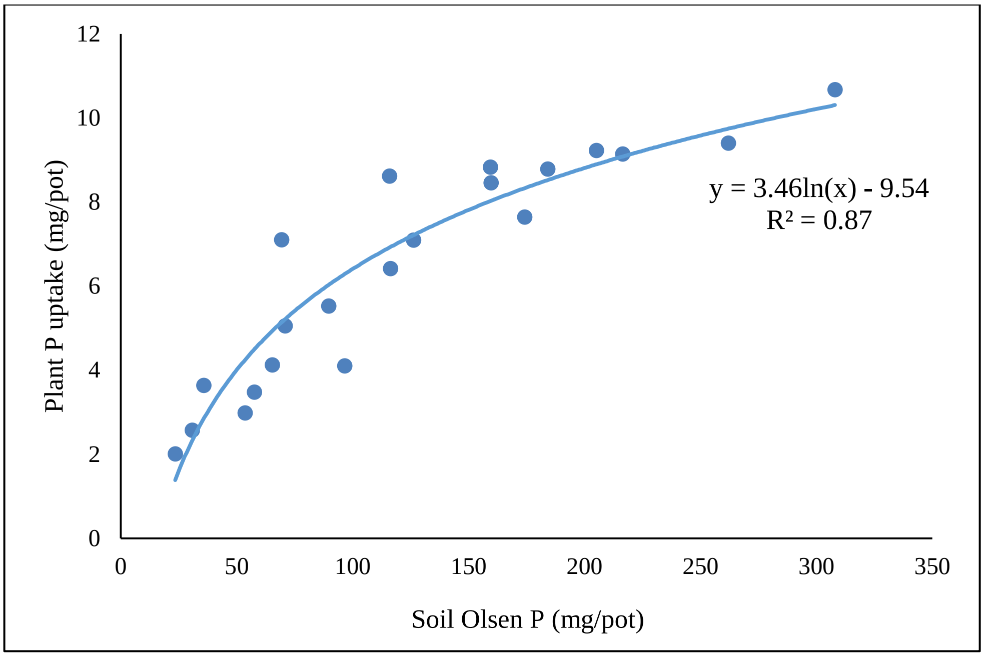

Figure 7.12: Relation between soil Olsen P and plant P uptake (n = 21).

7.4.3 Effect of organic acid addition on soil pH and Olsen P

The addition of organic acids significantly increased soil pH compared to control both by individual and combined addition (Figure 7.6). The observed soil pH by citric acid addition in this study is consistent with the soil pH observed in a previous incubation study at 60 days (Figure 6.1, Chapter 6) and was also slightly higher in case of benzoic and citric+ benzoic acid treatments. In this experiment, the soil pH was measured at the end of the experiment after harvesting of the plant (at 56 days) and the organic acids were added at a 10 times lower rate compared to the previous study in Chapter 6. The initial proton contribution and later microbial degradation of organic acid that was explained as the mechanisms for initial decrease and later increase in soil pH in Chapter 6, was also expected to occur in this study.

In the case of soil Olsen P, only the combined addition of citric and benzoic acid showed a significant increase compared to the control when P_1 and P_2 were added (Figure 7.7). This was due to the delayed degradation of the benzoic acid and prolonged contribution of the organic anions as also discussed in Chapter 6. In this study, the increase in soil Olsen P was due to the decrease in the P sorption sites through the formation of organometallic complexes in the soil rather than the dissolution of minerals or substitution of previously fixed P, as no difference in the soil Olsen P was observed when organic acids were added to the soil with P_0 and P_1. The M3 extractable Al and Fe also decreased in concentration in the citric and citric+ benzoic acid treatment when added with P_0 compared to the control. This may support the previous hypothesis of the formation of organometallic complexes between Al and Fe and organic anion and an increase in soil P availability.

7.4.4 Effect of organic acid addition on plant biomass and P uptake

The addition of organic acids did not have a significant effect on increasing plant biomass and P uptake compared to control. There are two possible reasons to explain this phenomenon. Either all the organic acids were degraded by the microbial action or the concentration of addition of organic acids added were too low to provide a significant effect in this study. Initially, it was attempted to grow lettuce with a higher concentration of organic acids (at the rate of 0.4% C, w/w basis) but this resulted in toxicity to the plant. The concentration of the organic acid would be phytotoxic if it is more than 10 mM (Chatterjee et al., 2015).

Although the addition of organic acids showed no significant difference in soil P availability and plant P uptake, the combined addition showed an increasing effect in soil P availability and plant P uptake compared to their individual addition. Therefore the combined addition of aliphatic and aromatic organic acid may have a prolonged effect on soil P availability and plant P uptake compared to their individual addition but further experiments are needed to explore this more.

7.5 Conclusions

The addition of organic amendments increased soil P availability with or without P addition. The main mechanisms include P supply from organic amendments and reduction in the soil P adsorption.

The low P addition from organic amendments (FWR and FWB) resulted in the low soil P availability and plant growth and plant P uptake. Furthermore, the organic amendments with a low ratio of phenolic to carbonyl C content and abundance of phenolic and carbonyl C content (FWR and FWB) resulted in lower availability of P that was added from KH_2PO_4 in the soil and also in plant growth and plant P uptake. However, the ratio of phenolic to carbonyl C content and total abundance of phenolic and carbonyl C of OA showed a moderate correlation with the availability of P added from KH_2PO_4 (ΔP_1 and ΔP_2) due to the addition of OA and P simultaneously to the soil. I recommend that the ratio of phenolic to carbonyl C content and total abundance of phenolic and carbonyl C of OA would better predict the soil Olsen P availability if OA added to the soil before P.

The addition of organic acid did not show any significant difference compared to the control which may be due to the addition of organic acid at a very lower rate in this study (approximately 10 times lower compared to the rate used in Chapter 6).

However, the combined addition of citric and benzoic acid showed an increase in soil Olsen P, plant growth and plant P uptake compared to their individual addition. Therefore, I conclude that the presence of both phenolic and carbonyl C content at equal abundance would be highly effective in increasing soil P availability, however further studies with the appropriate rate of organic acids will be needed to confirm this hypothesis.

Chapter 8: Summary, conclusions and recommendations for further work

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This thesis aimed to utilize the signature C and P compounds from a range of organic amendments to predict their effect on soil P availability. To achieve this aim this study utilized two major waste streams, food waste and biosolid, as sources of organic amendments in three different forms, unprocessed or raw, biochar and compost of food waste (raw food waste, FWR; food waste biochar, FWB; and food waste compost, FWC) and biosolid (raw biosolid, BSR; biosolid biochar, BSB and biosolid compost, BSC) were prepared. The raw and biochar product was produced from similar feedstock materials where the compost of food waste (FWC) and biosolid (BSC) were collected from commercial compost producing companies. In this study, I utilized Nuclear Magnetic Resonance (NMR) spectroscopy (both solid-state ^{13}C NMR and solution-state ^{31}P NMR) to identify changes in the abundance of forms of C and P compounds in OA across different sources and processing (Chapter 4). Further, a 110-day incubation experiment with organic materials (FWR, FWB, FWC, BSR, BSB and BSC) was conducted to understand their effect on soil P availability and soil P sorption (Chapter 5) and was correlated with organic anion producing C compounds (phenolic and carbonyl C) of the organic amendments. A significant correlation ($P < 0.01$) between the ratio of phenolic to carbonyl compounds of the organic amendments with the soil P sorption capacity was observed (Chapter 5). To further verify the effect of phenolic and carbonyl compounds on soil P availability, some naturally occurring aromatic organic acids (representative of phenolic compounds) (benzoic, 4-hydroxybenzoic and protocatechuic acid) and aliphatic organic acid (representative of carbonyl compounds) (oxalic acid and citric acid) were incubated for 110 days (Chapter 6). Finally, a plant bioassay experiment was conducted with both organic materials and some selected organic acids to further investigate the proposed hypothesis in earlier experiments in chapters 5 and 6 through plant P uptake (Chapter 7). In addition to Chapters 5 and 6, in this study, the effect of organic amendments and organic acids on the availability of P from added P sources was studied.

8.1 Key findings and conclusions

In Chapter 4, the solid-state ^{13}C NMR identified that the dominant forms of C in raw organic amendments were alkyl C (principally aliphatic lipids, fatty acids and waxes) and O-alkyl C (oxygenated C in carbohydrate which includes sugars and polysaccharides). Pyrolysis of the raw materials decreased the abundance of O-alkyl compounds and increased the aryl C (alkyl-substituted aromatic compounds), O-aryl C (phenolic compounds) and carbonyl C (carboxylic, amide and ketone compounds) compounds. In composted materials, the most abundant form of C was O-alkyl C (oxygenated C in carbohydrate which includes sugars and polysaccharides).

The solution-state ^{31}P NMR identified orthophosphate as the most abundant form of inorganic P in case of FWB, FWC and BSC and orthophosphate monoesters as the abundant form of organic P in case of FWR. The high Fe concentration in the BSR and BSB caused the broadening (due to paramagnetic effect) and merged the orthophosphate and orthophosphate monoester peak, which were recorded as the abundant forms of P in those materials.

In Chapter 5, the soil was incubated with the FWR, FWB, FWC, BSR, BSB and BSC and their effect on soil P availability was correlated with the signature C (phenolic and carbonyl C) and P (orthophosphate) compounds (determined in Chapter 4). The incubation result showed that the addition of the OA increased the Olsen P in an order of total P added from those materials. However, the mass balance calculation showed a lower observed soil Olsen P compared to the expected Olsen P when orthophosphate content of the OA was considered to calculated expected Olsen P concentration. It was speculated that the overestimation of the orthophosphate content by NMR spectroscopy was responsible for such lower observed Olsen P compared to the expected Olsen P in soil. An additive effect of soil Olsen P was observed when the expected Olsen P was calculated using Olsen P contribution from OA. There were three mechanisms expected to explain this additive effect in soil Olsen P. Firstly, the mineralization of the organic P (both from soil and OA) to inorganic P, secondly, the rise in the soil pH and thirdly the substitution of previously fixed P and formation of organometallic complexes in the soil by the organic anion producing compounds of the OA.

The concentration of soil Olsen P in the control treatment was fairly constant throughout the experiment. Moreover, the abundant form of organic P was orthophosphate monoester in OA, which is known for its less bioavailability due to the formation of stable complexes with soil cations. Therefore, the contribution of mineralized organic P was considered as a non-dominant phenomenon in this experiment.

The observed soil pH ranged from 3.7 to 4.7 in this study, which is within the range for maximum P fixation in the soil by soil cations. Therefore, the substitution of previously fixed P in the soil and the formation of organometallic complexes by the action of organic anion producing compounds of the OA (phenolic and carbonyl organic acid compounds) was considered as the main mechanism for obtaining that additive increase in soil Olsen P. Also a strong positive correlation between the ΔOlsen P (the difference between observed and expected Olsen P) and phenolic and carbonyl C content of the OA was observed, which further provide evidence in the support of the third hypothesis.

Further, a P sorption experiment was conducted with the incubated soil to understand the change in soil Phosphorus Buffering Capacity (PBC). All the organic amendments significantly ($P \leq 0.05$) decreased the soil P buffering capacity compared to control. Again, as hypothesized earlier the organic anion producing C compounds (phenolic and carbonyl C) of OA showed a strong negative correlation with the soil ΔPBC (the difference between treatment and control). However, the correlation was stronger with the ratio of phenolic to carbonyl C content of organic amendments compared to the total abundance. The soil PBC decreased as the ratio of phenolic to carbonyl C content of the OA was increased. Due to the contrasting nature of phenolic and carbonyl compounds, they could complement each other and influence soil P availability. Therefore, this experiment concluded that the role of the OA on soil P availability could be predictable from the ratio of phenolic to carbonyl C content.

In Chapter 6, to further validate the hypothesis of the effect of phenolic and carbonyl C compounds on soil P availability, some naturally occurring phenolic compounds (aromatic organic acids such as benzoic, 4-hydroxybenzoic and protocatechuic) and carbonyl compounds (aliphatic organic acids such as oxalic and citric) were incubated with soil for 110 days. The aliphatic and aromatic organic acids were added individually or in a combination of a 1:1 ratio in this study. The result suggested that the aliphatic organic acids were performed better in increasing soil P availability relative to phenolic organic acids. In addition to that, the effect of aliphatic organic acid was extended when applied in combination with phenolic organic acids. It was hypothesized that the combined addition of phenolic and carbonyl C compound had complementary effects on each other. For instance, phenolic compounds are known to be toxic to the soil microbes which may delay the microbial degradation of carbonyl C and supply organic anions for a longer period. Therefore, it was recommended that the ratio of phenolic to carbonyl C content of OA would be able to predict better the soil P availability compared to their total abundance.

In Chapter 7, a plant bioassay experiment was conducted where organic amendments and some selected organic acids (citric and benzoic) were added to the soil with or without an additional P source (at three different doses such as 0 (P_0), 50 (P_1) and 100 (P_2) kg/ha). The effect of organic amendments and organic acids on soil P availability and plant P uptake both from OA and from added P sources were studied. The experimental results with organic materials followed the results observed in the previous incubation experiment in Chapter 5, the addition of OA increased soil P availability. Similar to Chapter 5, the additive effect of OA addition to soil on Olsen P was calculated (ΔP_0, the difference between observed and expected Olsen P) and a strong correlation with the ratio of phenolic and carbonyl C content of the OA was expected. However, there was no significant correlation between ΔP_0 and phenolic and carbonyl C content of the OA was observed. It was speculated that the differences in experimental type in Chapter 5 and Chapter 7 were responsible for this non-significant relationship.

The OA also increased the soil P availability from added external sources of P (P_1 and P_2) compared to control treatment. The formation of organometallic complexes by the organic anions was reported as the main mechanisms for the increase in soil P availability from added P and a strong correlation between ΔP (includes ΔP_1, P_1-P_o and ΔP_2, P_2-P_0) and the phenolic and carbonyl C content of the OA was expected. However, a weak to moderate correlation between the ΔP (ΔP_1 and ΔP_2) and phenolic and carbonyl C content of the OA was observed. In this study, OA and P were added simultaneously to the soil. Therefore, a competition between organic anions (which was coming from the dissociation of organic acid compounds of OA) and P to be adsorbed and was expected to increase P availability in the soil. However, the preferential sorption of P by Al and Fe compared to the formation of organometallic complexes with organic anions was speculated as to the main reason for the observed weak to moderate correlation between the ΔP (ΔP_1 and ΔP_2) and phenolic and carbonyl C content of the OA. The phenolic and carbonyl C content of OA would correlate strongly with the soil P availability if OA were added first (which will reduce P sorption by forming organometallic complexes) and then P to the soil as also observed in Chapter 5. Therefore, it was concluded that the phenolic and carbonyl C content of the OA would predict soil P availability better if OA were added first (which would form organometallic complexes) and then P to the soil compared to their simultaneous addition.

Plant P uptake showed a strong positive correlation with the soil Olsen P content. The plant P uptake increased as the soil Olsen P was increased until it reached a plant P limited yield. Therefore, it was concluded that soil Olsen P was a good indicator of plant P availability.

The effect of organic acids on soil P availability and plant P uptake was non-significant compared to the control for most of the cases in this experiment and was not consistent with the results obtained from Chapter 6. Organic acids were added at 10 times lower concentration in this experiment compared to the concentration used in Chapter 6 and may have been the reason for obtaining non-significant effects. This experiment recommended conducting further studies in the future with appropriate rates of organic acid addition to understand their role in soil P availability and plant P uptake.

Based on the results from Chapters 5, 6 and 7, I concluded that the maximum P availability would be achieved if organic amendments were firstly added to soil and then to follow with P application to soil. The ratio of the phenolic to carbonyl C content of the organic amendments could be used to predict the impact of organic amendments on increasing P availability in acidic soil. The availability of P, which would be added in the form of fertilizer with OA could also be predicted by phenolic and carbonyl C content of the OA, if OA were added first and then P added to the soil.

8.2 Limitations of this study and suggestions for future work

In this study, I tested the effect of organic amendments on soil P availability in just a single acidic soil. P availability is generally considered to be a function of soil pH (acidic/alkaline), mineral content and cation concentrations. The reactions of the OA could be different if soil pH and P status were higher. The organic matter content of the soil also varies depending on land use. Different organic matter content of the soil may have different effects on soil P availability. In this study, I observed a strong correlation between the phenolic and carbonyl C of the OA and the P availability in acid soil. In the future, I recommend testing the effect of organic amendments against a wider range of soils from different pH domains and that the reproducibility of the findings from this study should be assessed.

This study utilized actual waste streams (food waste and biosolid) with three different processed forms, dried (raw), compost and biochar. However, these waste streams varied in their composition and potentially influenced the response. Organic amendments should be sourced from other plant and animal sources such as manure, plant/food processing residues, litter, wood sieving, urban green waste with associated processing such as compost, pyrolysis (biochar), dehydration, anaerobic digestion, incineration and other chemical treatments. The abundance of the forms of C and P compounds are expected to vary depending on their sources and processing. In this work, there was a tendency for compost (FWC and BSC) to be more useful compared to biochar and raw products in increasing soil P availability. Therefore, in the future, the physical, chemical and biological limitations of signature C and P assessment should be assessed.

This study included only a few controlled laboratory incubations and pot experiments on a laboratory scale with the measurement of soil Olsen P, which although a valuable tool, may not be the best test for P availability. Ultimately a better indicator is field performance but this has its own constraints. Field conditions are much more varied and influenced by various factors depending on the crop, soil type and climate conditions compared to those of controlled laboratory incubations and pot experiments. In the field condition, it is difficult to control environmental factors such as temperature and rainfall. Temperature and rainfall influence soil microbial activity, which controls the degradation of the organic compounds that are added to the soil from OA. As our ultimate goal is to apply OA at a field scale for crop growing by the farmers or agricultural landholders for increasing P availability, a field-level test to understand the impact of the OA on soil P availability and how the phenolic and carbonyl compounds predict that behavior should be assessed.

Another limitation of this study is the lack of microbial measurements. The degradation of the organic acids (which were from the OA) is due to the soil microbial community and this regulates soil P availability. Therefore, further studies with the inclusion of the microbial measurements, their impact on the transformation of the organic compounds and possible effect on soil P availability would be useful. The effect of organic acids on soil microbial biomass, genetic diversity and abundance should be assessed.

Soil P availability depends on the cation concentrations in the soil. The organic amendments form organometallic complexes by the organic anions in order to increase soil P availability. Under the traditional approaches, to understand the interaction between soil cations and P availability involved different chemical extraction processes where concentration of the soil cations and P are measured separately and then compared. This is an indirect process where soil needs to go through different processing (drying, grinding and mixing with specific chemical/chemicals) and also dependent on the efficiency of the extractant. In recent times, synchrotron techniques are becoming popular and successful in understanding the P chemical speciation in soil (Schefe et al., 2011). The positive side of the synchrotron work is, this technique allows us to have direct information on soil P chemical speciation compared to chemical extraction. The synchrotron-based X-ray technique can determine directly the sorption reactions of P on the surface of soil involving µ-XRF (X-ray fluorescence) which can map and quantify elements such as P and Al in the soil at a sensitivity level of mg/kg. Further synchrotron-based µ-XANES (X-ray absorption near-edge structure) spectroscopy could provide information on the chemical speciation of P directly from the soil. I submitted a proposal (Appendix 4) to the Australian Synchrotron, Clayton, Victoria, Australia as a part of this PhD project with an aim to map and quantify P and Al compounds directly from soil after incubation with organic acids involving XRF and then use of XANES spectroscopy to understand soil P chemical speciation, but it was unsuccessful. In the future, the incorporation of chemical extraction with synchrotron work would be useful to quantify and understand the effect of organic waste materials/organic acids on soil P and cation concentration and their chemical speciation directly involving XRF and XANES spectroscopy.

8.3 Applications of this study

Processing of organic waste through drying, composting and pyrolysis and then application to agricultural land as a source of plant nutrients is an important resource recovery strategy. Besides supplying nutrients, the organic waste addition increases soil organic matter content, which improves soil physical, chemical and biological properties.

The world phosphate rock (main source of inorganic P fertilizer) reserve is decreasing and is expected to reach its peak production soon in a few years. The addition of organic waste to agricultural land may be able to reduce the P fertilizer addition to some extent and ease the demand for phosphate rock. Between the two waste streams used in this study, biosolid has a greater potential to provide plant-available P and increase P uptake due to their high P content compared to food waste. Among the three processed forms of OA used in this study, compost tends to increase soil P availability most by decreasing soil P sorption capacity. Biochar products of both food waste and biosolid were more effective in increasing soil P availability and reducing soil P adsorption compared to their raw product due to the increase in phenolic and carbonyl functional groups and reactivity with soil cations. Therefore, organic waste can potentially be applied to the agricultural land to reduce the P fertilizer addition. Processed compost/biochar would perform better compared to their unprocessed (raw) product for increasing P availability in the soil.

As this study demonstrated that, the impact of organic amendments on increasing soil P availability could be predicted by the ratio of phenolic to carbonyl C content, the traditional approaches of testing organic materials could be replaced by the identification of signature C compounds. The usual traditional approaches are several laboratory, pot and field experiments, which are somewhat expensive, time-consuming and laborious. Furthermore, traditional approaches are most of the time unable to demonstrate expected outcomes due to limited mechanistic insights. Therefore, farmers, landholders and producers of OA could adopt and implement knowledge from this study to assess their organic materials/fertilizer's impact on soil P availability based on the abundance of phenolic and carbonyl C compounds in the quickest possible time. In this study, I used solid-state ^{13}C NMR spectroscopy for the identification of forms of C in organic amendments and the abundance of phenolic and carbonyl C compounds showed a significant ($P < 0.01$) correlation with soil P availability. At present, the accessibility of NMR facilities and the requirement for specialist knowledge to interpret spectra prohibits routine use. However if the benefits of this technology for prediction of the appropriateness of organic amendment were more broadly established and coupled with the ever-decreasing cost of such technology, then farmers would have greater confidence in the long-term benefit of returning waste streams to the farm.

Appendix 1: FTIR, GC-MS and LCMS analysis of selected organic amendments

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All the organic materials such as food waste (FWR), biosolid (BSR) and their processed form such as biochar (FWB and BSB) and compost (FWC) were analyzed using FTIR (to identify functional groups), GCMS (to determine compounds, extracted using methanol and hexane as extractant) and LCMS (to determine the presence of both aliphatic and phenolic organic acids). All the materials used here for analysis were used in further experiments in Chapters 4, 5 and 7.

A1.1 FTIR analysis

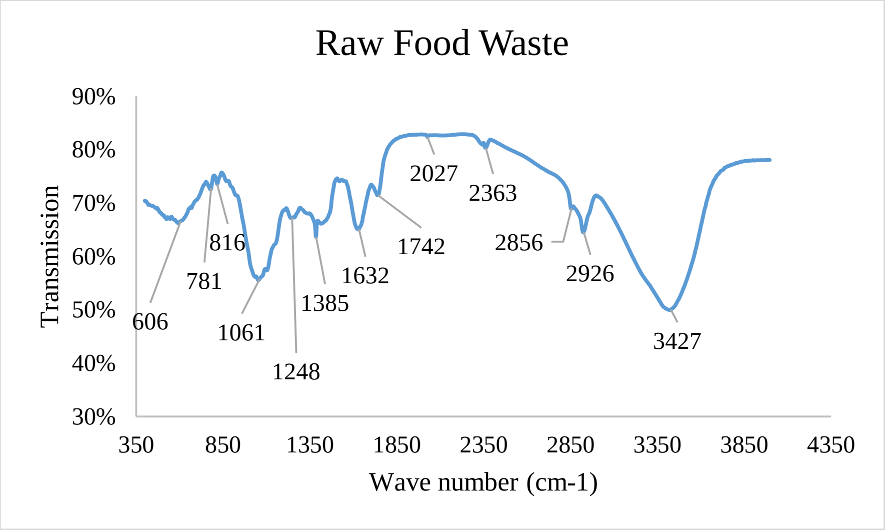
The FTIR analysis was conducted to identify different functional groups in organic materials. The samples were processed following KBr (potassium bromide) method. In this method, KBr was oven-dried at 105° C for 48 hours to illuminate all the moisture. Then 100 mg of KBr was mixed thoroughly with less than ~1 mg of organic materials. A very thin disc was produced using a pressure pump and then the transmission was obtained at different wavenumber.

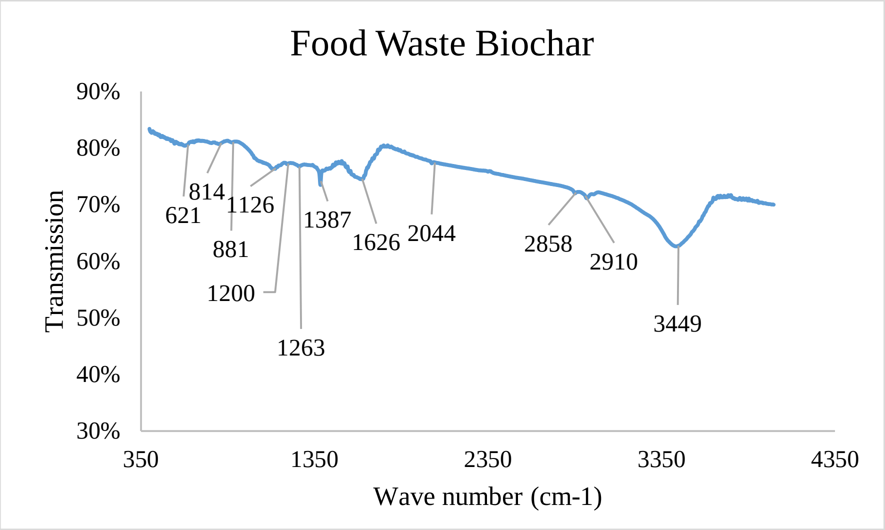
A1.2 GC-MS analysis

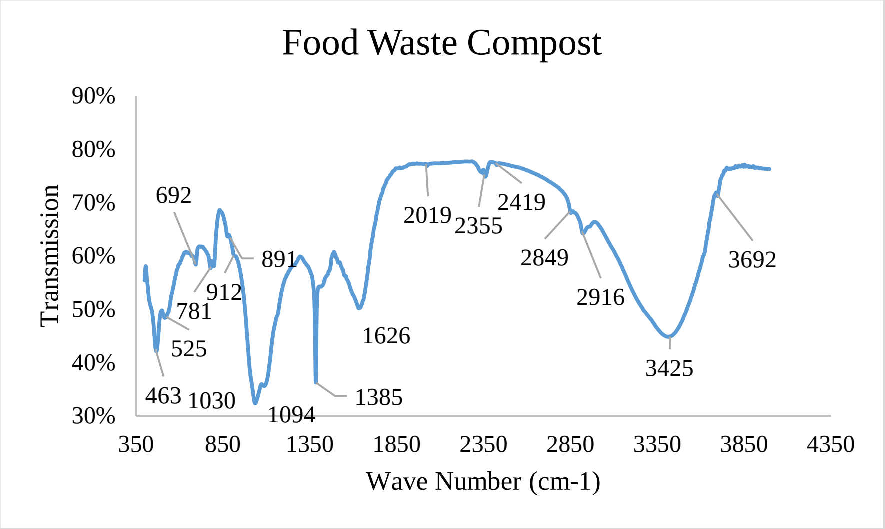
Finely ground samples (0.5 mm) were extracted with Methanol and Hexane at a 1:10 ratio to identify different compounds present in organic materials. About 1 ± 0.02g of organic materials were taken into a conical flask. 10 ml of organic solvent (methanol and hexane) were added to the flask and then sonicated for 30 minutes. A piece of parafilm was used to cover the conical flask top. After sonication, the extracts were filtered through cotton to the GC-MS sample vial for analysis.

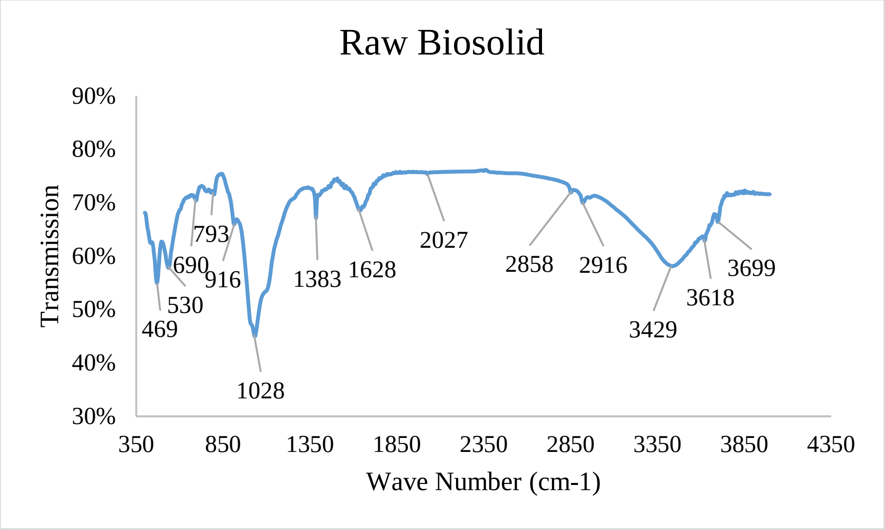
Appendix 1

FTIR Results








Raw Biosolid

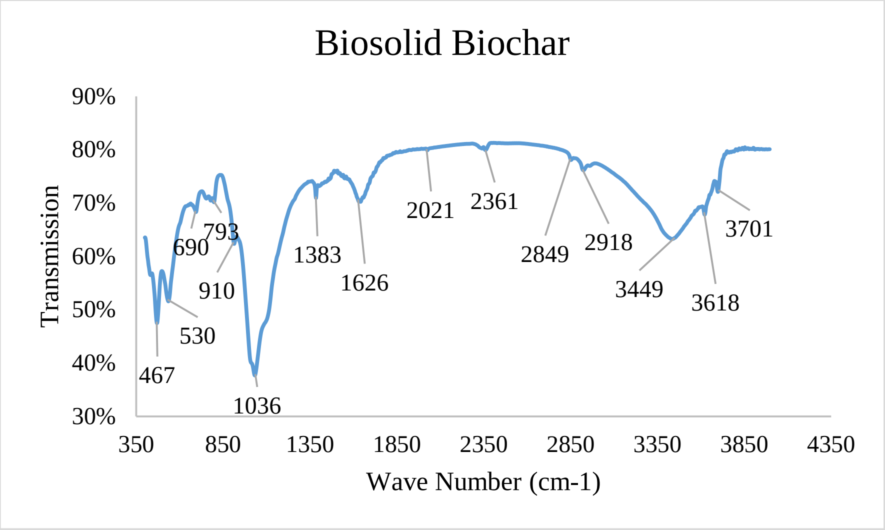

Biosolid Biochar

Figure A1.1: FTIR spectra for FWR, FWB, FWC, BSR and BSB

Table A 1.1: Interpretation of FTIR results. The FTIR spectra have been interpreted based on the following paper (Coates, 2000). WN indicating wave number. S and Br are indicating sharp and broad peak sizes, respectively.

WN	Functional groups FWR	WV	Functional groups FWB	WN	Functional groups FWC	WN	Functional groups BSR	WN	Functional groups BSB
816 S	Aromatic	881 S	Aromatic	798 S	Aromatic	793 S	Aromatic	793 S	Aromatic
1061 Br	Alkyl-substituted ether C-O stretch	1126 S	C-O stretch (Alkyl-substituted ether/ Cyclic ethers)	891 S	Aromatic	916 S	C-H	910 S	C-H Stretch
1248 S	aryl-O stretch	1200 S	Aromatic phosphates (P-O-C stretch)	1030 Br	CN Stretch	1028 Br	Aromatic	1036 Br	Aromatic
1385 S	Methyl or Phenol	1263 S	aryl-O stretch	1094 S	C-O stretch (Alkyl-substituted ether/ Cyclic ethers)	1383 S	Phenol	1383 S	Phenols
1632 S	NH bend / C=C stretch	1387 S	Phenol / Methyl (−CH3)	1385 S	Phenol / Methyl (−CH3)	1628 S	NH bend / (-C=N-)/ C=C	1626 S	NH bend / (-C=N-)/ C=C
742 S	Ester/ Carboxylic acid/Ketone/Aldehyde	1626 Br	NH bend / C=C	1626 Br	NH bend / (-C=N-)/ C=C	2027 S	Carbonyls	2021 S	Carbonyls
2027 S	carbonyls	2044 S	carbonyls	2019 S	carbonyls	2858 S	C-H stretch	2849 S	C-H stretch
2856 S	C-H	2858 S	C-H stretch	2849 S	C-H stretch	2916 S	C-H stretch	2918 S	C-H stretch
2926 S	C-H	2910 S		2916 S	C-H stretch	3429 Br	NH stretch	3449 Br	NH stretch
3427 Br	OH stretch	3449 Br	H-bonded OH stretch	3425 Br	H-bonded OH stretch	3618 S	H-bonded OH stretch	3618 S	H-bonded OH stretch
				3692 S	H-bonded OH stretch	3699 S	H-bonded OH stretch		

Results from GC-MS Analysis

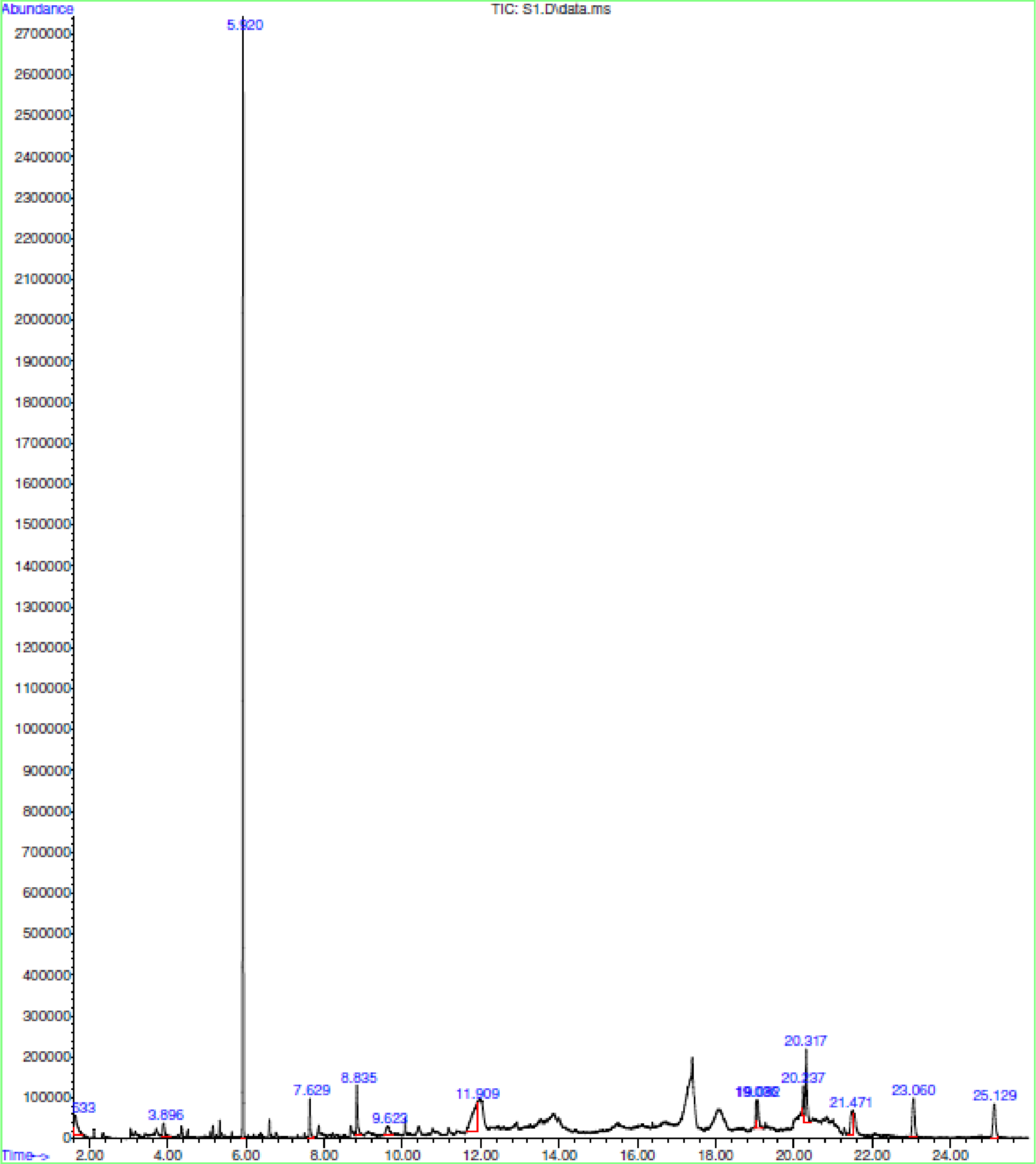


Figure A 1.2: Compounds in Raw Food Waste (Methanol Extract)

Table A1. 2: Compounds in Raw Food Waste (Methanol Extract)

No	Peak #	Rt (min)	Compound	CAS number* * Registry Number	Qual
1	1	1.633	Tetradecamethylcycloheptasiloxan	000107-50-6	93
2	1	1.633	3-isopropoxy-1,1,1,7,7,7-hexamet	071579-69-6	38
3	2	3.896	Phosphine, triethyl-	000554-70-1	37
4	3	5.920	L-limonene	005989-54-8	98
5	3	5.920	Limonene	000138-86-3	98
6	4	7.629	2,3-dihydro-3,5-dihydroxy-6-meth.	000000-00-0	72
7	4	7.629	4h-pyran-4-one, 2,3-dihydro-3,5-...	028564-83-2	72
8	5	8.835	2-furancarboxaldehyde, 5-(hydrox...	000067-47-0	91
9	5	8.835	5-hydroxymethylfurfural	000000-00-0	91
10	6	9.623	3-ethyl-d5-thiopyridine	057420-70-9	35
11	6	9.623	2,5-difluorophenylhydrazine	097108-50-4	32
12	6	9.623	Acetamide, n-(3-oxo-4-isoxazolid...	051541-30-1	25
13	7	11.909	Xanthosine	000146-80-5	40
14	7	11.909	Guanosine	000118-00-3	32
15	7	11.909	Trans-cyclopentane-1,3-diol-2,2-...	056772-13-5	22
16	8	19.036	Linoleic acid	000060-33-3	99
17	8	19.036	9,12-octadecadienoic acid	000060-33-3	97
18	9	19.082	9,12-octadecadien-1-ol	001577-52-2	94
19	9	19.082	Heptadecene-(8)-carbonic acid-(1)	000000-00-0	94
20	9	19.082	9-octadecenoic acid	000112-80-1	93
21	10	20.237	Benzene	000886-66-8	25
22	10	20.237	7h-furo[3,2-g][1]benzopyran-7-on…	002009-24-7	22
23	11	20.317	Vanadium, bis(.eta.8-1,3,5,7-cyc..	035796-61-3	59
24	11	20.317	P-tolyl trichloromethyl sulfone	000000-00-0	35
25	11	20.317	2,6-piperidinedione, 1,4,4-trime...	025115-67-7	35
26	12	21.471	Eicosamethylcyclodecasiloxane	018772-36-6	35
27	12	21.471	Methyl ester of di-o-methylisoph...	071295-03-9	27
28	12	21.471	Tetracosamethylcyclododecasiloxa...	018919-94-3	27
29	13	23.060	Tetracosamethylcyclododecasiloxa...	018919-94-3	50
30	13	23.060	Eicosamethylcyclodecasiloxane	018772-36-6	35
31	13	23.060	Cis-3-propoxy-b-methyl-b-nitrost...	000000-00-0	25
32	14	25.129	Eseroline, 7-bromo-, methylcarba...	000000-00-0	59
33	14	25.129	Tetracosamethylcyclododecasiloxa...	018919-94-3	50
34	14	25.129	Eicosamethylcyclodecasiloxane	018772-36-6	38

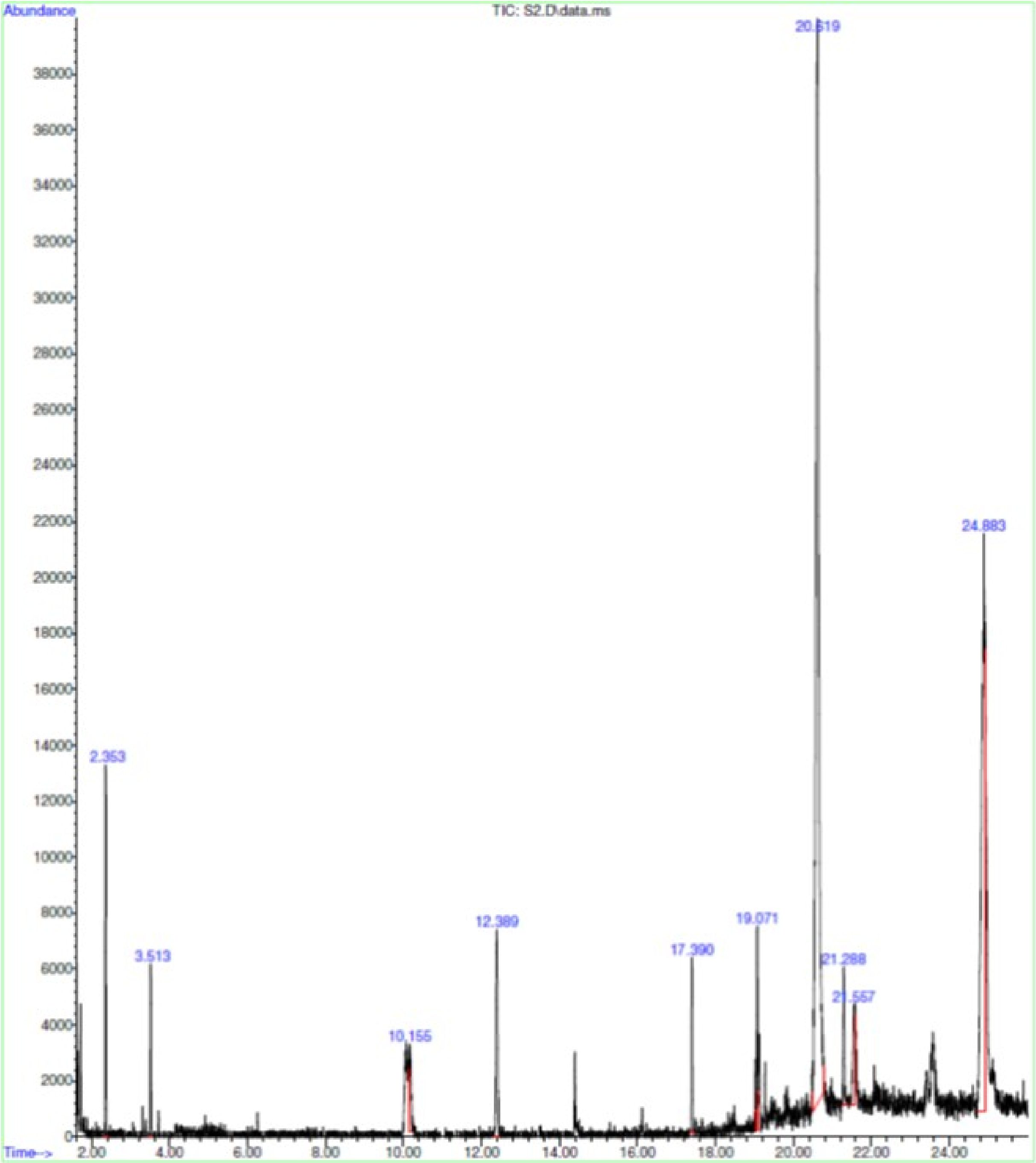


Figure A 1.3: Compounds in Raw Biosolid (Methanol Extract)

Table A 1.3: Compounds in Raw Biosolid (Methanol Extract)

No	Peak #	Rt (Min)	Compound	CAS Number** Registry Number	Qual
1	1	2.353	2,2-Dimethoxybutane	000000-00-0	74
2	1	2.353	Methyl 1-Methyl-D3-2-Propenyl Ether	000000-00-0	38
3	1	2.353	Methyl 1-Deuterio-2-Butenyl Ether	000000-00-0	10
4	2	3.513	Sym-Tetramethyldimethoxydisiloxa...	018187-24-1	42
5	2	3.513	Phenanthridine	000229-87-8	9
6	2	3.513	1,4-Benzenedicarboxylic Acid, Me...	039379-10-7	9
7	3	10.155	Cyclohexasiloxane, Dodecamethyl-...	000540-97-6	72
8	4	12.389	Tetradecamethylcycloheptasiloxan...	000107-50-6	53
9	4	12.389	1,1,1,3,5,7,9,9,9-Nonamethylpent...	084409-41-6	38
10	5	17.390	Hexadecanoic Acid	000057-10-3	70
11	6	19.071	Cyclopentadecanone, 2-Hydroxy-	004727-18-8	43
12	6	19.071	7-Octadecenoic Acid, Methyl Este...	057396-98-2	38
13	6	19.071	9-Octadecenoic Acid (Z)-, Ethyl ...	000111-62-6	38
14	7	20.619	Tetracosamethylcyclododecasiloxa...	018919-94-3	42
15	7	20.619	Octadecamethylcyclononasiloxane ...	000556-71-8	27
16	7	20.619	Eicosamethylcyclodecasiloxane	018772-36-6	22
17	8	21.288	2-1-d2-ethylthio-6-methyl-pyridine	054244-78-9	38
18	8	21.288	2-Methoxy-3-Tosyl-1-Propanol	000000-00-0	38
19	8	21.288	3-Chloroformanilide	000139-71-9	32
20	9	21.557	Gibberellin A3	000077-06-5	35
21	9	21.557	2,3-dinaphthyl-2,3-dihydro-1h-1,...	000000-00-0	17
22	9	21.557	1,1-Diphenylpropene $$ Benzene, ...	000778-66-5	16
23	10	24.883	Bistrimethylsilyl n-acetyl eicos...	000000-00-0	50
24	10	24.883	Eicosamethylcyclodecasiloxane	018772-36-6	35
25	10	24.883	Benzoic Acid, 2,4-Bis[(Trimethyl...	010586-16-0	35

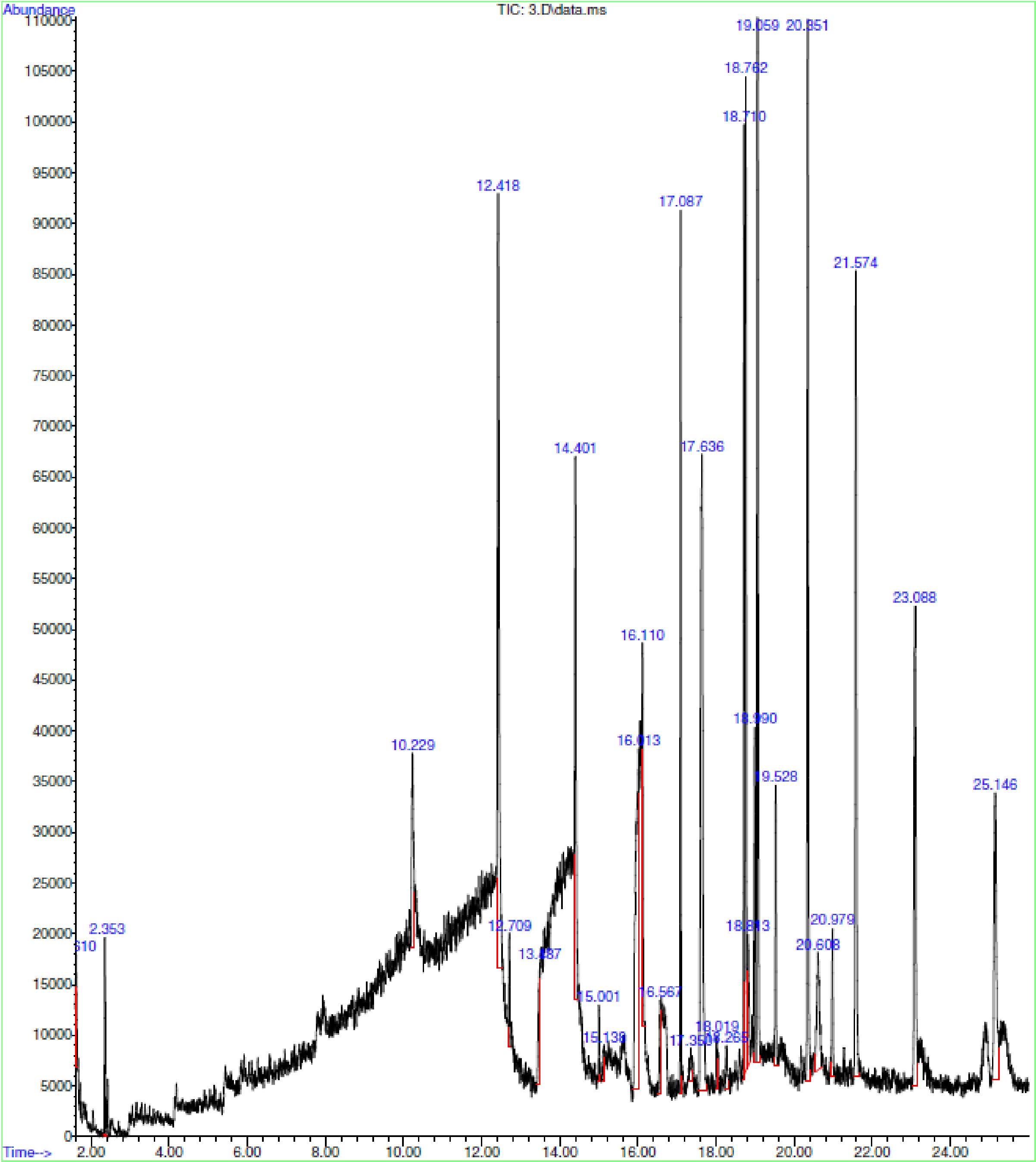


Figure A 1.4: Compounds in Food Waste Biochar (Methanol Extract)

Table A 1.4: Compounds in Food Waste Biochar (Methanol Extract)

No	Peak #	Rt (Min)	Compound	CAS Number* * Registry Number	Qual
1	1	1.610	Cyclohexasiloxane, dodecamethyl-	000540-97-6	83
2	1	1.610	1,3,5,7,9-Pentaethylcyclopentasi...	017995-44-7	38
3	2	2.353	2,2-dimethoxybutane	000000-00-0	74
4	2	2.353	2-Propenoic acid, 2-chloro-, met...	000080-63-7	59
5	2	2.353	Methyl 1-Methyl-d3-2-propenyl Ether	000000-00-0	58
6	3	10.229	Cyclohexasiloxane, dodecamethyl-...	000540-97-6	87
7	4	12.418	Tetradecamethylcycloheptasiloxan...	000107-50-6	90
8	4	12.418	3-Isopropoxy-1,1,1,7,7,7-hexamet...	071579-69-6	37
9	5	12.709	5a,6,6a,9,10 -pentahydro-4,5-epo...	000000-00-0	9
10	5	12.709	Propanoic acid	000079-09-4	7
11	5	12.709	1,1-Dideuterio-1-silacyclobutane...	013883-12-0	7
12	6	13.487	Tetracosamethylcyclododecasiloxa...	018919-94-3	52
13	6	13.487	Benzoic acid, 2,4-bis[(trimethyl...	010586-16-0	50
14	6	13.487	Benzeneacetic acid, .alpha.,3,4-...	055268-65-0	46
15	7	14.401	Silane, [[4-[1,2-bis[(trimethyls...	056114-62-6	90
16	7	14.401	Benzeneacetic acid, .alpha.,3,4-...	037148-65-5	55
17	8	15.001	Tetradecanoic acid, methyl ester...	000124-10-7	50
18	9	15.138	1,1,3,3,5,5,7,7,9,9,11,11-DODECA...	000000-00-0	17
19	9	15.138	1-Methyl-2-(4-nitrophenyl)benzim...	000000-00-0	14
20	9	15.138	1-methyl-2-(p-nitrophenyl)-benzi...	000000-00-0	14
21	10	16.013	Bis(trimethylsilyl)-oxazepam	000000-00-0	46
22	10	16.013	Bistrimethylsilyl n-acetyl eicos...	000000-00-0	42
23	10	16.013	1,1,1,5,7,7,7-Heptamethyl-3,3-bi...	038147-00-1	38
24	11	16.110	4.alpha.-Methyl-24-ethyl-5.alpha...	000000-00-0	53
25	11	16.110	Morphine, bis(o-trimethylsilyl) ...	055449-66-6	38

No	Peak #	Rt (Min)	Compound	CAS Number* * Registry Number	Qual
26	11	16.110	1,1,1,5,7,7,7-Heptamethyl-3,3-bi...	038147-00-1	37
27	12	16.567	9.alpha.-hydroxy-17.beta.-(trime...	000000-00-0	64
28	12	16.567	Dimethoxyglycerol docosyl ether	000000-00-0	40
29	13	17.087	Hexadecanoic acid, methyl ester ...	000112-39-0	97
30	13	17.087	Methyl hexadecanoate	000000-00-0	96
31	14	17.350	1,1,3,3,5,5,7,7,9,9,11,11,13,13,...	000000-00-0	37
32	14	17.350	9,12-Octadecadienoic acid (Z,Z)-...	054284-45-6	17
33	15	17.636	Eicosamethylcyclodecasiloxane	018772-36-6	90
34	15	17.636	Tetradecamethylcycloheptasiloxan...	000107-50-6	52
35	15	17.636	1,1,1,5,7,7,7-Heptamethyl-3,3-bi...	038147-00-1	43
36	16	18.019	1,1,3,3,5,5,7,7,9,9,11,11,13,13,...	000000-00-0	25
37	16	18.019	1,1,1,3,5,7,7,7-octamethyltetras...	000000-00-0	10
38	17	18.265	Silicone grease, Siliconfett	000000-00-0	37
39	17	18.265	Octadecamethylcyclononasiloxane ...	000556-71-8	37
40	17	18.265	1,1,1,5,7,7,7-Heptamethyl-3,3-bi...	038147-00-1	23
41	18	18.710	8,11-Octadecadienoic acid, methy...	056599-58-7	99
42	18	18.710	9,12-Octadecadienoic acid (Z,Z)-...	000112-63-0	98
43	18	18.710	10,13-Octadecadienoic acid, meth...	056554-62-2	97
44	19	18.762	Methylelaidate	000112-62-9	99
45	19	18.762	9-Octadecenoic acid (Z)-, methyl...	000112-62-9	99
46	19	18.762	9-Octadecenoic acid, methyl este...	001937-62-8	99
47	20	18.813	3-Methylflav-3-ene $$ 2H-1-Benzo...	088214-83-9	27
48	20	18.813	3,3,6,9,9,10-Hexamethyl-2,10-dia...	000000-00-0	27
49	20	18.813	7-methoxy-6-hydroxy-2,2-dimethyl...	074094-44-3	27
50	21	18.990	Octadecanoic acid, methyl ester ...	000112-61-8	97
51	21	18.990	Heptadecanoic acid, 16-methyl-, ...	005129-61-3	97

No	Peak #	Rt (Min)	Compound	CAS Number* * Registry Number	Qual
52	22	19.059	Tetracosamethylcyclododecasiloxa...	018919-94-3	83
53	22	19.059	Benzeneacetic acid, .alpha.,3,4-...	037148-65-5	43
54	23	19.528	Bowdensine	001354-75-2	38
55	23	19.528	7-Chloro-2,3-dihydro-3-(4-nitrob...	055056-33-2	14
56	23	19.528	(1rs,2sr,3sr)-2-benzyl 1-methyl ...	131939-07-6	14
57	24	20.351	Eseroline, 7-bromo-, methylcarba...	000000-00-0	86
58	24	20.351	Morphine, bis(o-trimethylsilyl) ...	055449-66-6	55
59	24	20.351	2H-1,4-Benzodiazepin-2-one, 7-ch...	055319-93-2	45
60	25	20.608	5,6,8,9-tetramethoxy-2-methylpep...	074199-94-3	35
61	25	20.608	Methyl ester of di-o-methylisoph...	071295-03-9	32
62	25	20.608	2-ethyl-6-(2,4,6-trimethylphenyl...	070118-55-7	25
63	26	20.979	3,3-Diethoxy-1,1,1,5,5,5-hexamet...	000000-00-0	14
64	26	20.979	(24)orthoparaorthoparacyclophane...	066726-65-6	14
65	26	20.979	1,1,1,3,5,7,9,9,9-nonamethylpent...	084409-41-6	10
66	27	21.574	Eicosamethylcyclodecasiloxane	018772-36-6	35
67	27	21.574	Bistrimethylsilyl n-acetyl eicos...	000000-00-0	32
68	27	21.574	Octadecamethylcyclononasiloxane ...	000556-71-8	27
69	28	23.088	Eseroline, 7-bromo-, methylcarba...	000000-00-0	70
70	28	23.088	Eicosamethylcyclodecasiloxane	018772-36-6	47
71	28	23.088	4.alpha.-methyl-24-ethyl-5.alpha...	000000-00-0	35
72	29	25.146	Tetracosamethylcyclododecasiloxa...	018919-94-3	58
73	29	25.146	Eicosamethylcyclodecasiloxane	018772-36-6	47
74	29	25.146	1,1,1,5,7,7,7-Heptamethyl-3,3-bi...	038147-00-1	43

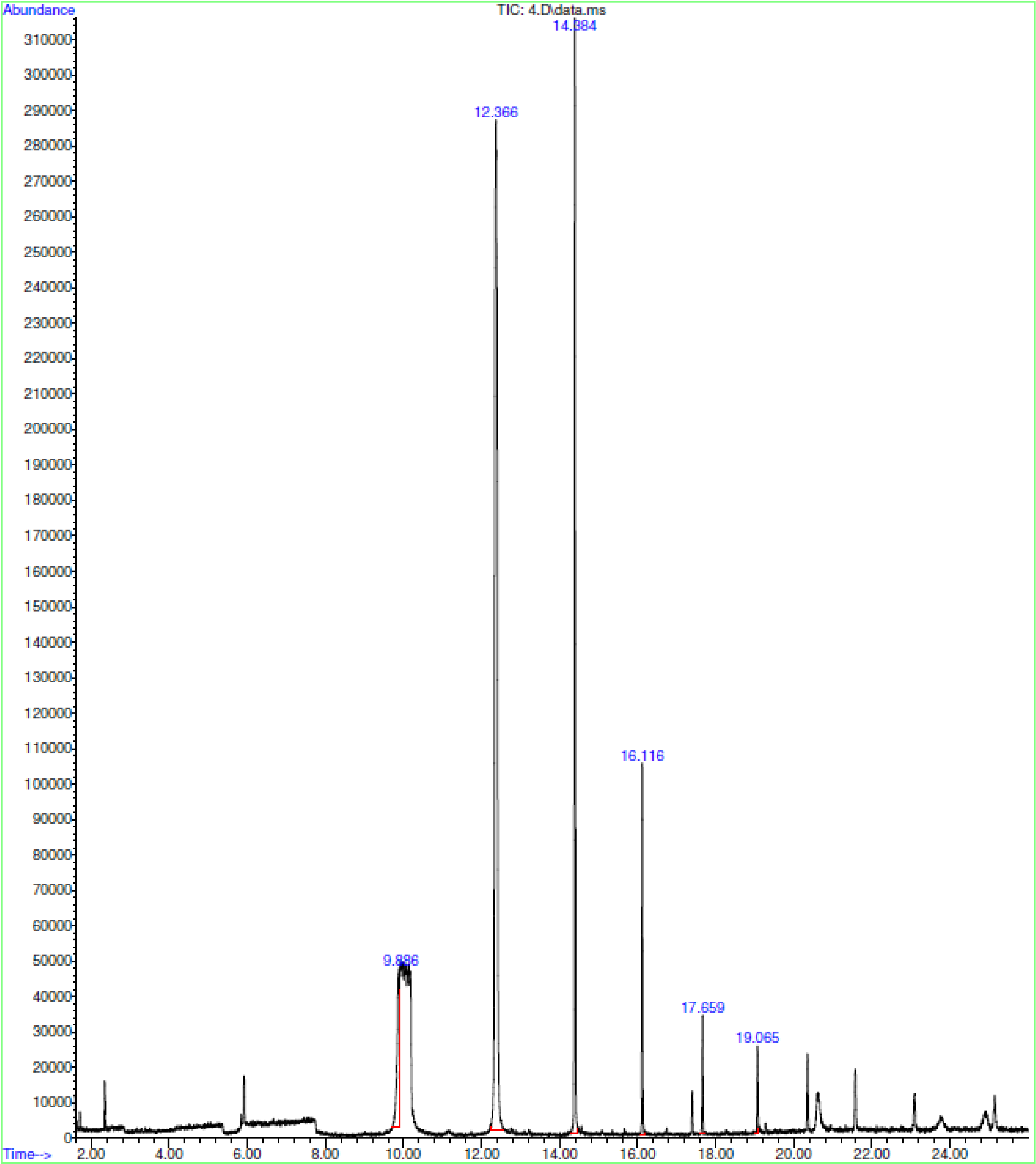


Figure A 1.5: Compounds in Biosolid Biochar (Methanol Extract)

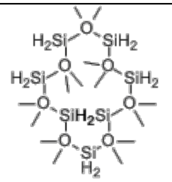
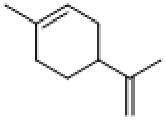
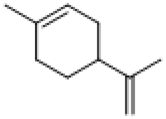
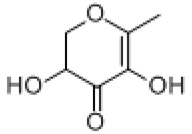
Table A 1.5: Compounds in Biosolid Biochar (Methanol Extract)

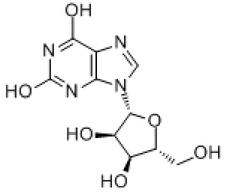
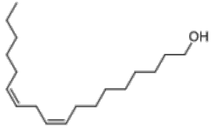
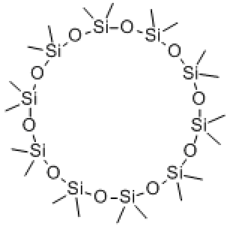
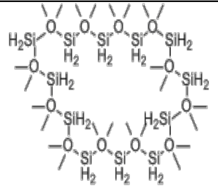
No	Peak #	Rt (Min)	Compound	CAS Number** Registry Number	Qual
1	1	9.886	Cyclohexasiloxane, dodecamethyl-...	000540-97-6	91
2	1	9.886	2,4-di(trimethylsiloxy)-6,7-(met...	000000-00-0	49
3	2	12.366	Tetradecamethylcycloheptasiloxan...	000107-50-6	91
4	2	12.366	3-Isopropoxy-1,1,1,7,7,7-hexamet...	071579-69-6	37
5	3	14.384	Cholan-24-oic acid, 3,7-dihydrox...	000474-25-9	56
6	3	14.384	Benzeneethanamine, N-[(pentafluo...	055429-13-5	49
7	3	14.384	N-(Trifluoroacetyl)-N,O,O',O"-t...	000000-00-0	47
8	4	16.116	1,3,5,7,9,11-hexaethylbicyclo[5....	073113-17-4	47
9	4	16.116	Estra-1,3,5(10)-trien-17-one, 2-...	077883-26-2	38
10	4	16.116	Morphine glucuronide-pentatms $$...	052092-53-2	32
11	5	17.659	Eicosamethylcyclodecasiloxane	018772-36-6	58
12	5	17.659	Tetradecamethylcycloheptasiloxan...	000107-50-6	43
13	6	19.065	Tetracosamethylcyclododecasiloxa...	018919-94-3	81
14	6	19.065	Benzeneacetic acid, .alpha.,3,4-...	037148-65-5	38

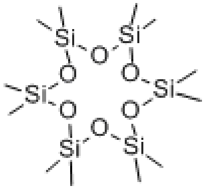
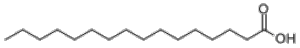
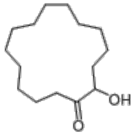
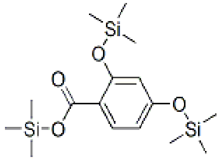
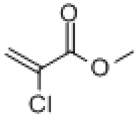
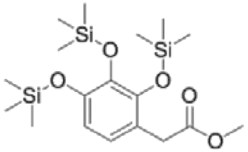
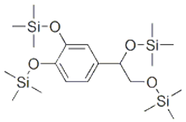
Compilation of compounds from GC-MS Analysis

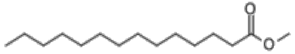
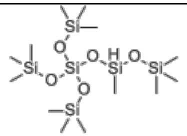
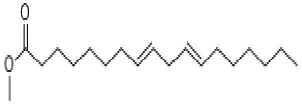
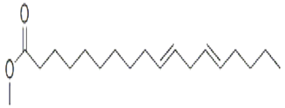
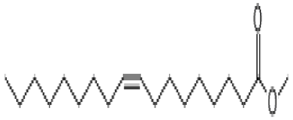
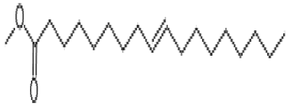
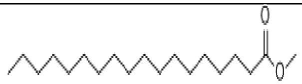
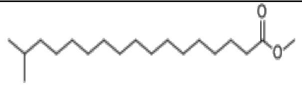
The compounds have been obtained from GC-MS analysis with methanol extraction at a 1:10 ratio of sample to solvent. Presence of compounds on the different product then categorized using CAS number and selected based on qual no ≥40.

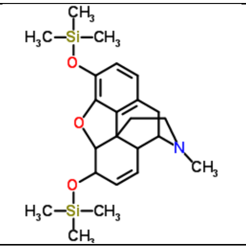
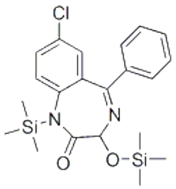
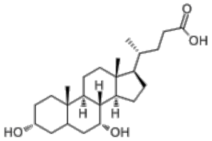
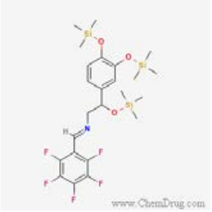
Table A 1.6: Identified compound, functionality and sources.

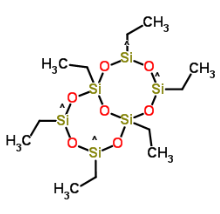
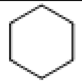
No	CAS No	Compound	FWR	BSR	FWB	BSB	Structure	Functionality	Source
S1	000107-50-6	Tetradecamethylcycloheptasiloxan	93	53	90	91		Siloxane Organosilicon	Used for pharmaceutical and food production
S4	005989-54-8	L-limonene	98					Cyclic hydrocarbon	Citrus peel
S5	000138-86-3	Limonene	98					Cyclic hydrocarbon	Citrus peel
S6	028564-83-2	4H-Pyran-4-one,2,3-dihydro-3,5-dihydroxy-6-methyl	72					Heterocyclic hydrocarbon	
S7	000067-47-0	5-Hydroxymethylfurfural	91					Aldehyde and alcohol	Dehydration product of sugar

S11	000146-80-5	Xanthosine	40					N-Containing compound	Caffeine precursor (Tea/coffee)
S14	000060-33-3	Linoleic acid/ 9,12-octadecadienoic acid	99					Fatty acid	Derived from olive oil
S15	001577-52-2	9,12-octadecadien-1-ol	94					Fatty alcohol	Reduction of Linoleic acid
S16	000112-80-1	9-octadecenoic acid	93					Fatty acid	Beef or mutton fat
S21	018772-36-6	Eicosamethylcyclodecasiloxane			47	58		Siloxane Organosilicon	Used for pharmaceutical and food production
S23	018919-94-3	Tetracosamethylcyclododecasiloxane	50	42	83	81		Siloxane Organosilicon	Used for pharmaceutical and food production
S24	018187-24-1	Sym-Tetramethyldimethoxydisiloxane		42				Siloxane Organosilicon	Used for pharmaceutical and food production

S27	000540-97-6	Cyclohexasiloxane,2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl		72	87	91		Siloxane Organosilicon	Used for pharmaceutical and food production
S29	000057-10-3	Hexadecanoic Acid		70				Saturated fatty acid	Fruit of pam oil
S30	004727-18-8	Cyclopentadecanone, 2-Hydroxycyclopentadecanone		43				Saturated alicyclic ketone	
S37	010586-16-0	2,4-Bis[(trimethylsilyl) oxy]benzoic acid trimethylsilyl ester		35	50			Ester	Naturally occur in plants
S39	000080-63-7	2-Propenoic acid, 2-chloroacrylic acid, methyl ester			59			Methyl ester	Animal and vegetable oil
S42	055268-65-0	α,3,4-Tris(trimethylsiloxy)benzeneacetic acid methyl ester			46			Methyl ester	Animal and vegetable oil
S43	056114-62-6	[[4-[1,2-Bis[(trimethylsilyl)oxy]ethyl]-1,2-phenylene]bis(oxy)]bis(trimethylsilane			90			Siloxane Organosilicon	Used for pharmaceutical and food production

S44	037148-65-5	Benzeneacetic acid			55	38			
S45	00124-10-7	Tetradecanoic acid, methyl ester			50			Methyl ester	Butter, milk, oil
S46	038147-00-1	1,1,1,5,7,7,7-HEPTAMETHYL-3,3-BIS			43			Siloxane Organosilicon	Used for pharmaceutical and food production
S49	056599-58-7	8,11-Octadecadienoic acid, methyl ester			99			Methyl ester	Bread, flour
S50	000112-63-0	9,12-Octadecadienoic acid (Z,Z)-, methyl ester			98			Methyl ester	
S51	056554-62-2	10,13-Octadecadienoic acid methyl ester			97			Methyl ester	
S52	000112-62-9	(Z) 9-Octadecenoic acid methyl ester / Methylelaidate			99			Methyl ester	
S53	001937-62-8	9-Octadecenoic acid, methyl ester			99			Methyl ester	
S56	000112-61-8	Octadecanoic acid, methyl ester			97			Methyl ester	
S57	005129-61-3	Heptadecanoic acid,16-methyl-, methyl ester			97			Methyl ester	

S61	055449-66-6	Morphine, bis(o-trimethylsilyl)			55				Pain medication
S62	055319-93-2	2H-1,4-Benzodiazepin-2-one, 7-chloro-1,3-dihydro-5-phenyl-1-(trimethyl silyl)-3-[(trimethylsilyl)oxy			45				Drug
S66	000474-25-9	Chenodeoxycholic acid Cholan-24-oic acid, 3,7-dihydrox...				56			Synthesized in liver from fat
S67	055429-13-5	Benzeneethanamine, N-[(Pentafluorophenyl)methylene]-β,3,4-tris(trimethylsilyloxy)benzeneethanamine				47		Amine	Epoxy resins

S68	073113-17-4	1,3,5,7,9,11-Hexaethylbicyclo[5.5.1]hexasiloxane-3,5,9,11-tetrayl				47		Siloxane Organosilicon	Used for pharmaceutical and food production
S71	000110-82-7	Cyclohexane							Cleaning product

A1.3 LCMS analysis for identification of organic acids

Organic C from OA was extracted following the water extraction method described in (Guigue et al., 2014) with slight modification of 1 to 10 sample to water (miliQ) ratio. Then carboxylic compounds were identified by a liquid chromatography-mass spectrometry (LCMS) (Waters Micromass) in negative electrospray mode with a cone voltage of 20 V scanning from 50 to 250 amu. Separations were performed on a Zorbax SB-C8 column (250 mm x 4.6 mm ID; 5 µm) maintained at 30 °C using a gradient of 95% A: 5% B for 2 minutes then to 100% B at 20 minutes and held for 20 minutes. Solvent A was 0.5% (v:v) formic acid in water and solvent B was 0.5% (v:v) formic acid in methanol. Acids were quantified from the peak areas recorded for:

Malic m/z 133 (~ 1.6 min)

Oxalic m/z 89 (~ 2.0 min)

Citric m/z 191 (~ 6.0 min)

Benzoic m/z 121 (~ 16.0 min)

4-Hydroxybenzoic m/z137 (~ 19.4 min)

Protocatechuic m/z/151 (~ 25.0 min)

Table A 1.7: Identified organic acids in organic amendments and soil.

Organic amendments	**Malic acid**	**Oxalic acid**	**Citric acid**	**Benzoic acid**	**4-Hydroxy benzoic acid**	**Protocatechuic acid**
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
FWR	106	7	231	<1	2	4
FWB	1	40	8	13	4	<1
FWC	<1	<1	<1	<1	<1	<1
BSR	<1	<1	<1	<1	1	<1
BSB	<1	<1	<1	<1	<1	<1
BSC	<1	2	<1	<1	<1	<1
Soil	<1	<1	<1	<1	1	<1

Appendix 2: Incubation experiment to test the hypothesis and methodologies

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This experiment investigated the role of differently processed organic amendments (OA) such as compost, biochar and biosolid on P availability in acidic soil. This experiment was designed to test the hypothesis that the organic amendments can increase soil P availability and also test the methodologies used in chapters 5, 6 and 7.

Collection and processing of soil and organic amendments

A dairy soil from the Dookie campus of the University of Melbourne and 4 different types of organic amendments such as Food waste compost (Compost), Biosolid Biochar, Biosolid and NEWSOIL (a mixture of Biosolid and Sand) were collected. The compost and biochar were collected from two former PhD students Dr Hang Gao and Dr Bhawana Bhatta at the University of Melbourne. The Biosolid and NEWSOIL (NS) were collected from the North East Water Victoria.

Setup of the incubation experiment with OA

100 g of soil were taken into a 500 mL plastic vial and pre-incubated at a moisture content of 60% WHC of soil for 1 week to stabilize microbial activity. The incubation was conducted in an incubator at 25°C. 1g of OA was added to each vial. The moisture content was checked every two days. Data were collected in 7, 14, 21 and 28 days through destructive sampling. Each time of sample collection had separate controls. Each treatment had 3 replications. At each time point of sample collection, the soil Olsen P and pH were determined following the methods described in Chapter 5.

P sorption experiment

Sorption experiment was conducted with incubated soil at each time sample collection by the method described in chapter 5. Exactly 2.5 g of incubated soil was taken into a 50 ml centrifuge tube and 25 ml of 0.01 M $CaCl_2$ solution containing different concentrations of P ranged from 0.025, 0.05, 0.1, 1, 2.5 and 5 mg P/L from $KH_2PO_4$was added. Two drops of chloroform were added to suppress microbial growth. Then it was shaken for 17 h using an end-over-end shaker, centrifuged and filtered (Whatman no 5 filter paper) to collect the supernatant. The phosphate concentration in the supernatant was determined colorimetrically following Murphey and Riley (1962) method using a segmented flow analyzer (Skalar SAN++).

Statistical analysis

Data were statistically analyzed by analysis of variance (ANOVA) using the software package Minitab 18 (Akers, 2018). Treatment means were separated using the least significant differences (LSD) value at the 5% level of probability at a specific sample collection point.

Results

Characterization of soil and organic amendments

The pH of the soil was 5.8 with an Olsen P of 25 mg/kg. Fe was the dominant form of element in this acidic soil followed by Al (Table 1).

The pH of the OA ranged from 5.8 to 7.6. The Olsen P and total P content of the OA varied with different forms of processing. The compost had the highest Olsen P content 799 mg/kg where biochar had the highest total P content of 24957 mg/kg. The total C content of OA was ranged from 0.9 to 49%. The detailed characterization of soil and OA presented in Table A 2.1.

Table A2.1: Characterization of soil and organic amendments

Parameters	Soil	Compost	Biochar	Biosolid	NEWSOIL
pH	5.8	7.6	7.5	6.1	5.8
EC µs/cm	84	11330	768	1653	1091
Olsen P (mg/kg)	25	799	298	282	177
Total P (mg/kg)	410	7994	24957	8223	4811
Total C %	1.5	49	34	5.8	0.9
Total N %	0.13	1.9	1.4	0.88	0.24
Total Al (mg/kg)	10497	928	30867	30491	10571
Total Fe (mg/kg)	20411	869	22643	20278	7177
Total Mg (mg/kg)	488	1255	6760	4225	1601
Total Na (mg/kg)	27	6922	2608	679	189
Total K (mg/kg)	1293	5803	5024	3769	1563
Total Ca (mg/kg)	1204	38661	22311	6445	3685
Total S (mg/kg)	134	1769	1654	1955	657
Total Zn (mg/kg)	15.7	52	761	181	88
Total Mn (mg/kg)	1282	20	315	452	144

Effect on Soil Olsen P

The addition of OA significantly increased the soil Olsen P at all the time compared to control (Figure A 2.1) with few exceptions with NEWSOIL at 14 and 21 days. There was no significant difference was observed among different treatments in soil Olsen P at 7 days. There was no significant difference in soil Olsen P was observed among compost, biochar and biosolid at any time. The soil Olsen P remained constant by the compost and biochar at 7 and 14 days and then increased at 21 and 28 days. Whereas the biosolid had the highest increase in 21 days and then decreased at 28 days. The NEWSOIL had the lowest impact on increasing soil Olsen P among all the OA.

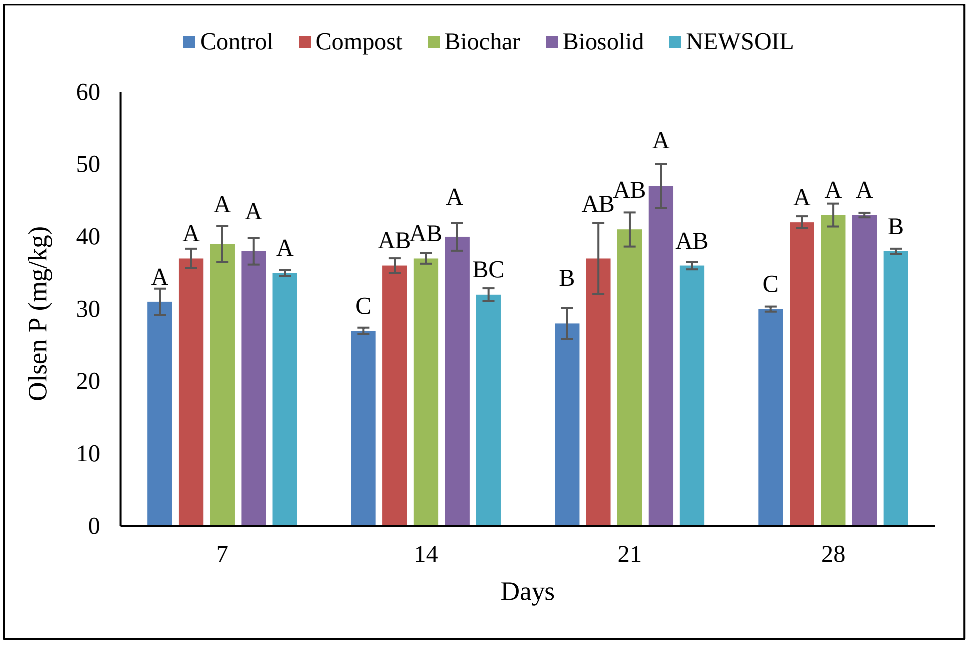


Figure A 2.1: Effect of organic amendments addition on Olsen P availability at different time. Line on the top of the bar indicating standard error (n=3). Different letters are indicating statistically significant at P ≤ 0.05 at a specific time.

Effect of organic amendments on soil pH

Addition of OA increased the soil pH at all the time compared to control (Figure A 2.2). The highest pH was obtained initially at 7 days and then decreased for all the treatments. The soil pH was significantly higher in biochar treatment compared to control at all the time. The biosolid had significantly higher pH at 7 and 14 days compared to control. In case of NEWSOIL no significant difference was observed at 14, 21 and 28 days compared to control. Compost however recorded the highest pH at 7 days among all the treatments and compared with control no significant difference was observed at 28 days. Between compost and biochar only significant difference was observed in 21 days and no significant difference was observed in 7, 14 and 28 days.

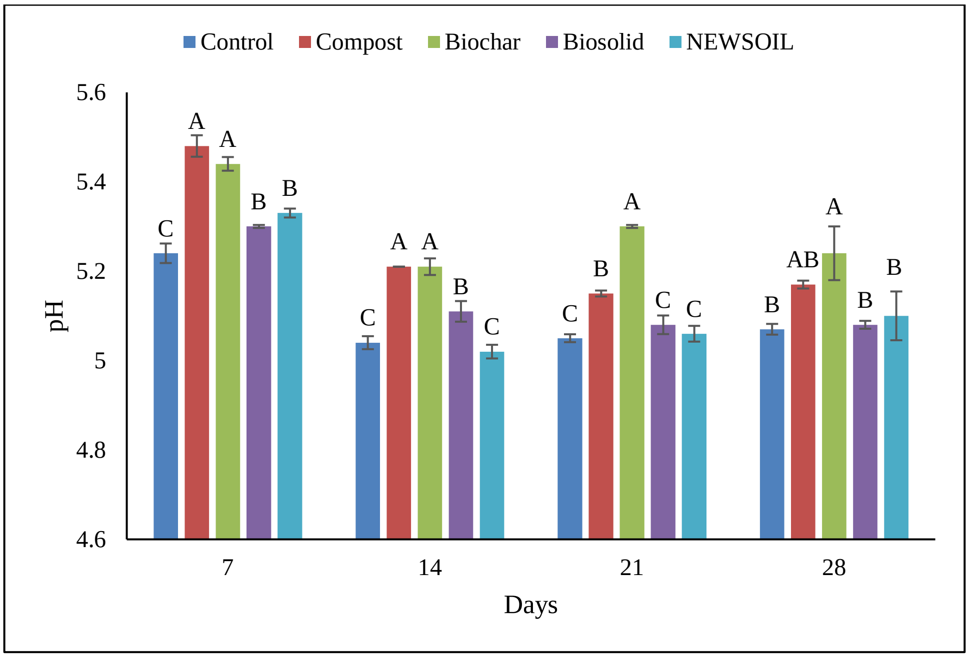


Figure A 2.2: Effect of organic amendments addition on soil pH at different time. Lines on the top of the bar are indicating standard error (n=3). Different letters are indicating statistically significant at P ≤ 0.05 at a specific time.

Effect of organic amendments on soil P sorption and EPC

The addition of OA were decreased the soil P sorption compared to control at all the time (Figure A 2.3). The lowest P sorption was observed by compost at all the time followed by biochar, biosolid and NEWSOIL, respectively.

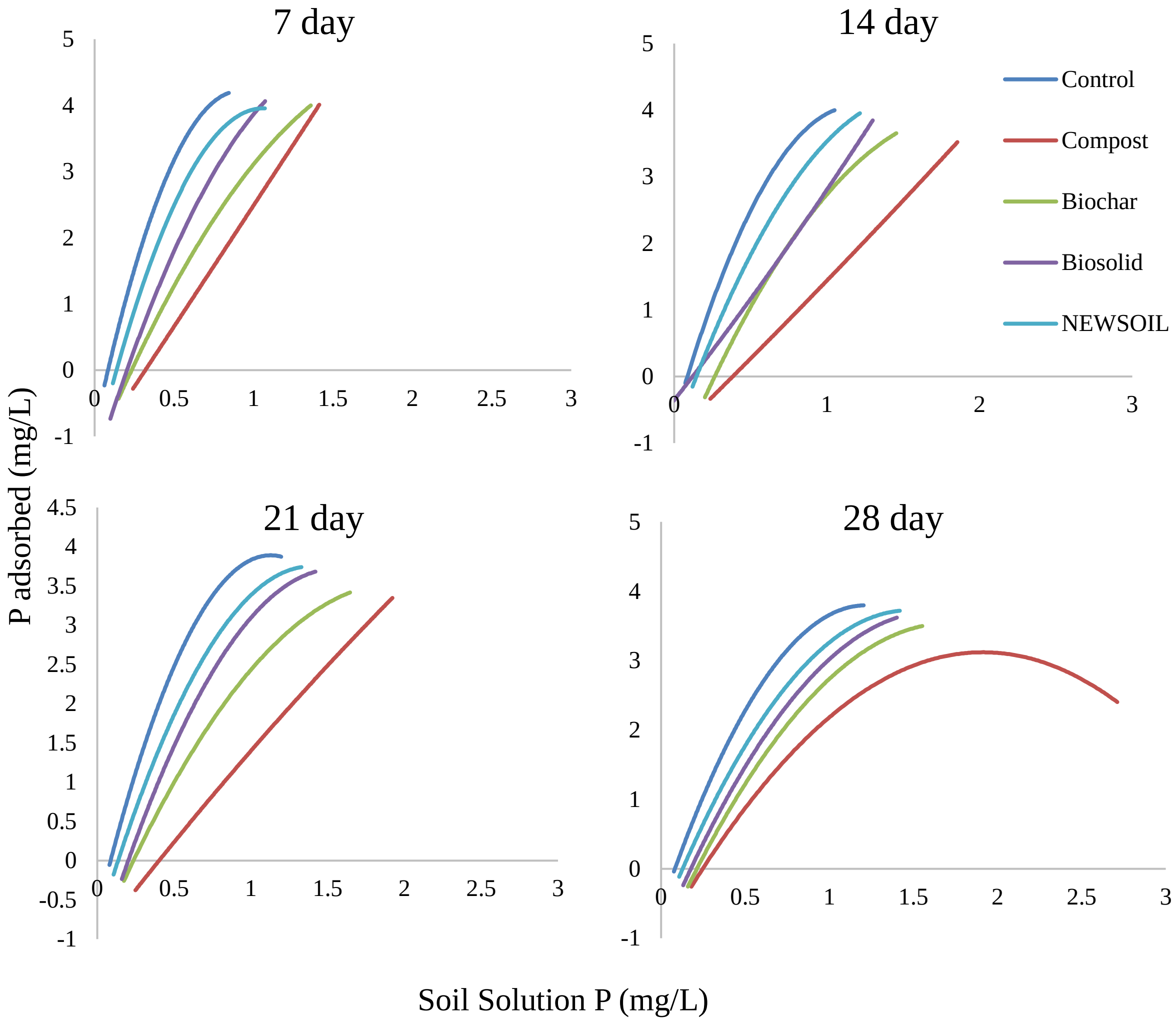


Figure A 2.3: Effect of organic amendments on soil P sorption at different times. The sorption curves were fitted with polynomial equations.

Appendix 3: Identification of rate of organic acid addition

An incubation study was conducted to determine the rates of organic acids addition for having a significant change in soil P availability.

Incubation Experiment

100 g of soil were incubated in a 250 mL plastic vial at 60% WHC in an incubator at 20°C for 2 weeks. About 15ml water was required to reach 60% WHC of the soil. The soil was pre-incubated for three days for 3 days with 7ml of water. Then different rates of C such as 0, 0.2g, 0.4g, 0.8g and 1g were added with rest 8ml water after pre-incubation. Citric acid was used as a source of carbon in this experiment. To add different rates of treatment 1g of C water was prepared as stock and then diluted accordingly for the rest of the treatment. The treatments were added as described in Table 1. The treatments were added in 3 replications. The moisture content of the soil was maintained throughout the period. The effect of different rates of C on soil Olsen P and pH was determined on 7 and 14 days after incubation.

Table A 3.1: Calculation of treatments

Rate of C	mL of 1g added	Water added (mL)
0	0	8
0.2g	1.6	6.4
0.4g	3.2	4.8
0.8g	6.4	1.6
1g	8	0

Results

Effect on soil Olsen P

The addition of citric acid increased the soil Olsen P compared with no addition (Figure A 3.1). Soil Olsen P increased as the rate of citric acid addition increased and the highest Olsen P was recorded at the rate of 1g C. The increase of soil Olsen P was significantly different by the citric acid addition at the rate of 0.4, 0.8, and 1g C, respectively compared to zero addition. There was no significant difference was observed in case of 0 and 0.2 g C addition. However, the soil Olsen P decreased as time progressed in 14 days compared to 7 days.

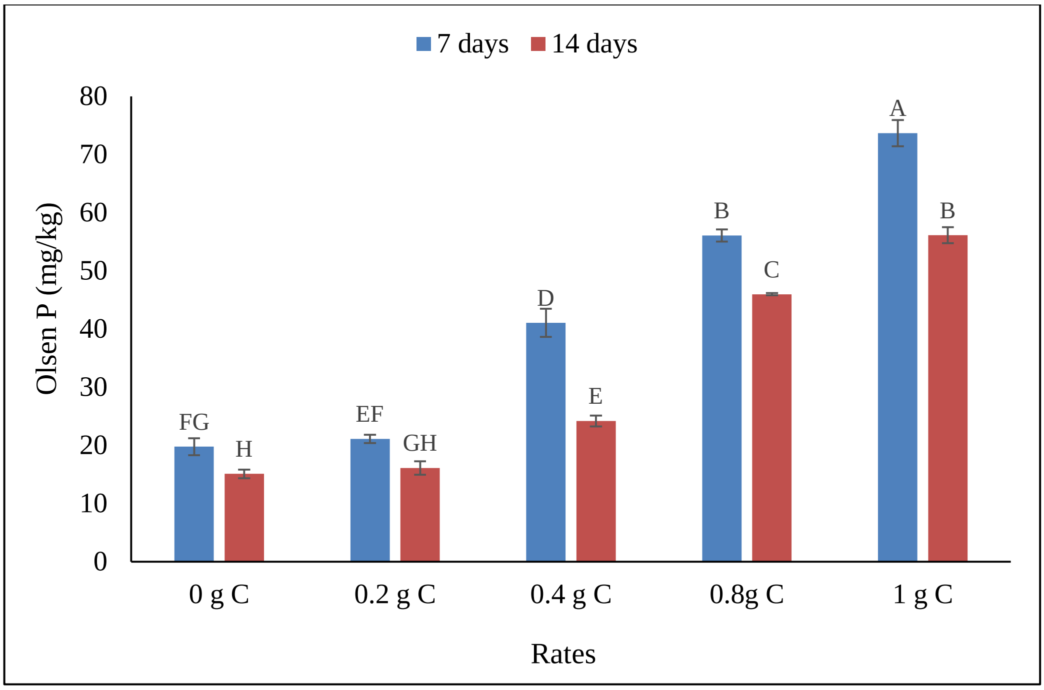


Figure A 3.1: Effect of Citric acid on soil Olsen P. The line on the top of the bars represent standard error (n=3). Different letters are indicating statistically significant at P ≤0.05.

Effect on soil pH

The addition of citric acid decreased the soil pH compared with no addition (Figure A 3.2). The soil pH decreased as the addition rate increased up to 0.8g C. No difference in soil pH was observed between 0.8 and 1 g C addition. Similarly to soil Olsen P, between 0 and 0.2 g C addition had no significant difference on soil pH. The addition of 0.4g C was the lowest rate where a significant difference was observed compared to their zero amd 0.2g C addition rate. In general, the soil decreased initially in 7 days and then increased in 14 days.

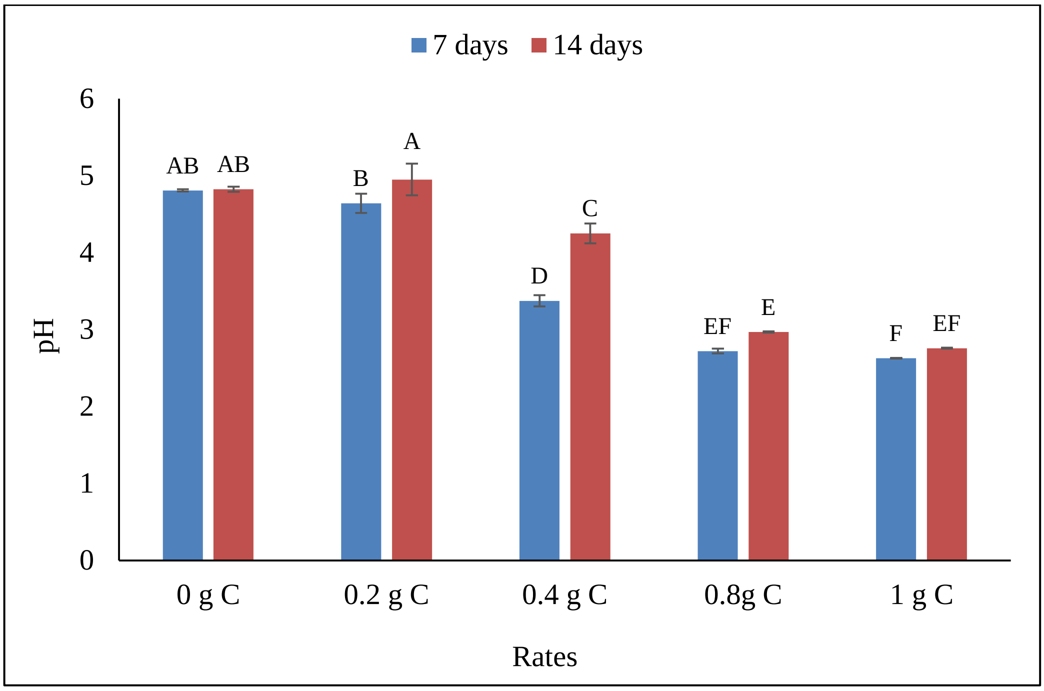


Figure A 3.2: Effect of Citric acid on soil pH. The lines on the top of the bars are presenting standard error. Different letters are indicating statistically significant at P ≤0.05.

Appendix 4: Proposal for Synchrotron study

Title: Do carboxylic acids change the speciation of phosphorus adsorbed onto soil surfaces: implications for organic amendment processing for improved nutrient availability in agricultural systems.

Abstract:

This experiment will determine how organic waste materials may improve the efficiency of phosphorus (P) fertilizer in agricultural soil through inhibiting soil fixation processes, while also understanding the importance of source and processing on their efficacy. The use of both bulk amendments and model carboxylic compounds will provide a strong connection between theoretical systems and the reality of application of heterogeneous materials. The learnings from this experiment will provide a starting point to communicate to industry and fellow researchers on the fundamental differences between these materials, and how organics could be better placed to more effectively utilize this valuable resource.

Scientific Purpose, and the Importance of the Proposed Research:

There has been an increasing amount of interest in the use of organic waste in agriculture as a source of nutrients, with the associated benefits of increased microbial activity, greater water infiltration and storage, and enhanced nutrient cycling. Concomitant with this, landfill avoidance, particularly for urban waste streams, requires the development of new avenues for recycling. These dual benefits mean organic waste addition to agricultural land is an attractive option.

However, not all organic waste materials are created equal. While the raw materials differ in their composition and nutrient status (eg food waste vs biosolid), the processes that these materials go through prior to application to land may also have a significant impact on their functionality (compost vs pyrolysis).

Agricultural production requires the sustainable addition of nutrients for plant growth. Next to nitrogen, phosphorus is the most limiting nutrient and its supply is reliant on a finite source of phosphate rock, with predictions of shortages within the next 100 years. Therefore, a step-change in phosphorus use efficiency is required to extend the life of these limited resources.

Previous research has shown that naturally occurring carbon compounds can increase soil P availability by controlling soil chemical processes (Iyamuremye et al., 1996). Experiments using individual aliphatic and aromatic carboxylic acids have demonstrated that they can alter P chemical speciation and increase soil P availability (Schefe and Tymms, 2013), which has also been described in XANES experiments (Schefe et al, 2009; 2010). However, these single-addition laboratory studies have not made the connection to common organic waste materials, nor have they examined the impact of carboxylic-type compounds on soil P availability when present in a heterogeneous material.

This research aims to start building that connection, through identification of the types of organic carbon present in two important urban waste materials, food waste and biosolid, and then examining if their effect on sorption and availability of fertilizer P is modified when processed through either composting or through pyrolysis (heating in the absence of oxygen to produce ‘biochar’). This is being done in parallel with simpler experiments which have determined the effect of aliphatic and aromatic carboxylic acids on subsequent P availability.

Results to date indicate that the combination of an aliphatic and aromatic carboxylic acid may provide unique benefits to the availability of applied P fertilizer. Results further indicate that both the source and processing of organic waste materials play a significant role in their ability to improve the availability of applied P fertilizer.

Understanding these fundamental processes will provide a more robust approach to the evaluation of organic waste materials so that their suitability for application to land can be considered based on their chemical composition and the form of processing that they have been subjected to, rather than a ‘one size fits all’ approach. Not only will this ensure that the organic material applied to land is more likely to increase P fertilizer efficiency, it will also assist in removing some of the vagaries of working with organic materials, where the effects of application often appear random and non-reproducible due to a lack of knowledge of the underlying fundamental processes involved.

National Benefit & Applications of the Proposed Research:

As Federal, state and local governments commit to reducing the amount of organic waste materials headed to landfill, there is increasing pressure to divert those materials to agricultural soils. However, the type of material involved ranges significantly from putrescible food waste to biosolid, each with a unique composition and nutritive content. Furthermore, the processing of these materials may also have a significant effect on their ability to positively impact on the soil environment, with the forms of processing ranging from stockpiling (minimal change from raw materials) to composting (moderate shift in composition) through to pyrolysis and the formation of biochar (large shift in composition).

Organic materials have previously been considered as an interchangeable product however their ability to improve the soil environment varies markedly and this has affected their commercial viability, particularly in the farming community.

If organic materials were categorized on their ability to make a positive change to the soil, and plant nutrition, then options increase, with different organics being preferentially used for different applications (fit for purpose); some could be used to stimulate microbial activity, some for improved nutrition for plant growth, and others could be used for carbon sequestration purposes.

The proposed experiment will improve our understanding of why two contrasting organic materials (food waste and biosolid) vary in their ability to improve the plant-availability of applied P, and the importance of different processing pathways (raw, composted, pyrolysis) in changing these effects. If the source and processing of organic materials have a significant effect on the ability of these materials to improve the efficiency of applied fertilizer (and so have to apply less P to have the same plant growth response), this would provide a key point of differentiation between these products and increase confidence for use of organic waste streams in the farming sector.

The learnings from this experiment will then be used as the starting point to educate organics processors, local governments and fellow researchers on the fundamental differences between these materials, and how organics could be better placed to more effectively utilize this valuable resource. Considering that Victoria recovers over 1 million tons of recycled organics annually (Sustainability Victoria), with at least 6 million tons recovered nationally (Australian Organic Recycling Association), there is a huge potential to improve the allocation of this resource for more efficient nutrient cycling and sequestration of carbon.

Supplementary Information

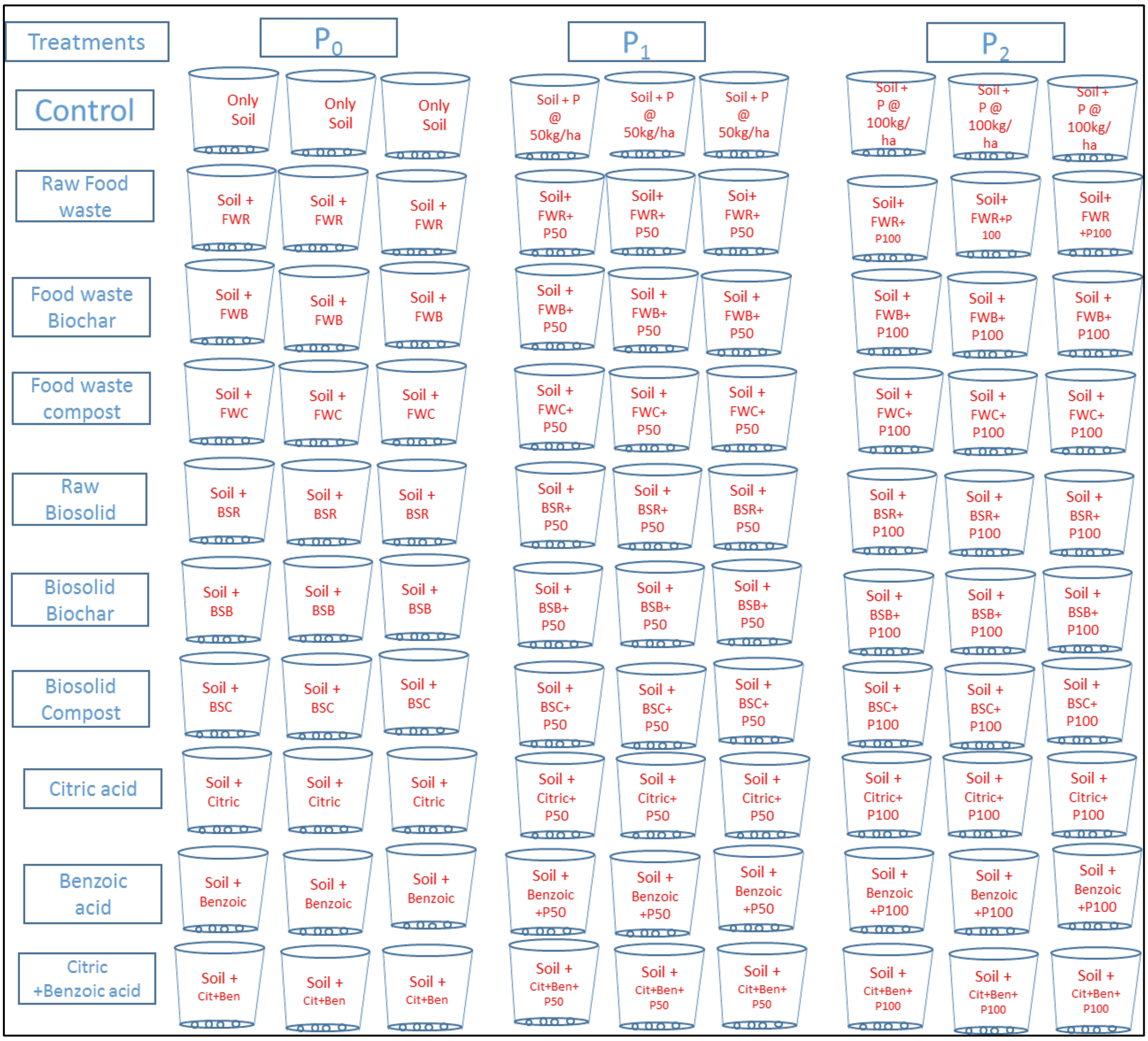
Chapter 5

Table S5.1: Pearson's correlation study between the change in soil PBC (ΔPBC) and ΔpH, ΔM3 Al, and ΔM3 Fe at each time. The values representing Pearson's correlation coefficient (r) (n= 24).

Days	ΔpH	ΔM3 Al (mg/kg)	ΔM3 Fe (mg/kg)
7	0.18^{ns}	0.33^{ns}	0.16^{ns}
30	-0.32^{ns}	$- 0.20^{ns}$	$- 0.34^{ns}$
60	$- 0.32^{ns}$	0.19^{ns}	$- 0.11^{ns}$
110	-0.53^{**}	0.18^{ns}	$- 0.15^{ns}$

**significant at $P < 0.05$ and ns- non-significant.

Chapter 7



Treatments	P_0			P_1			P_2		
Control	Only Soil	Only Soil	Only Soil	Soil + P @ 50kg/ha	Soil + P @ 50kg/ha	Soil + P @ 50kg/ha	Soil + P @ 100kg/ ha	Soil + P @ 100kg/ ha	Soil + P @ 100kg/ ha
Raw Food waste	Soil + FWR	Soil + FWR	Soil + FWR	Soil+ FWR+ P50	Soil+ FWR+ P50	Soil+ FWR+ P50	Soil+ FWR+ P100	Soil+ FWR+P 100	Soil+ FWR +P100
Food waste Biochar	Soil + FWB	Soil + FWB	Soil + FWB	Soil + FWB+ P50	Soil + FWB+ P50	Soil + FWB+ P50	Soil + FWB+ P100	Soil + FWB+ P100	Soil + FWB+ P100
Food waste compost	Soil + FWC	Soil + FWC	Soil + FWC	Soil + FWC+ P50	Soil + FWC+ P50	Soil + FWC+ P50	Soil + FWC+ P100	Soil + FWC+ P100	Soil + FWC+ P100
Raw Biosolid	Soil + BSR	Soil + BSR	Soil + BSR	Soil + BSR+ P50	Soil + BSR+ P50	Soil + BSR+ P50	Soil + BSR+ P100	Soil + BSR+ P100	Soil + BSR+ P100
Biosolid Biochar	Soil + BSB	Soil + BSB	Soil + BSB	Soil + BSB+ P50	Soil + BSB+ P50	Soil + BSB+ P50	Soil + BSB+ P100	Soil + BSB+ P100	Soil + BSB+ P100
Biosolid Compost	Soil + BSC	Soil + BSC	Soil + BSC	Soil + BSC+ P50	Soil + BSC+ P50	Soil + BSC+ P50	Soil + BSC+ P100	Soil + BSC+ P100	Soil + BSC+ P100
Citric acid	Soil + Citric	Soil + Citric	Soil + Citric	Soil + Citric+ P50	Soil + Citric+ P50	Soil + Citric+ P50	Soil + Citric+ P100	Soil + Citric+ P100	Soil + Citric+ P100
Benzoic acid	Soil + Benzoic	Soil + Benzoic	Soil + Benzoic	Soil + Benzoic +P50	Soil + Benzoic +P50	Soil + Benzoic +P50	Soil + Benzoic +P100	Soil + Benzoic +P100	Soil + Benzoic +P100
Citric +Benzoic acid	Soil + Cit+Ben	Soil + Cit+Ben	Soil + Cit+Ben	Soil + Cit+Ben+ P50	Soil + Cit+Ben+ P50	Soil + Cit+Ben+ P50	Soil + Cit+Ben+ P100	Soil + Cit+Ben+ P100	Soil + Cit+Ben+ P100

Figure S7.1: Experimental design and treatment combination used in Chapter 7. P_0, P_1 and P_2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

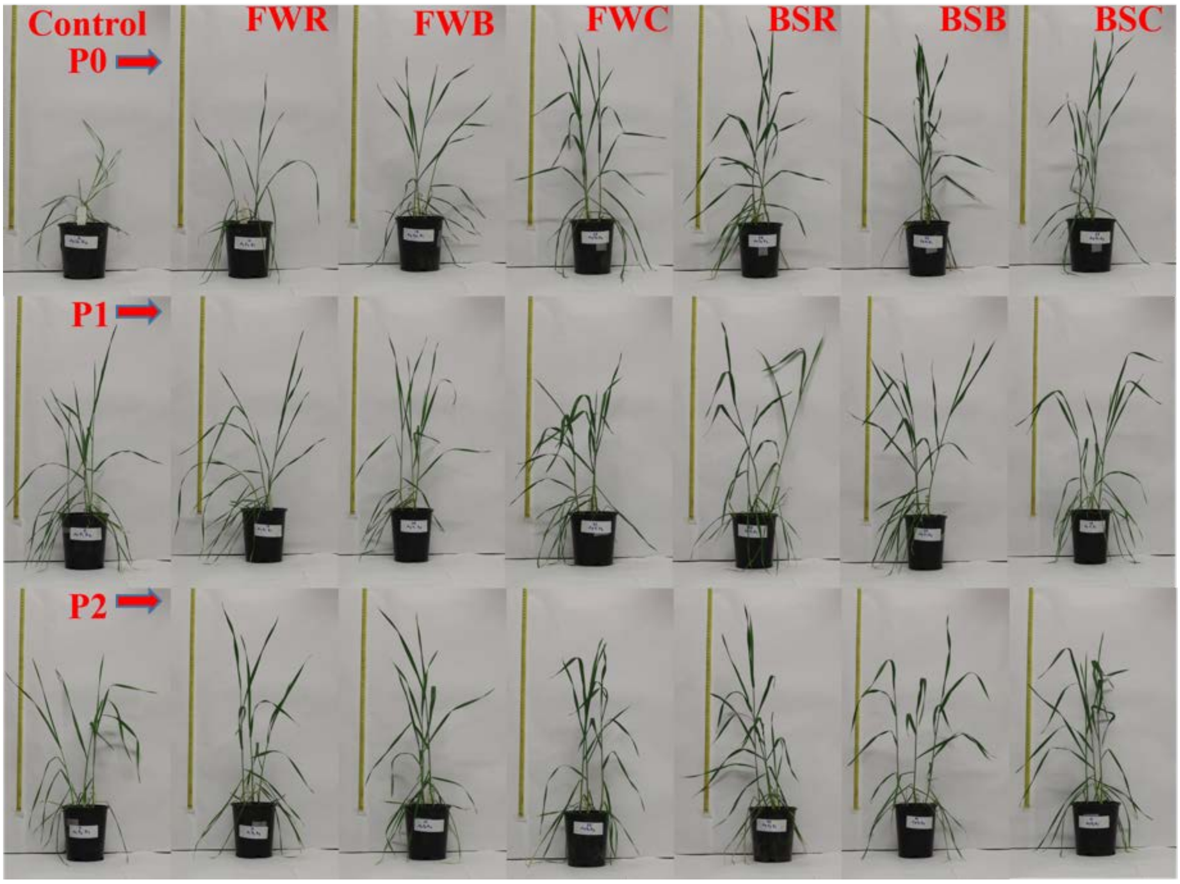


Figure S7.2: Effect of organic amendments along with three different rates of P addition on plant growth. The photo was taken just before the harvesting of the plant (after 8 weeks from the date of Transplanting. P_0, P_1 and P_2 represent 0, 50 and 100 kg/ha P addition, respectively from KH_2PO_4.

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