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FINAL PROJECT REPORT

Waste-derived fertiliser products, nano-porous materials for pesticide delivery, and moisture retention and microbial carrier technologies: Review and meta-analysis

Project 3.1.01

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EXECUTIVE SUMMARY

This scoping project report covers three major research priorities themes that include:

Part I. Developing New, Targeted, High-Performance Waste-derived Fertilisers

Australia generates approximately 64 Mt of waste annually. A significant fraction of the waste is rich in organic carbon and nutrients such as nitrogen, phosphorus, and potassium. Part 1 provides a brief background into the concept of beneficial reuse of waste for nutrient recovery and production of fertilisers and soil amendments. Part 2 consists of a comprehensive review of the main types of wastes with potential for beneficial reuse as fertilisers and soil amendments. The waste streams reviewed include crop waste, livestock and poultry, food waste of commercial, and industrial and municipal solid waste including biosolids. Part 3 describes the main waste-derived organic fertilisers and soil amendments in Australia (composts, meat blood and bone meal, manures and biosolid by-products, fish hydrolysates, crop residues and biochar). It also reviews the current and emerging technologies for production of fertilisers and soil amendments from waste, and identifies the key challenges. Part 4 contains a quantitative meta-analysis of the characteristics of various wastes and waste-derived products, and their effectiveness as a nutrient source and soil amendments across crop types. The key findings include: (1) wastes are highly variable in the physico-chemical properties; (2) biosolids and composts are particularly effective for improving soil health and crop yield; (3) crops with below-ground marketable yield components (e.g., potato) respond well to waste-derived fertilisers; and (4) waste-derived fertilisers perform equally well to conventional synthetic fertilisers in terms of improving crop yield. Part 5 outlines the main challenges and opportunities for Australian waste industry and end-users regarding waste-derived fertilisers. Key recommendations for further research investment are described in Part 6.

Part II. Developing New, Targeted and Low Residual Pesticide/ Herbicide Delivery System

Increasing world population and food demand has triggered increasing pressure on agricultural productivity, which relies on the use of large amount of pesticide/herbicides. However, a major issue regarding agricultural application of pesticide/herbicide is the residue effect of pesticide/herbicide which pose risks to environment and human health. Thus cost-effective targeted pesticide application and management of insects and weeds is critical to achieve both sustainable agricultural production and environmental protection. This theme focuses on the utilisation of various materials and technologies for pesticides/herbicide delivery which help reduces loss, residue, targeted release and sustainable release. The information summarised covered background information on application of controlled releasing pesticide/herbicide system, key materials being investigated for the delivery, limitations of different materials and future considerations for development of cost-effective and environmental friendly pesticides/herbicides.

Part III. Developing New Microbial Carriers for Delivering Beneficial Microorganism and Moisture Retention

Microbial inoculants (e.g., rhizobia) has contributed greatly to soil health and crop productivity. The key issues associated with microbial carriers include low capacity of moisture retention, low microbial survival rate and short shelf life of the microbial inoculants. Among the various organic and inorganic carriers studied, peat remains as the carrier of choice for many years. This theme focused on addressing the gaps in microbial carrier technology to develop an alternative carrier material with suitable habitants and adhesion, strong capacity of moisture retention and water activity for microorganisms as a sustainable, economical and environementally friendly alternative to peat. The cost-effective agricultural by-products (e.g., organic wastes, biochar and other naturally available inorganic materials) can be explored as low cost, easily available and efficient carrier material alternatives.

OBJECTIVES	RESULTS
1) to collate the information and data on the sources quantity/, geographic distribution of waste streams and relevant industries; 2) to undertake a meta-analysis of the characteristics (carbon, nutrients and contaminants of different wastes) and to evaluate the potential beneficial values and environmental risks, and management strategy of these wastes to be used for developing new targeted high-performance waste-derived fertilisers, efficient and low residue pesticide/ herbicide delivery systems and effective moisture retention and microbial carrier products; 3) to assess and undertake meta-analysis of the effectiveness of current commercially available (existing and emerging) waste-derived fertilisers, pesticide/ herbicide delivery systems and moisture retention and microbial carrier products; 4) to identify the novel and cost-effective technologies that can be employed to develop the above novel products and undertake the economic and environmental analyses to address their viability, technical challenges and environmental risks; 5) to identify the key potential issues/ barriers related to the development and manufacturing of the above-mentioned products by the relevant industries and the adoption by farmers 6) to identify the research opportunities and recommend the future research investment and directions for a) new, targeted and high performance fertiliser products, b) new, targeted and low residual pesticide/ herbicide delivery systems) and c) effective delivery mechanisms for beneficial microorganisms) and/ or high performance in moisture retention of Program 3.	**Part I. Waste-derived fertilisers** a) Approximately 64 Mt of wastes are generated annually while these wastes are highly variable in their chemical and physical properties; b) New technologies are being developed to extract key nutrients (phosphorus) from various organic wastes (e.g. biosolids, liquid wastes); b) Some of these wastes are being applied to soil and different crops either directly or as waste-derived fertiliser (e.g., composts); d) Meta-analysis showed that waste-derived fertilisers perform equally well to conventional synthetic fertilisers in improving crop yield. **Part II. Pesticide/ herbicide delivery system** a) Growing agricultural productivity highly depends on utilisation of pesticide/ herbicides for managing insects and weeds; b) Efficient delivery of pesticides with low residue is a key challenge; c) Nanoencapsulated pesticide has the potential for efficient delivery of pesticides/ herbicides; d) Utilization of various materials for pesticides/ herbicide delivery will help reduce loss and residue, with targeted and sustainable release. **Part III. New microbial carriers & moisture retention materials** a) The major currently used microbial carriers include peat, granular clay pellets and liquid-based products; c) The key issues associated with currently used microbial carriers include low capacity of moisture retention, low microbial survival rate and short shelf-life of the microbial inoculants. d) Advanced technologies such as micro-encapsulation and polymeric nanomaterial-based carriers can be an effective solution to current microbial carrier issues; e) Agricultural by-products (organic wastes, biochar) and naturally-derived inorganic materials can be cost-effective, locally available, efficient alternative carriers (high moisture retention and effective microbial delivery).

NEXT STEPS - RECOMMENDATIONS	TIMING –N/A

Part I. Waste-derived fertilisers

a) Regional-scale quantification and characterisation of various solid (e.g., biosolids, manures, composts) and liquid (recycled water, daily effluent, piggery effluent) wastes produced in Australia for economic and effective application for specific soil type, crop type and climate condition;

b) Improved understanding of roles of organic C functionalities in waste-derived products for improving nutrient recycling, water and nutrient retention and soil structure for increasing crop yield.

c) Optimising existing technologies to recover nutrients efficiently from waste streams, minimise contaminants and commercialize these nutrient products for maximising profitability;

d) Synergistic and antagonistic effects and economic viability of co-utilization of waste-derived fertiliser products with commercially available inorganic fertilisers

e) Developing sound strategies for minimising environmental risks (nutrient pollution, greenhouse gas emission) associated with the use of waste-derived fertiliser products.

Part II. Pesticide/ Herbicide Delivery System

a) Developing a ‘smart’ pesticide delivery system using nanomaterials to achieve ‘control’ and ‘targeted’ release of pesticide for efficient delivery;

b) Investigating the size and dissolubility of nanocarriers and evaluate biotransformation of nanocarriers to the environment;

c) Innovative, cost-effective, new technologies for encapsulation of pesticides to produce slow and targeted release pesticide products;

d) Minimising environmental impacts of non-targeted release of selected pesticide and the impacts of residual pesticides/herbicides on soil health and crop productivity;

e) Testing pest control effectiveness of new pesticide formulations and pesticide placement technologies for targeted release.

Part III. New Microbial Carriers and Moisture Retention Products

a) Identifying cost-effective, locally available, efficient (high moisture retention and effective microbial delivery) agricultural by-product (e.g., organic wastes, biopolymers, biochar) and naturally-derived inorganic materials;

b) Integrating advanced technologies such as microencapsulation and nanomaterial based bio-polymeric substances in carrier preparation;

c) Testing the effectiveness of the new microbial inoculant formulations for their moisture retention, microbial survival and their applicability for different soil and climatic conditions;

d) Evaluating adverse effects of the selected carrier materials on crop growth, soil health and environment;

PART I: DEVELOPING NEW, TARGETED, HIGH-PERFORMANCE WASTE-DERIVED FERTILISERS

By Maryam Esfandbod, Orpheus Butler, Mehran Rezaei Rashti and Chengrong Chen, School of Environment and Sciences and Australian Rivers Institute, Griffith University, May 2018.

Executive summary

An enormous amount of waste is generated in Australia and around the world every year. A significant fraction of this waste is rich in organic carbon (C) and nutrients such as nitrogen (N), phosphorus (P), and potassium (K). Thus, by converting this waste into high-performance fertilisers and/or soil amendments it will be possible to recover increasingly scarce nutrients (e.g. P), achieve critical environmental outcomes (e.g. reduce nutrient pollution and the amount of waste going to landfill), and deliver economic benefits for farmers by improving soil health and increasing crop yield at similar costs to conventional fertilisers. Part 1 of this Scoping Project Report provides a brief background into the concept of beneficial reuse of waste for nutrient recovery and production of fertilisers and soil amendments. Part 2 consists of a comprehensive review of the main types of wastes with potential for beneficial reuse as fertilisers or soil amendments. This has been conducted, with special attention paid to rate and geographic distribution of waste generation, and the chemical properties of wastes as reported in the literature. The waste types reviewed include agricultural waste from crops (particularly grain crops, sugar cane, and banana), livestock and poultry (beef, poultry and piggery manure and carcasses and abattoir waste), food waste from the commercial, industrial and municipal solid waste streams, and biosolids. Part 3 describes the main types of waste-derived organic fertilisers and soil amendments available or under development in Australia (including composts, meat blood and bone meal, manures and sewage by-products, fish hydrolysates, crop residues and biochar). This part also reviews the current and emerging technologies for production of fertilisers and soil amendments from waste, and identifies the key challenges involved in using waste for such purposes. Part 4 contains a quantitative meta-analysis of the properties of various wastes and waste-derived products and their effectiveness across a range of crop types. This meta-analysis reveals several key findings, including: (1) wastes are highly variable in the chemical properties; (2) biosolids and composts are particularly effective for improving yield; (3) crops with below-ground marketable yield components (roots, tubers and bulbs) respond particularly well to waste-derived fertilisers; and (4) in general, waste-derived fertilisers perform equally well to conventional synthetic fertilisers in terms of improving crop yield. Part 5 outlines the main challenges and opportunities for Australian waste industry and end-users regarding waste-derived fertilisers. Finally, key recommendations were made in Part 6 for further research and investment.

1. Background

Intensive agriculture and long-term loss of organic matter from soils through harvesting have led to land degradation (e.g. declines in soil organic matter and health, nutrient deficiency, loss of soil structure and moisture, salinity, sodicity and acidity, etc.). These constraints, together with inefficient use of fertiliser and pesticides/ herbicides, have greatly limited the productivity and sustainability of many agricultural systems in Australia, such as wheat, cotton, sugarcane, and wool, dairy and meat production.

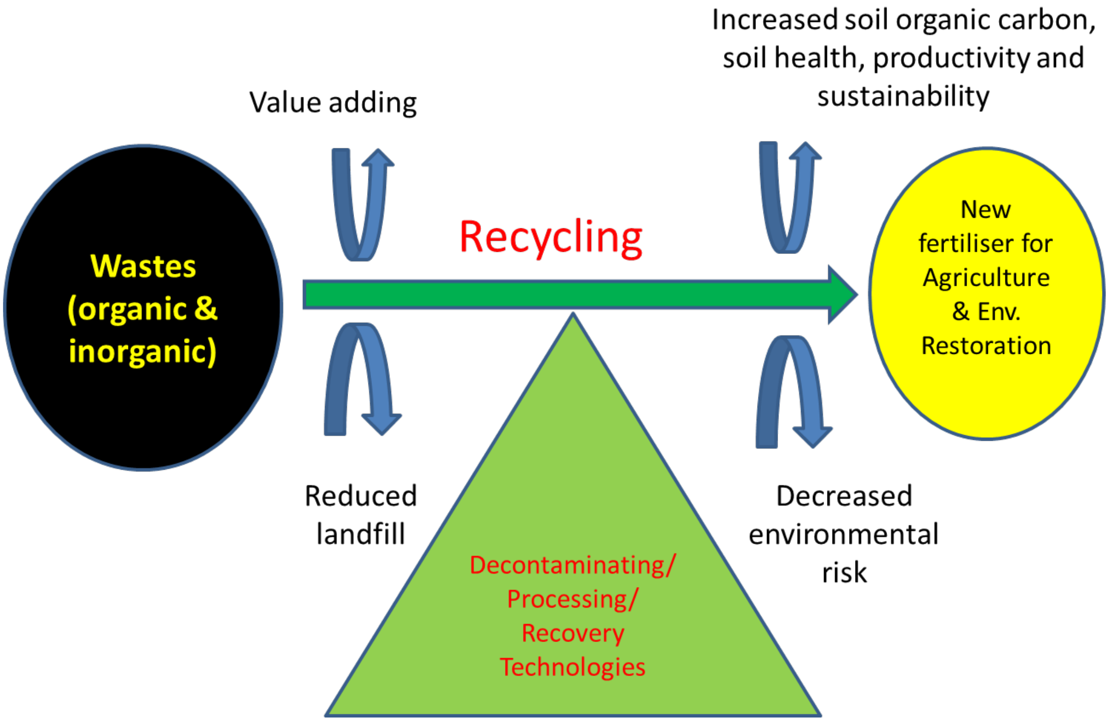


Figure 1.1. Recycling of wastes to improve soil performance and sustainability.

On the other hand, increasing amounts of wastes are generated as population increases. Much of this waste is rich in nutrients and carbon, and thus has strong potential to be used in the manufacturing of new, high-performance fertilisers (Fig. 1.1). However, some issues such as heterogeneity of the waste materials and associated contaminants need to be addressed prior to their reuses. Currently a limited range of products are available for farmers to manage complex soil constraints. To address soil fertility constraints, increase crop yield and minimise environmental risks, there is an urgent need to employ cost effective and innovative technologies to develop novel slow-release-fertilisers and soil amendments to enhance soil performance.

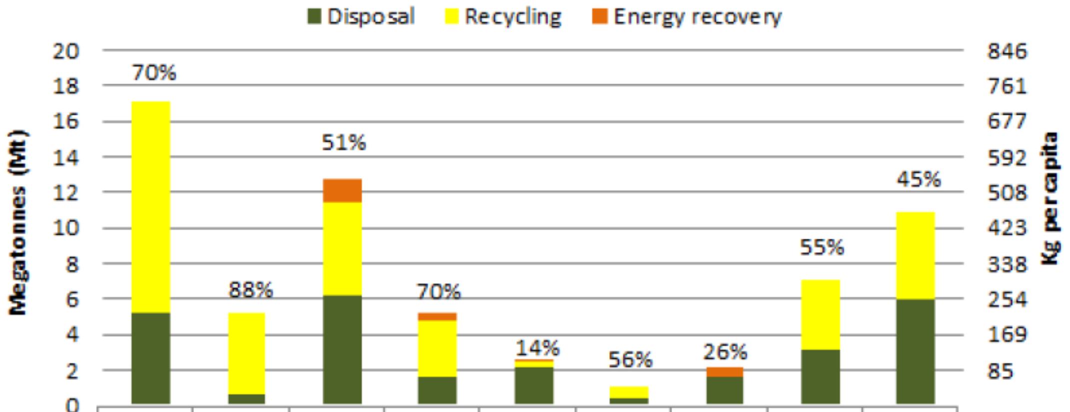
2. Availability and composition of waste in Australia

2.1 An overview of the generation and fate of waste in Australia

According to the Australian National Waste Report (ANWR; 2016), Australia generated approximately 64.3 Mt of waste in 2014—15 (Fig. 1.2). Overall, Australia's generation of waste is decreasing on a per capita basis and an increasing proportion of this waste is being re-used. However, when fly ash (a major by-product of energy generation through coal burning) is excluded, Australia has produced 1% more waste per person each year from 2006 to 2015 (ANWR 2016).

Commercial and industrial (C&I) waste and construction and demolition (C&D) waste constituted 48.2% and 31.1% of total waste generated, and the remaining 20.7% was comprised of municipal solid (MS) waste (ANWR 2016). In 2015-16, 41.9% of C&I waste, 35.5% of C&D waste and 48.9% of MS waste was fated for disposal (i.e. landfill). Thus, there were ca. 13 Mt of C&I, 7.1 Mt of C&D and 6.5 Mt of MS wastes that together represented a tremendous opportunity for beneficial re-use for recovery of increasingly scarce mineral nutrients, production of compost and fertiliser for use in food production, and amelioration of soils in degraded and marginal landscapes.

The ANWR (2016) identified nine major waste streams in Australia including: masonry materials (largely from demolition activities), metals, organic materials, paper and cardboard, plastics, glass, hazardous waste (including contaminated and non-contaminated bio-solids), fly ash, and ‘other’ waste. Among these, almost two-thirds of the ca. 27 Mt of waste that was fated for landfill in 2014-15 was comprised of organic materials (23.0% of total), fly ash (21.9% of total), and masonry materials (19.3% of total; ANWR 2016). Importantly, while the generation of organic waste and fly ash has gradually decreased on a per capita basis from 2006 to 2015, the recovery rate of these waste streams is only 45% and 51%, respectively. At the same time, while recovery rates of masonry waste have been relatively high compared to most other waste streams (70% recovery), the generation of masonry waste has increased in recent years (ANWR 2016).



	Masonry mat.	Metals	Organics	Paper & c'board	Plastics	Glass	Other	Hazwaste	Fly ash
Generation (kg/cap)	726	219	542	223	107	45	91	298	460
Generation (Mt)	17	5.2	13	5.3	2.5	1.1	2.1	7.0	11
En recovery (Mt)			1.4	0.5	0.02		0.5	0.0	
Recycling (Mt)	12.0	4.6	5.2	3.2	0.3	0.6	0.1	3.9	4.9
Disposal (Mt)	5.2	0.6	6.2	1.6	2.2	0.5	1.6	3.2	5.9

Figure 1.2. Different categories of wastes generated and recovery in Australia in 2014-2015 (Australian National Waste Report 2016).

Of the remaining waste streams, metals had by far the highest rate of re-use in 2014-15 (88%) and plastics showed the highest rate of disposal (86%). Over the same period, glass made up only 1.7% of total waste generated and 1.9% of landfill-fated waste. Approximately 70% of the 5.3 Mt of paper and cardboard waste were recycled or used for energy recovery in 2014-2015, with the remaining 1.6 Mt going to landfill. This amount has remained steady despite a decline in the overall amount of paper and cardboard waste generated from 2006 to 2015. Around 3.2 Mt of disposed waste was defined as ‘hazardous’ in the ANWR (2016) and this included contaminated soils, asbestos, tyres and biosolids.

Queensland, NSW and Victoria tend to generate the most waste, with Queensland always contributing the most or the second-most in the material categories of organics, paper and cardboard, hazardous waste, masonry, and fly ash in 2014-15 (Table 1.1; ANWR 2016). Together, QLD and NSW contributed ≥ 50% of organic waste, paper and cardboard waste, and hazardous waste in 2014-15, while QLD and WA together contributed 58.9% of masonry waste. Further, QLD dominates the fly ash generation, contributing 73.0% of the national total in 2014-15 (ANWR 2016).

Table 1.1. Amounts of landfill-fated waste by material category (kilotons [% of national category total]) for each Australian state and territory; data derived from the ANWR 2016.

	Organics	Paper & cardboard	Hazardous waste[†]	Masonry	Fly ash
ACT	83 (1.3%)	31 (2.0%)	9 (0.3%)	14 (0.3%)	0 (0.0%)
NSW	1802 (28.8%)	347 (21.9%)	1020 (32.1%)	773 (14.9%)	801 (13.5%)
NT	111 (1.8%)	29 (1.8%)	0 (0.0%)	139 (2.7%)	0 (0.0%)
QLD	1541 (24.6%)	445 (28.1%)	938 (29.5%)	1480 (28.5%)	4332 (73.0%)
SA	292 (4.7%)	48 (3.0%)	338 (10.6%)	217 (4.2%)	0 (0.0%)
TAS	152 (2.4%)	44 (2.8%)	96 (3.0%)	63 (1.2%)	0 (0.0%)
VIC	1387 (22.1%)	393 (24.8%)	668 (21.0%)	932 (17.9%)	645 (10.9%)
WA	899 (14.3%)	248 (15.6%)	111 (3.5%)	1578 (30.4%)	160 (2.7%)
TOTAL	6267	1585	3180	5196	5938

[†]Including contaminated and non-contaminated bio-solids

The following section reviews information about the forms of waste within these major waste streams that are likely to be of high value for nutrient recovery and the production of compost and fertiliser. Where possible, information has been derived from Australian studies and industry reports. The focus is on organic waste materials; however, some inorganic waste materials are discussed due to their potentially high mineral content. The highlighted organic wastes are mainly associated with the food cycle (production, consumption and human waste [i.e. biosolids]) and include agricultural waste from crops, meat production and processing (beef, poultry, pigs and abattoirs), downstream food waste from MS waste (i.e. household food waste) and C&I waste streams, and biosolids. The discussed inorganic wastes are mainly associated with the C&D waste stream and include plasterboard and concrete.

2.2 Generation and properties of key organic wastes in Australia

The ANWR (2016) described organic waste as non-hazardous organic materials including “food, garden organics and timber” but excluding paper and cardboard. Other waste streams of an organic origin, but that were treated as ‘hazardous wastes’ in the ANWR (2016), included biosolids, abattoir and tannery wastes, and grease trap sludge. Chatterjee et al. 2017 summarised some of the main categories and sources of organic wastes (Table 1.2).

In order to characterise organic wastes according to their generation and properties, they have been divided into the following sections in this scoping study report: (1) waste from agricultural crops, (2) waste from meat production (beef, poultry, piggeries and abattoirs), (3) commercial and industrial food waste and (4) municipal (i.e. household) food waste.

Table 1.2. Sources of recycled organics in Australia (Chatterjee et al. 2017).

Group	Type of wastes	Source of wastes
Plant wastes	Crop residues	Field crop residues and biomass
	Kitchen wastes	Daily kitchen wastes
	Green market wastes	Fruits and vegetable market wastes
	Coconut-arecanut/perennials wastes	By products of these crops
	Forest biomass	Natural forest biomass and by-products.
	Road side vegetation	Weeds and invasive plants biomass
	Aquatic plant biomass	Biomass of aquatic plants
Animal wastes	Animal dung and urine	Faeces and urine of domestic animals and dairies
	Poultry excreta	Poultry droppings of boiler and layering farm.
	Fish meal and fish wastes	Fish wastes arise from fresh water fish and sea fish industries
Other wastes	City garbage	City garbage and municipal solid wastes
	Biogas slurry	By-product of biogas plant
	Biosolid, Sewage and sludge	Industrial/municipal waste water treatment plants
	Sugar industry and distillery wastes	Spent and effluent of sugar industry
	Paper mill industrial wastes	Spent and effluent of the paper mill
	Fly ash	Fly ash generated from thermal power plants.

2.2.1 Agricultural waste from crops

The main crops grown in Australia in terms of economic value are wheat, oats, barley, sorghum, rice, cotton, canola, and sugar cane, which in 2015-16 were produced to the value of around $13.5 billion dollars (ABS 2018). Fruit and vegetables (including grapes) also generate a large amount of revenue (ca. $9.1 billion in 2015-16; ABS 2018). However, many of these economically essential food crops generate a large amount of ‘wasted’ biomass from crop productivity (hereafter ‘crop residues’, although some of this may be waste generated during processing post-harvest).

According to the Australian Government Rural Industries Research and Development Corporation (RIRDC), grain crops, grapes, nuts, and sugarcane are all generating enough waste biomass to make each of them viable for biofuel production (RIRDC 2013a). The high volume of waste generated suggests that crop residues are a potentially valuable source of organic feedstock for the production of organic fertilisers and soil amendments. The following sections present a summary of the volume of waste generated by several economically important crops, some properties of these crop residues, and discussion about their potential value as organic fertilisers (e.g. green manure or compost). The list is not exhaustive, but instead serves as examples of the level of waste generated by Australian cropping systems and the potential value of ‘green manure’ as an organic fertiliser.

Grain crops

Australia grows in excess of 22.2 Mt of wheat, 8.9 Mt of barley, 1.8 Mt of sorghum, 1.3 Mt of oats, and 0.4 Mt of maize annually as of 2017 (ABS 2018). The grain crops, such as wheat which makes up the vast proportion of Australian grain crop production, are mainly produced in the southern half of the continent, close to the south east and west coasts and inland (Fig. 1.3). The highest levels of production occur in southern NSW, Victoria and SA. Reportedly, around half of overall grain crop biomass is left unharvested (RIRDC 2013a). If this figure is accurate, then roughly 17.6 Mt of wasted ‘crop residue’ are generated from grain crop production each year. The grain crop residues are mostly low in nutrients, but can still be considered as an excellent source of C for production of compost or other soil amendments (e.g. biochar), particularly in combination with nutrient-rich organic waste streams.

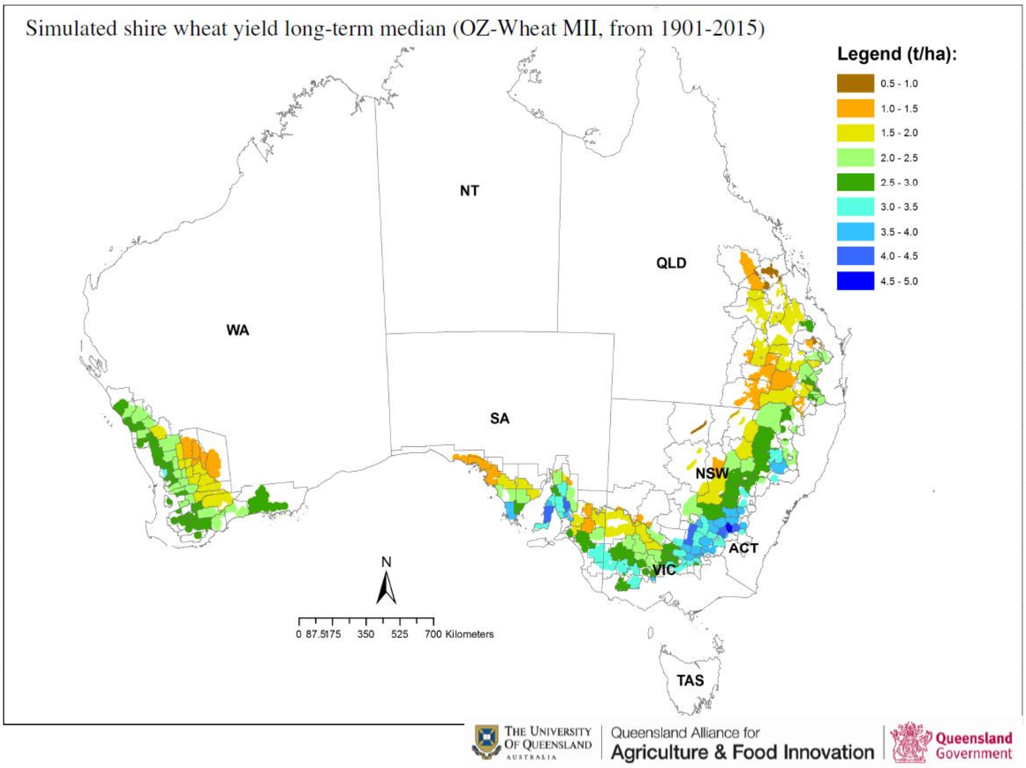


Figure 1.3. Long-term median wheat yield from 1901-2015 based on OZ-Wheat MII simulations; (National Wheat Outlook Australia 2016).

Sugarcane bagasse and mill mud

As of 2015-16, Australian sugarcane production was valued at around $1.48 billion (ABS 2018). This figure corresponds to approximately 34.4 Mt of sugarcane cut for crushing in the same period. Most of this production is focused in coastal QLD (particularly in sub-tropical and tropical coastal QLD). The fibrous material remaining after crushing and extraction of sugar from cane is called *bagasse*, and for each tonne of sugarcane crushed, about 300 kg of bagasse is leftover (on a wet basis), which equates to roughly 10.3 Mt of bagasse produced annually in Australia. Bagasse has many potential uses as a fibre or biofuel (Loh et al. 2013). Similar to grain crop residues, bagasse is not nutrient-rich, but it may be valuable for compost and biochar production.

Another ‘waste’ product of sugarcane production is *mill mud*, which is residue from the milling process and is comprised of soil and fibre, and sometimes ash from mill boilers (which often use sugarcane bagasse to generate energy). Mill mud tends to contain higher levels of nutrients than bagasse, with levels of total N = 1.1%, total P = 1.2% and total K = 0.3% reported in industry fact sheets (Australian Macadamia Society Fact Sheet), and similar values reported in the scientific literature: for example, 1.57% N, 1.59% P, 0.23% K and 35.2% C (Ostatek-Boczynski et al. 2013). Thus, mill mud appears to have C:N and C:P ratios around 22, and N:P ratios < 1, which suggests it is likely to be most effective for P-intensive or P-limited crops, or in P-deficient soils.

Bananas

Banana is an economically- and nutritionally-important crop for Australia. It is particularly important to the economy of northern QLD, which produced 94% of the 414,000 tonnes of bananas in Australia in 2016-17 (Australian Banana Grower’s Council 2018). Meeting retail standards of size and appears entails a large amount of wasted fruit for banana growers, as highlighted recently on the ABS program ‘*War on Waste*’ (Fig. 1.4) and as has been identified elsewhere (Horticulture Innovation Australia 2017). Retaining the value of this lost product has been identified as a key opportunity for the banana industry (HIR 2017).

Figure 1.4. Wasted bananas generated on a high-production farm in one day; (image: ABC’s *‘War on Waste’* 2017).

On a dry basis bananas contain around 3.25% protein (equivalent to 0.55% N), 0.015% Ca, 0.081% Mg, 0.066% P, 1.07% K (USDA 2018). The nutrient contents vary based on fruit size and are also different between fruit flesh and fruit peels. However, these values, along with the large volume of mass generated by the banana industry at various stages, indicate the strong potential for use of banana crop residue for nutrient recovery and production of organic fertilisers (i.e. compost or green manures). In this context, bananas serve as an example of the potential for farm-wasted fruit and vegetables as feed stocks for production of organic fertilisers.

2.2.2 Agricultural waste from livestock and poultry

Beef production

Beef cattle production is highly intensified in the Limestone Coast region of SA, the Great Ocean Road and Gippsland regions of VIC, around Perth in WA and in various regions of inland NSW (Fig. 1.5). Beef production is extremely widespread but generally less intensive (i.e. fewer cattle per square kilometre) in QLD.

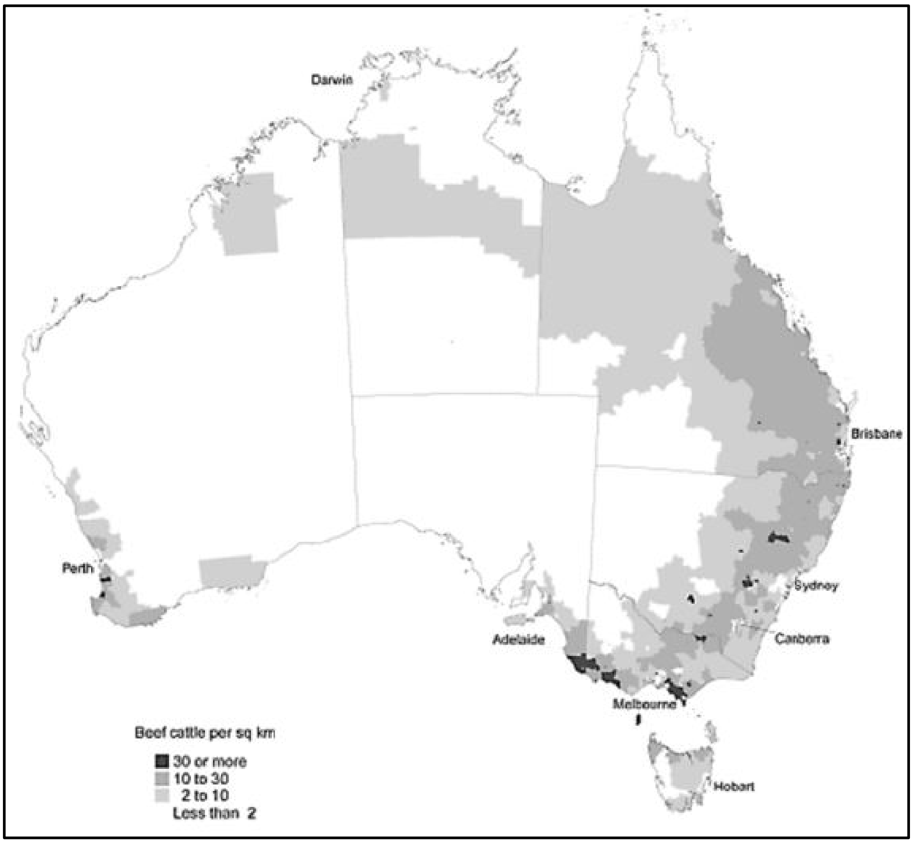


Fig. 1.5. Geographical distribution of beef cattle production in Australia as per 2011 (PriceWaterhouseCoopers 2011, based on ABS data).

Manure is main form of on-farm waste generated by beef production. The amount of raw manure removed from cattle pens can vary widely depending on farm practices and pen construction, but conservative estimates are approximately 400 kg manure (total dry matter) per standard cattle unit (equivalent to one 600 kg animal) per year (Tucker et al. 2015). Given the 23.3 million beef cattle in Australia as of June 2017 (ABS 2018), this equates to around 9.3 million tonnes of dry manure generated by the beef industry on a yearly basis.

Cattle manure is rich in nutrients, but the chemical properties of manure vary from farm to farm and depend on management practises. Table 1.3 shows values of total C, N, P, and K concentrations and C:N:P ratios of raw manure (i.e. manure straight from the pen) reported in some Australian studies. Table 1.4 is from Tucker et al. (2015) and provides data on several other chemical properties of cattle manure.

Mortality (other than slaughter) of beef cattle is the second important form of on-farm organic waste generated by beef production. The rate of mortality is below 1% (Tucker et al. 2015). However, even a mortality rate as low as 0.5% is equivalent to 116,500 mortalities per year based on the 2017 beef cattle population, equating to 69,900 tonnes of cattle biomass. Animal biomass has higher nutrient content than manure (Williams 2007; Tucker et al. 2015), and carcass compost has a higher nutrient content than manure compost.

Table 1.3. Select chemical and stoichiometric properties of raw cattle manure reported by a subset of prior studies of Australian cattle manure.

Total C (%)	Total N (%)	Total P (%)	C:N	C:P	N:P	Reference
-	2.5	0.96	-	-	2.60	Tucker et al. 2015
36.8	3.20	-	11.5			Eldridge et al. 2013
-	0.023†	0.15†	-	-	0.15	Gopalan et al. 2013
29.3	2.70	1.81	10.9	16.2	1.49	Mitchell 1997

†Reported on a fresh basis - this does not affect stoichiometric ratios.

Table 1.4. Average elemental composition of beef cattle pen manure (Tucker et al. 2015).

Parameter	Average level	Minimum level	Maximum level	No. of samples
Dry matter (%)	66.0	19.6	95.6	161
Total nitrogen (% db)	2.5	0.95	4.1	85
Total phosphorus (% db)	0.96	0.75	1.21	21
Potassium (% db)	1.86	0.73	2.92	21
Sodium (% db)	0.33	0.08	0.50	27
Sulfur (% db)	0.44	0.31	0.56	26
EC1:5 (dS/m)	14.7	9.1	18.8	21
Ammonia-N (mg/kg db)	1,797	130	6,430	53
Nitrate-N (mg/kg db)	120	1	390	38
Copper (mg/kg db)	43.8	11.0	68.0	23
Iron (mg/kg db)	11,783	1900	27,000	23
Zinc (mg/kg db)	280	79	430	23

Poultry

Poultry production is typically situated close to large cities, as well as Mareeba (northern QLD) and inner NSW (Fig. 1.6). The poultry industry (primarily chicken and chicken egg production) generates a large amount of organic waste of potentially high value for nutrient recovery and fertiliser manufacture. According to the Australian Government Rural Industries Research and Development Corporation (RIRDC) report on the 'Conversion of Waste to Energy in the Chicken Meat Industry' (2013), this waste occurs primarily in the forms of spent litter (which is comprised of bedding material, poultry excrement, feathers and spilled poultry feed), hatchery waste and chicken mortalities.

The RIRDC (2013b,c) report indicates that, among these three waste streams, poultry litter is the largest contributor to poultry industry waste. It has been estimated that Australia produced approximately 775,000 tonnes of poultry litter waste (on a fresh basis) annually, and that this amount was increasing rapidly over time (Dorahy and Dorahy 2008). The chemical properties of poultry litter are extremely variable and largely depend on the nature of the bedding material. Common bedding materials include sunflower husks, paper, straw, sawdust and rice hulls. In addition, the chemical properties vary based on the feed type and amount, the age of the animal and general poultry shed management practices. Nutrients in litter mainly come originally from the poultry feed.

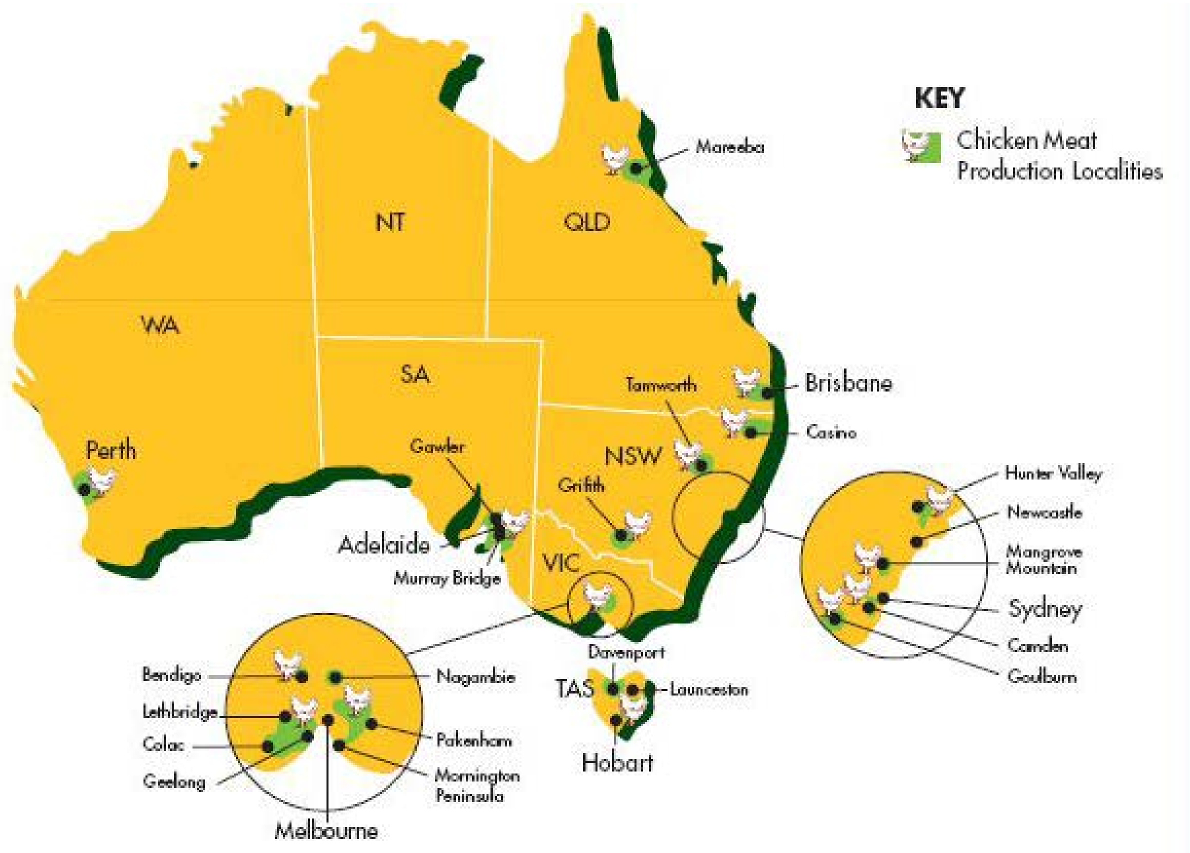


Figure 1.6. Map of chicken production localities in Australia (www.chicken.org.au).

Dorahy and Dorahy (2008) summarised the chemical properties of poultry litter from five Australian studies (Table 5). These data show that poultry litter has a high organic C and nutrient content. In particular, P content in poultry litter is very high, ranging from 1.1—1.9% according to the studies summarised by Dorahy and Dorahy (2008) and the RIRDC reports (2013b,c). Based on the properties summarised in the RIRDC reports (2013b,c), the overall average organic C, N, P and K contents of poultry litter (on a dry basis) can be roughly estimated at 37.5% for C, 3.0% for N, 1.6% for P, and 1.25% for K. These values equate to C:N = 12.5, C:P = 23.4, C:K = 30.0, N:P = 1.88, and N:K = 2.4.

Table 1.5. Select chemical and stoichiometric properties of poultry litter reported by a subset of prior studies of Australian poultry litter.

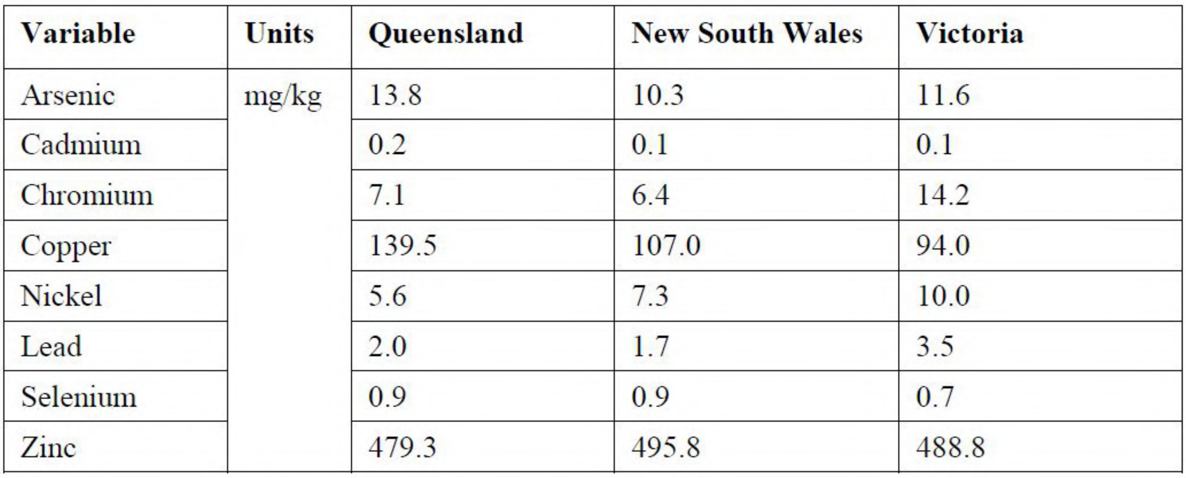
Total C (%)	Total N (%)	Total P (%)	C:N	C:P	N:P	Reference
38.7	3.94	-	9.8	-	-	Eldridge et al. 2013
39.0	3.0	1.36	13.0	29.0	2.21	Ahmad 2016
28.0	4.1	1.9	6.8	14.7	2.16	Dorahy & Dorahy 2008
32.0	3.1	-	10.3	-	-	Chan et al. 2008
36.0	2.6	1.8	22.5	20.0	1.44	Griffiths et al. 2004
-	2.6	1.8	-	-	1.44	DNRE[1] 1999
-	2.7	1.3	-	-	2.08	Parkinson et al. 1999

[1] DNRE = Department of Natural Resources and Environment.

There is some evidence that poultry litter contains heavy metal contaminants (Table 1.6; Nicholas, et al. 2007 in RIRDC 2013b). Further, poultry litter tends to contain large amounts of numerous pathogens, depending on various conditions (temperature, pH, animal age, management). Some of the key pathogens present in poultry litter include *Campylobacter jejuna*, *Clostridium botulinum*, and *Salmonella spp*. (RIRDC 2013d). There are also some reports indicating the existence of pesticide-contaminated poultry litter (e.g. Parkinson et al. 1999), but this is strongly dependent on the shed management.

Hatchery waste is made up of egg materials, dead embryos and dead chicks. The amount of hatchery waste generated in Australia ranges between farms, from 156 to 1170 tonnes per year (RIRDC 2013c). In some cases, eggshell material (and likely any beak and bone if present) is separated from the liquid protein by centrifuging the hatchery waste. Liquid protein comprises around 40% of hatchery waste (RIRDC 2013c) and is a rich potential source of organic N and C. The remaining 60% is likely to be comprised largely of eggshell waste, generated in the range of 94 to 702 tonnes per year. This represents a rich source of $CaCO_3$ (i.e. lime) and various amino acids (Nakano et al. 2003).

Table 1.6. Concentrations of heavy metal contaminants in poultry litter from Australian poultry farms (data originally from Nicholas et al. 2007, summarised and tabulated in the RIRDC 2013 report).

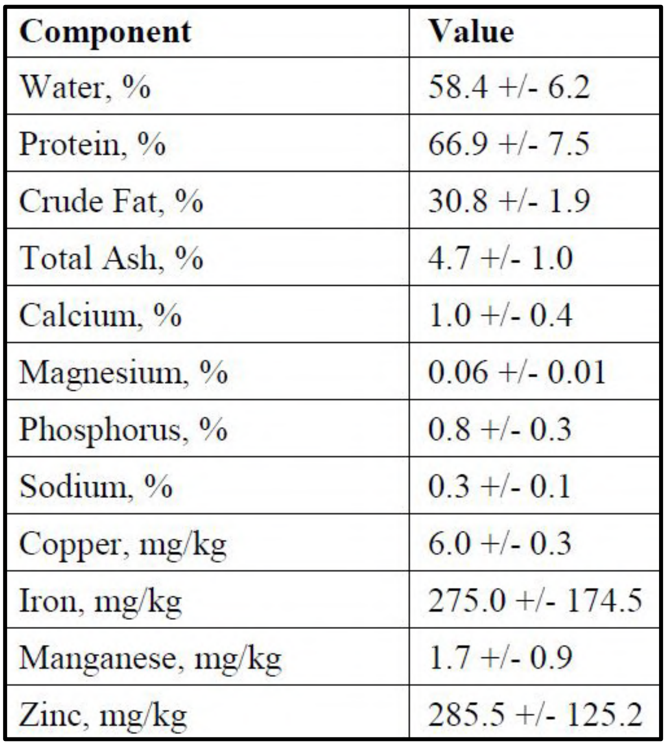


Variable	Units	Queensland	New South Wales	Victoria
Arsenic	mg/kg	13.8	10.3	11.6
Cadmium		0.2	0.1	0.1
Chromium		7.1	6.4	14.2
Copper		139.5	107.0	94.0
Nickel		5.6	7.3	10.0
Lead		2.0	1.7	3.5
Selenium		0.9	0.9	0.7
Zinc		479.3	495.8	488.8

A significant portion of hatchery waste was fated for landfill according to a survey conducted by Glatz and Miao (RIRDC 2013c), with 28.6% of survey respondents indicating that their hatchery waste was generally sent to landfill. Other methods of waste disposal included a combination of composting and landfill (14.3% of respondents) and rendering and composting (14.3% of respondents). According to Glatz and Miao (RIRDC 2013c), almost none of the survey respondents used any form of on-site hatchery waste processing, including composting.

The amount of poultry waste associated with chicken mortality prior to slaughter is variable and naturally depends on mortality rates. Mortality rates are subject to numerous factors, primarily related to shed management, but also the age of the chicken. Mortality rates are highest in the first week (1.54%), but generally decrease afterwards (0.48%; Yassin et al. 2009). Assuming a mortality rate of 0.48%, it can be roughly estimated that of the ca. 160 million chickens in Australian sheds at the end of 2017, around 768,000 did not survive to slaughter. Given the high nutrient content of chicken carcasses (Table 1.7), these chicken mortalities represent an important opportunity for nutrient recovery efforts and fertiliser production.

Table 1.7. Average chemical composition of chicken carcasses (RIRDC 2013c, data originally from Dierenfeld et al. 1994)



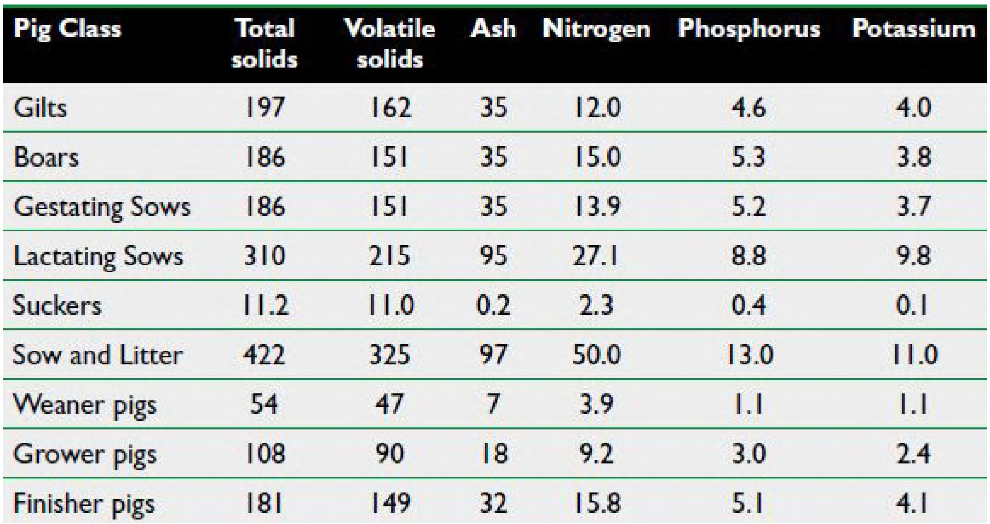
Component	Value
Water, %	58.4 +/- 6.2
Protein, %	66.9 +/- 7.5
Crude Fat, %	30.8 +/- 1.9
Total Ash, %	4.7 +/- 1.0
Calcium, %	1.0 +/- 0.4
Magnesium, %	0.06 +/- 0.01
Phosphorus, %	0.8 +/- 0.3
Sodium, %	0.3 +/- 0.1
Copper, mg/kg	6.0 +/- 0.3
Iron, mg/kg	275.0 +/- 174.5
Manganese, mg/kg	1.7 +/- 0.9
Zinc, mg/kg	285.5 +/- 125.2

Piggeries

As of December 2017 there were 1.3 million pigs in Australian piggeries. Piggeries are widespread throughout the country but tend to be focused around population centres (Cutler & Holyoake 2007). The main sources of wastes generated by piggeries are similar to those generated by beef and poultry production, namely manure and effluent, waste feed, used bedding and mortalities (National Environmental Guidelines for Piggeries [NEGP] 2010).

Piggery waste products are nutrient rich and their chemical composition varies based on feed type, shed type, bedding materials (if beds are used), and the class of pig (e.g. gilts, boars, sows, suckers, etc.; Table 8). Based on the total pig population in Australia (1.3 million) and the annual N and P output values in Table 1.8, the N- and P-waste outputs of piggeries could be in the order of 21,580 tonnes and 6,721 tonnes, respectively. Manure and waste feed may be stockpiled or composted, with the latter resulting in greater losses of volatilized N than the former. Eldridge et al. (2013) report total C and N values of pig (or ‘swine’) manure as 39.3% and 2.99% respectively (C:N = 13.1), and NH_4^+–N and NO_3^-–N values of 1300 ppm and 1.8 ppm respectively. Ahmad (2016) reported similar values, and found available P concentrations of 11,000 ppm in swine manure.

Table 1.8. Estimated amount of solid waste and nutrients generated for various classes of pig (kg per head per year; NEGP 2010).



Pig Class	Total solids	Volatile solids	Ash	Nitrogen	Phosphorus	Potassium
Gilts	197	162	35	12.0	4.6	4.0
Boars	186	151	35	15.0	5.3	3.8
Gestating Sows	186	151	35	13.9	5.2	3.7
Lactating Sows	310	215	95	27.1	8.8	9.8
Suckers	11.2	11.0	0.2	2.3	0.4	0.1
Sow and Litter	422	325	97	50.0	13.0	11.0
Weaner pigs	54	47	7	3.9	1.1	1.1
Grower pigs	108	90	18	9.2	3.0	2.4
Finisher pigs	181	149	32	15.8	5.1	4.1

Piggery effluent is generally collected in ponds and separated into irrigation effluent and sludge. These waste streams are nutrient-rich, although their exact chemical composition varies greatly based on a range of factors including climate, design and management of effluent ponds (NEGP 2010). Table 1.9 contains some examples of the N and P content and N:P ratios of piggery effluent products (irrigant and sludge) from studies of Australian piggeries.

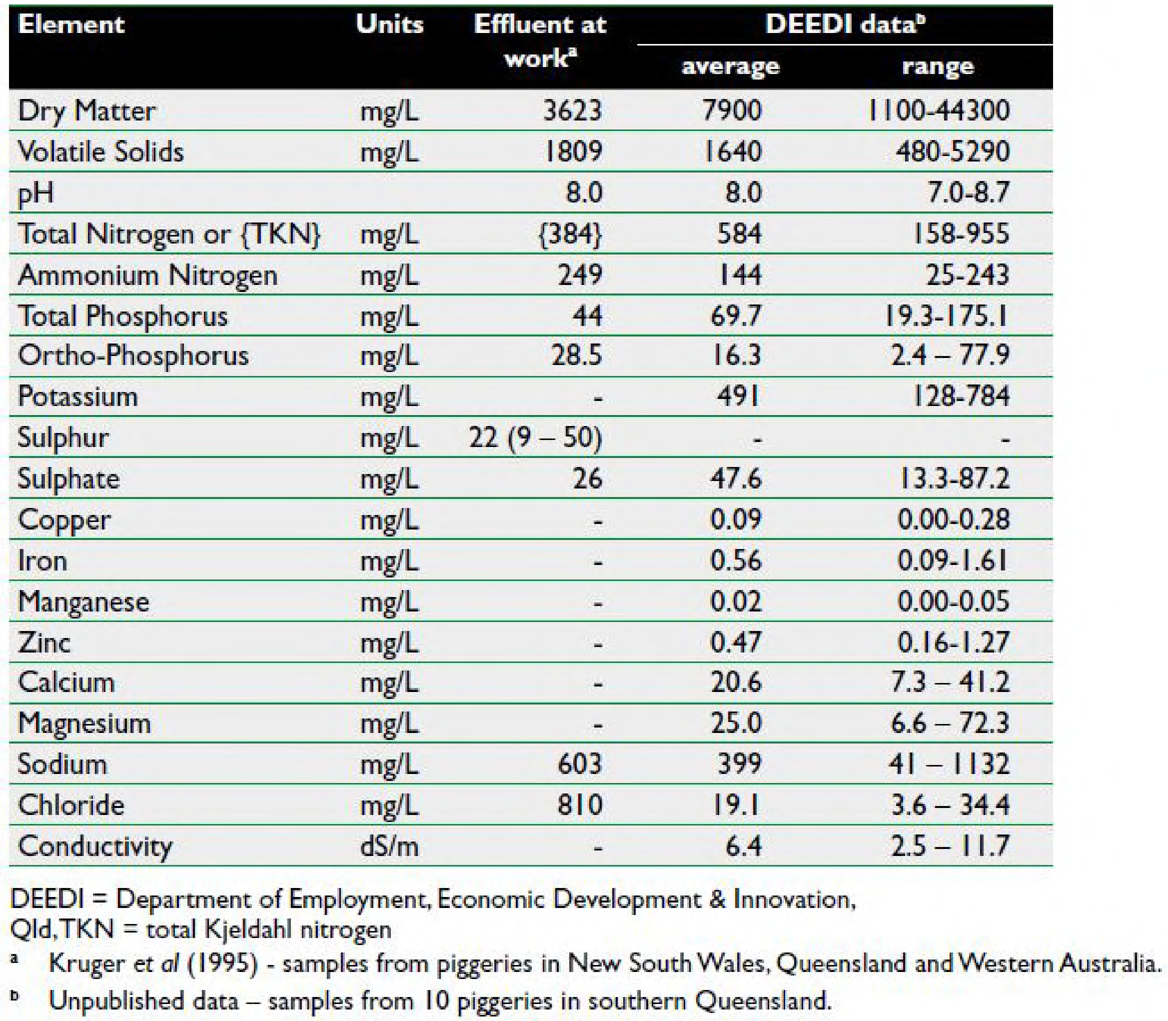
Table 1.9. N and P concentrations and N:P ratios of piggery effluent products from a small subset of prior studies of Australian piggeries.

Irrigant from piggery effluent			Sludge from piggery effluent			Reference
N	P	N:P	N	P	N:P	
384 mg L^{-1}	44 mg L^{-1}	8.7	2617 mg L^{-1}	1696 mg L^{-1}	1.54	Kruger et al. (1995)[†]
584 mg L^{-1}	70 mg L^{-1}	8.4	3.41%	4.69%	0.72	DEEDI (2010)[†]
-	-	-	4.6%	-	-	Kliese et al. (2005)

[†] Data were reported in the National Environmental Guidelines for Piggeries (NEGP) report (2010); DEEDI = Department of Employment, Economic Development and Innovation, QLD Government.

Tables 1.10 and 1.11 show further details of the chemical properties of piggery effluent products as reported by the NEGP (2010).

Table 1.10. Some measurements of chemical characteristics of irrigation effluent from piggeries in NSW and southern QLD (NEGP 2010).



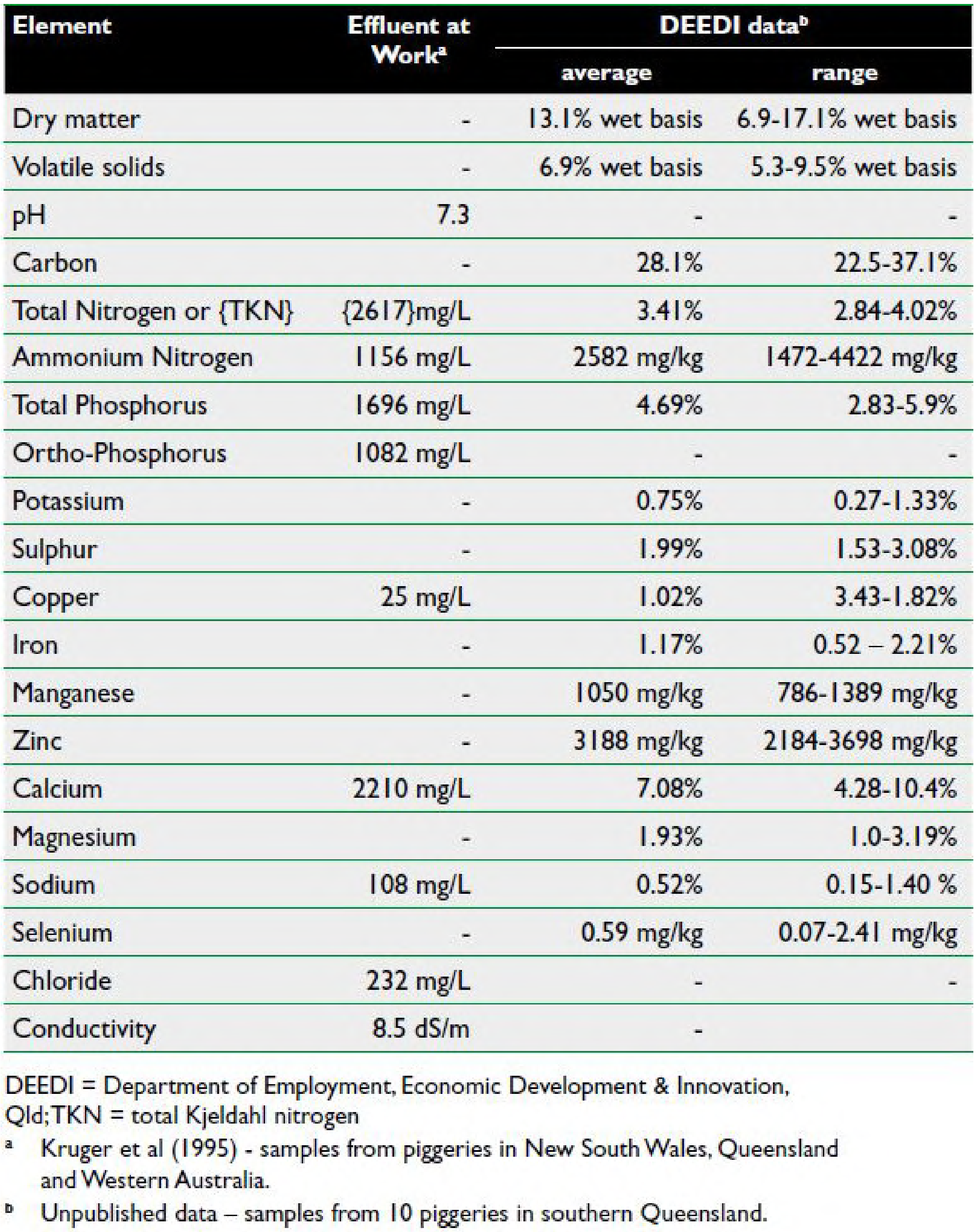
Element	Units	Effluent at work[a]	DEEDI data[b]	
			average	range
Dry Matter	mg/L	3623	7900	1100-44300
Volatile Solids	mg/L	1809	1640	480-5290
pH		8.0	8.0	7.0-8.7
Total Nitrogen or {TKN}	mg/L	{384}	584	158-955
Ammonium Nitrogen	mg/L	249	144	25-243
Total Phosphorus	mg/L	44	69.7	19.3-175.1
Ortho-Phosphorus	mg/L	28.5	16.3	2.4 – 77.9
Potassium	mg/L	-	491	128-784
Sulphur	mg/L	22 (9 – 50)	-	-
Sulphate	mg/L	26	47.6	13.3-87.2
Copper	mg/L	-	0.09	0.00-0.28
Iron	mg/L	-	0.56	0.09-1.61
Manganese	mg/L	-	0.02	0.00-0.05
Zinc	mg/L	-	0.47	0.16-1.27
Calcium	mg/L	-	20.6	7.3 – 41.2
Magnesium	mg/L	-	25.0	6.6 – 72.3
Sodium	mg/L	603	399	41 – 1132
Chloride	mg/L	810	19.1	3.6 – 34.4
Conductivity	dS/m	-	6.4	2.5 – 11.7

DEEDI = Department of Employment, Economic Development & Innovation, Qld, TKN = total Kjeldahl nitrogen

[a] Kruger *et al* (1995) - samples from piggeries in New South Wales, Queensland and Western Australia.

[b] Unpublished data – samples from 10 piggeries in southern Queensland.

Table 1.11. **Some measurements of chemical characteristics of in situ effluent sludge from piggeries in NSW and southern QLD (NEGP 2010).**



Element	Effluent at Work[a]	DEEDI data[b]	
		average	range
Dry matter	-	13.1% wet basis	6.9-17.1% wet basis
Volatile solids	-	6.9% wet basis	5.3-9.5% wet basis
pH	7.3	-	-
Carbon	-	28.1%	22.5-37.1%
Total Nitrogen or {TKN}	{2617}mg/L	3.41%	2.84-4.02%
Ammonium Nitrogen	1156 mg/L	2582 mg/kg	1472-4422 mg/kg
Total Phosphorus	1696 mg/L	4.69%	2.83-5.9%
Ortho-Phosphorus	1082 mg/L	-	-
Potassium	-	0.75%	0.27-1.33%
Sulphur	-	1.99%	1.53-3.08%
Copper	25 mg/L	1.02%	3.43-1.82%
Iron	-	1.17%	0.52 – 2.21%
Manganese	-	1050 mg/kg	786-1389 mg/kg
Zinc	-	3188 mg/kg	2184-3698 mg/kg
Calcium	2210 mg/L	7.08%	4.28-10.4%
Magnesium	-	1.93%	1.0-3.19%
Sodium	108 mg/L	0.52%	0.15-1.40 %
Selenium	-	0.59 mg/kg	0.07-2.41 mg/kg
Chloride	232 mg/L	-	-
Conductivity	8.5 dS/m	-	

DEEDI = Department of Employment, Economic Development & Innovation, Qld; TKN = total Kjeldahl nitrogen

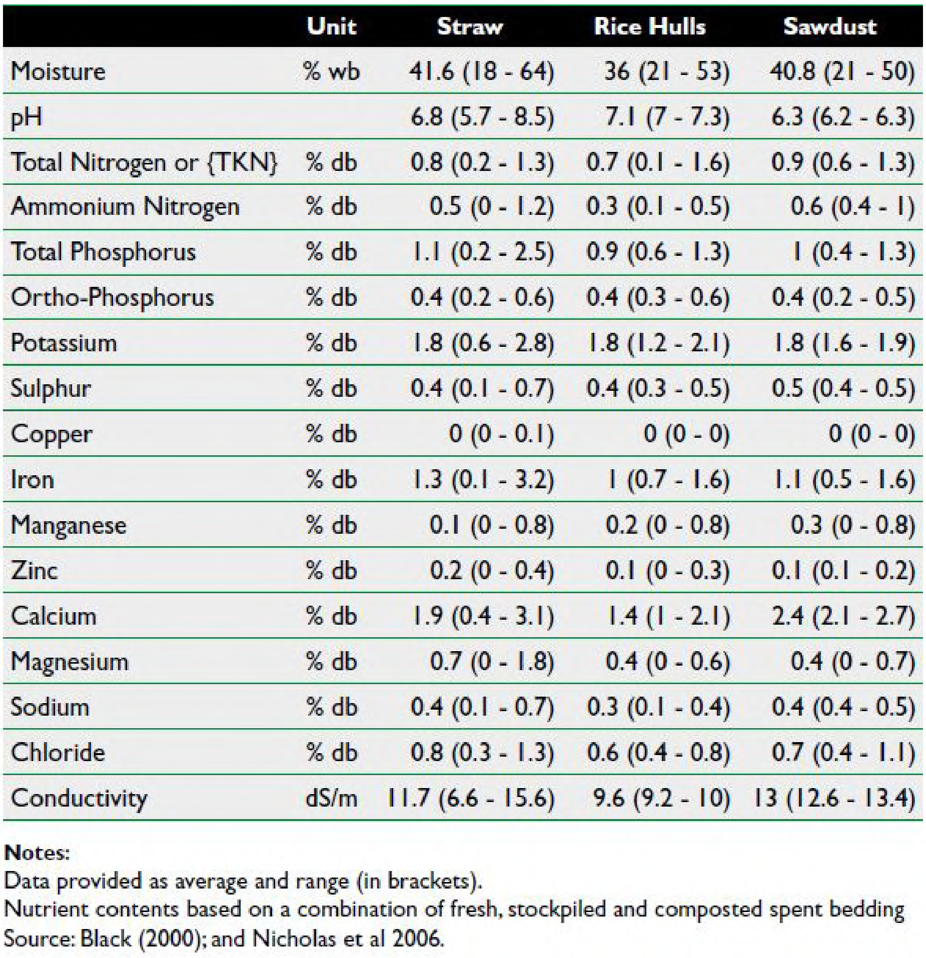
[a] Kruger et al (1995) - samples from piggeries in New South Wales, Queensland and Western Australia.

[b] Unpublished data – samples from 10 piggeries in southern Queensland.

A subset of piggeries use ‘deep-litter’ stalls, wherein pigs have a bed of organic fibre such as straw, rice hulls or sawdust. These stalls produce a large amount of spent litter waste which is a potentially valuable source of both C and nutrients (Table 1.12). The C and nutrient loading of spent litter varies on fibre type and farm practices. Tait et al. (2009) reported total organic C contents of 39%, 41% and 22% of soiled wheat straw, barley straw and rice husks. Based on these values, it can be estimated that the C:N ratios of spent piggery litter are around 46 (straw), 59 (rice husks) and 24 (sawdust). Similarly, these data suggest that C:P ratios of spent piggery litter are around 35 (straw), 46 (rice husks) and 22 (sawdust). Thus, piggery litter N:P ratios are likely to be around 0.7 (straw), 0.8 (rice husks) and 0.9 (sawdust).

By extrapolating the findings of Morrow and Ferket (1993) to 2018 piggery statistics, piggeries may generate around 26,000 tonnes of dead pigs annually. This figure may be somewhat lower if mortality rates have reduced over this time due to improved management practises and technology. However, given the high organic C and nutrient content of animal carcasses (as outlined for beef), it seems likely that pig carcasses could be an important resource for nutrient recovery and fertiliser production.

Table 12. Some measurements of the chemical properties of piggery litter after use (i.e. 'spent bedding'; NEGP 2010).



	Unit	Straw	Rice Hulls	Sawdust
Moisture	% wb	41.6 (18 - 64)	36 (21 - 53)	40.8 (21 - 50)
pH		6.8 (5.7 - 8.5)	7.1 (7 - 7.3)	6.3 (6.2 - 6.3)
Total Nitrogen or {TKN}	% db	0.8 (0.2 - 1.3)	0.7 (0.1 - 1.6)	0.9 (0.6 - 1.3)
Ammonium Nitrogen	% db	0.5 (0 - 1.2)	0.3 (0.1 - 0.5)	0.6 (0.4 - 1)
Total Phosphorus	% db	1.1 (0.2 - 2.5)	0.9 (0.6 - 1.3)	1 (0.4 - 1.3)
Ortho-Phosphorus	% db	0.4 (0.2 - 0.6)	0.4 (0.3 - 0.6)	0.4 (0.2 - 0.5)
Potassium	% db	1.8 (0.6 - 2.8)	1.8 (1.2 - 2.1)	1.8 (1.6 - 1.9)
Sulphur	% db	0.4 (0.1 - 0.7)	0.4 (0.3 - 0.5)	0.5 (0.4 - 0.5)
Copper	% db	0 (0 - 0.1)	0 (0 - 0)	0 (0 - 0)
Iron	% db	1.3 (0.1 - 3.2)	1 (0.7 - 1.6)	1.1 (0.5 - 1.6)
Manganese	% db	0.1 (0 - 0.8)	0.2 (0 - 0.8)	0.3 (0 - 0.8)
Zinc	% db	0.2 (0 - 0.4)	0.1 (0 - 0.3)	0.1 (0.1 - 0.2)
Calcium	% db	1.9 (0.4 - 3.1)	1.4 (1 - 2.1)	2.4 (2.1 - 2.7)
Magnesium	% db	0.7 (0 - 1.8)	0.4 (0 - 0.6)	0.4 (0 - 0.7)
Sodium	% db	0.4 (0.1 - 0.7)	0.3 (0.1 - 0.4)	0.4 (0.4 - 0.5)
Chloride	% db	0.8 (0.3 - 1.3)	0.6 (0.4 - 0.8)	0.7 (0.4 - 1.1)
Conductivity	dS/m	11.7 (6.6 - 15.6)	9.6 (9.2 - 10)	13 (12.6 - 13.4)

Notes:
Data provided as average and range (in brackets).
Nutrient contents based on a combination of fresh, stockpiled and composted spent bedding
Source: Black (2000); and Nicholas et al 2006.

Abattoir waste

Abattoirs generate a large amount of organic waste. Inedible parts of animals, which can make up as much as 45% of the animal, are considered waste (Franke-Whittle and Insam 2013). These animal parts can include organs, bone and feathers, ligaments and tendons, and blood vessels (Franke-Whittle and Insam 2013). There are >80 abattoirs throughout Australia, mainly situated along the east and south-east coast and inland Victoria (Fig. 1.7). In Queensland alone, at least 80,000 tonnes of abattoir organic waste were generated in 2015-16, and practically all of this is converted into beneficial products like pet food, compost and 'blood and bone' fertiliser (Department of Environment and Heritage Protection 2016). Given the similar numbers of abattoirs in NSW, Victoria and WA, the amount of abattoir waste generated on a national level is likely in the order of 200,000 tonnes per year in recent years as of 2018.

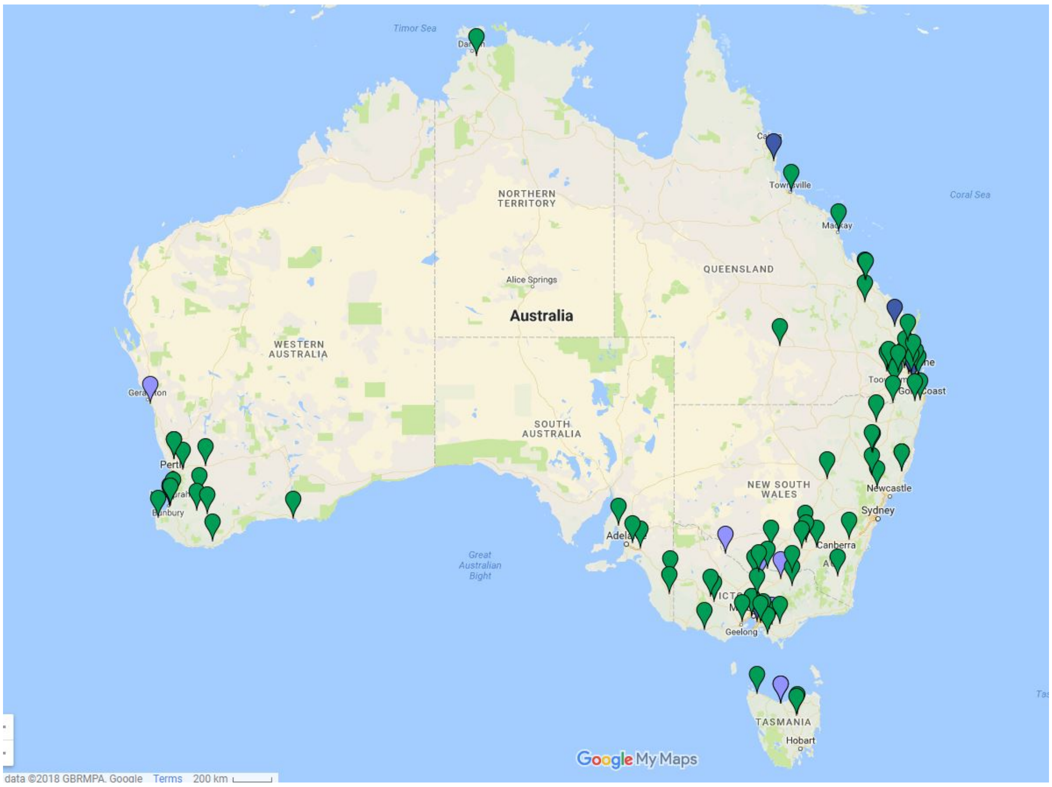
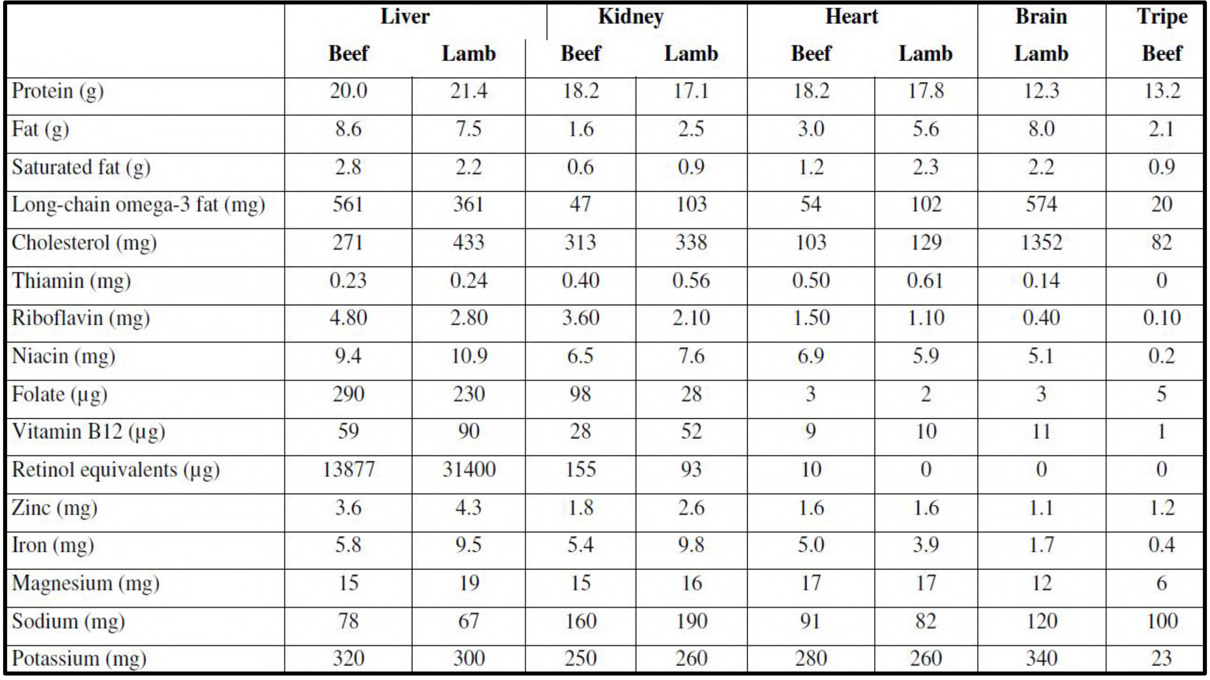


Figure 1.7. Locations of Aus-Meat listed abattoirs in Australia (blue = domestic abattoirs; green = international export abattoirs; (www.australianabattoirs.com).

Raw abattoir waste has very high organic C and nutrient content, although this varies based on the animal and the specific organs of the animal. Bone makes a large proportion (>50% of animal biomass) and is around 65% hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] and thus has a very high Ca and P content and low N:P (N:P = 0.8 on a molar basis; Sterner & Elser 2002). Other organs vary in their nutrient content, but all internal organs generally have high nutrient and organic carbon content. Table 1.13 contains examples of liver, kidney, heart, brain and tripe nutrient content (per 100 g on a fresh basis) of fresh beef and lamb.

Table 1.13. Amounts of selected nutrients (per 100 g fresh basis) in beef and lamb offal (Williams 2007).



	Liver		Kidney		Heart		Brain	Tripe
	Beef	Lamb	Beef	Lamb	Beef	Lamb	Lamb	Beef
Protein (g)	20.0	21.4	18.2	17.1	18.2	17.8	12.3	13.2
Fat (g)	8.6	7.5	1.6	2.5	3.0	5.6	8.0	2.1
Saturated fat (g)	2.8	2.2	0.6	0.9	1.2	2.3	2.2	0.9
Long-chain omega-3 fat (mg)	561	361	47	103	54	102	574	20
Cholesterol (mg)	271	433	313	338	103	129	1352	82
Thiamin (mg)	0.23	0.24	0.40	0.56	0.50	0.61	0.14	0
Riboflavin (mg)	4.80	2.80	3.60	2.10	1.50	1.10	0.40	0.10
Niacin (mg)	9.4	10.9	6.5	7.6	6.9	5.9	5.1	0.2
Folate (µg)	290	230	98	28	3	2	3	5
Vitamin B12 (µg)	59	90	28	52	9	10	11	1
Retinol equivalents (µg)	13877	31400	155	93	10	0	0	0
Zinc (mg)	3.6	4.3	1.8	2.6	1.6	1.6	1.1	1.2
Iron (mg)	5.8	9.5	5.4	9.8	5.0	3.9	1.7	0.4
Magnesium (mg)	15	19	15	16	17	17	12	6
Sodium (mg)	78	67	160	190	91	82	120	100
Potassium (mg)	320	300	250	260	280	260	340	23

2.2.3 Food waste from the MS and C&I waste streams

Food waste from the MS waste stream (i.e. household food waste) made up about 3.1 Mt of waste in 2014-15, with only around 6% of this being composted and another 23% being used for energy recovery. The remainder of this went to landfill (ANWR 2016). At the same time, the C&I waste stream created another 2.2 Mt of food waste (mainly generated at supermarkets, workplaces and retail food outlets). In total, about 3.1 Mt of food waste was fated for landfill (58.5% of food waste). The magnitude of food waste is closely linked with human population.

The heterogeneous nature of food waste and differences in diet among households means that the nutrient content of food waste is difficult to quantify with much accuracy. A study based in the United Kingdom found that fresh plant products (fruit and vegetables), ‘meat and fish’ and ‘eggs and dairy’ comprised approximately 36%, 13.0% and 7.4% of food waste (Quested et al. 2011). Assuming a similar overall dietary composition between the United Kingdom and Australia (and assuming that household and C&I food waste have reasonably similar compositions), this should be roughly equivalent to 1.9 Mt of fresh plant product, 0.7 Mt of meat and fish, and 0.4 Mt of eggs and dairy wasted in Australia in 2014-15.

Obviously, these food waste products have excellent nutritional value. To our knowledge, no studies have estimated the overall amount of lost nutrients associated with food waste in Australia. However, a recent study based in the United States (Spiker et al. 2016) estimated that 5.9 g dietary fibre (equivalent to ca. 2.18 g C; Sterner & Elser 2002), 33 g protein (equivalent to 17.5 g C and 5.61 g N; Sterner and Elser 2002), 450.3 mg P, 880 mg of K and 286 mg of Ca were lost through food wastage at retail and consumer levels per person per day. Applying these estimates to an Australian population as of 2018 (ca. 24,702,900; ABS 2018), it seems plausible that losses of C and nutrients in Australia from food waste could be in the order of 177 kt of C, 51 kt of N, 4.1 kt of P, 7.9 kt of K and 2.6 kt of Ca per year.

2.2.4 Biosolids

Biosolids are the solid phase of the end product of sewerage treatment, and constitute an enormous stream of nutrient-dense organic waste in Australia. Biosolids were not treated as ‘organic’ waste in the ANWR (2016) because they are processed very differently to the main waste streams. Approximately 327,000 tonnes of biosolids were generated in Australia in 2017 on a dry weight basis (Australian Water Association 2017), with this generation strongly coupled with human population density.

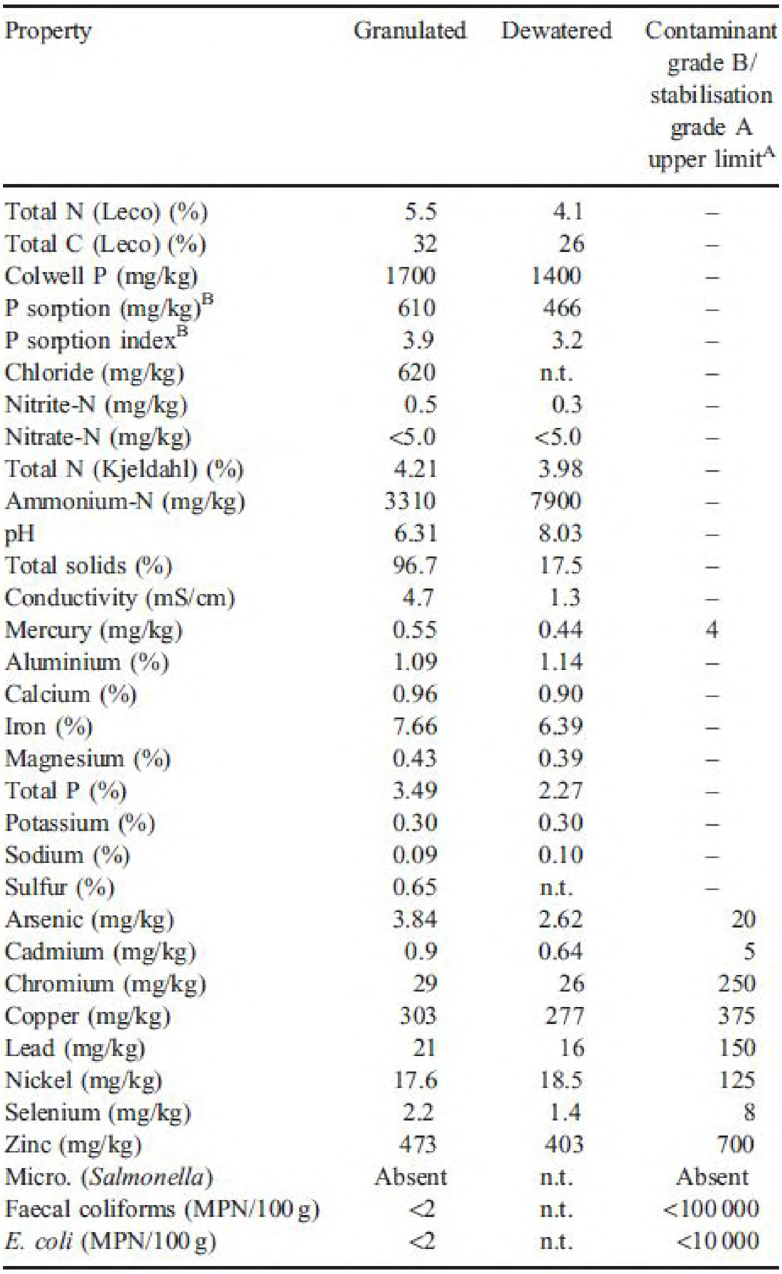
Biosolids are rich in nutrients, having total N contents as high as 5.5% and NH_4^+–N as high as 7900 ppm, depending on treatment and preparation processes (Eldridge et al. 2008). Total P content and available P concentrations in biosolids can be as high as 4.52% and 8600 ppm respectively (Ahmad 2016). Data in Eldridge et al. (2008) reported respective C:N, C:P and N:P ratios of 5.82, 9.17 and 1.58 in granulated biosolids, and 6.34, 11.45 and 1.81 for dewatered biosolids. The data included in Ahmad (2016) were consistent with this, with biosolid C:N, C:P and N:P ratios of 5.90, 6.39, and 1.08 respectively.

Despite their immense potential for nutrient recovery (particularly of P) and for production of organically-derived fertilisers, biosolids pose several challenges. The main concern is environmental contamination from heavy metals and microbial pathogens, which pose risks to human health and natural ecosystems. Table 14 is directly from Eldridge et al. (2008) and summarises the key chemical, heavy metal and pathogen-related properties of two biosolid products.

The risk of heavy metal contamination from biosolids is obviously increased when biosolids are applied to food crops, as several studies indicate that plants accumulate heavy metal contaminants in their biomass following soil amendment with biosolids (e.g. Wei and Liu 2005; Singh and Agrawal 2010). However, this is not always the case, as in some studies the positive effects of biosolids on crop yield do not coincide with increased contaminant levels in plant tissue (e.g. Evanylo et al. 2005; Garrido et al. 2005). There may be numerous options to reduce heavy metal uptake and accumulation in plants grown for food, such as finding the optimal application rate with consideration of the limiting nutrients (Singh and Agrawal 2010), or addition of biochar to adsorb Cd and Ni (Esfandbod et al. 2017).

Application of biosolids has strong potential to increase soil pathogen load, as biosolids themselves carry high levels of various pathogens, much like other manures, including *E. coli*, *Salmonella spp*. and faecal coliforms (Table 1.14). In many cases, the risks posed by soil-borne pathogens may be reduced by hygiene and other management practises, and by careful selection of appropriate crops. For instance, biosolids may be more appropriate for food crops where the consumable portion of the plant has minimal contact with soil (fruit trees, vines, etc.).

Table 1.14. Properties of two biosolid products produced in Australia (Eldridge, et al. 2008).



Property	Granulated	Dewatered	Contaminant grade B/ stabilisation grade A upper limit[A]
Total N (Leco) (%)	5.5	4.1	–
Total C (Leco) (%)	32	26	–
Colwell P (mg/kg)	1700	1400	–
P sorption (mg/kg)[B]	610	466	–
P sorption index[B]	3.9	3.2	–
Chloride (mg/kg)	620	n.t.	–
Nitrite-N (mg/kg)	0.5	0.3	–
Nitrate-N (mg/kg)	<5.0	<5.0	–
Total N (Kjeldahl) (%)	4.21	3.98	–
Ammonium-N (mg/kg)	3310	7900	–
pH	6.31	8.03	–
Total solids (%)	96.7	17.5	–
Conductivity (mS/cm)	4.7	1.3	–
Mercury (mg/kg)	0.55	0.44	4
Aluminium (%)	1.09	1.14	–
Calcium (%)	0.96	0.90	–
Iron (%)	7.66	6.39	–
Magnesium (%)	0.43	0.39	–
Total P (%)	3.49	2.27	–
Potassium (%)	0.30	0.30	–
Sodium (%)	0.09	0.10	–
Sulfur (%)	0.65	n.t.	–
Arsenic (mg/kg)	3.84	2.62	20
Cadmium (mg/kg)	0.9	0.64	5
Chromium (mg/kg)	29	26	250
Copper (mg/kg)	303	277	375
Lead (mg/kg)	21	16	150
Nickel (mg/kg)	17.6	18.5	125
Selenium (mg/kg)	2.2	1.4	8
Zinc (mg/kg)	473	403	700
Micro. (*Salmonella*)	Absent	n.t.	Absent
Faecal coliforms (MPN/100 g)	<2	n.t.	<100 000
E. coli (MPN/100 g)	<2	n.t.	<10 000

2.2.5 Summary

Which organic wastes have the best potential for recovering nutrients?

Based on the above findings related to the quantity and quality of organic waste generation, it seems clear that there is remarkable potential for recovering nutrients (particularly N and P) from the livestock and poultry waste streams, the sewerage and biosolids waste stream, and to a lesser extent the municipal solid food waste stream.

Which organic wastes will be best for making organic fertilisers and composts?

Each of the organic wastes produced at high volumes and described above have strong potential as feedstock for producing organic fertilisers, and the variation in C and nutrient content (and other chemical properties) among the different waste types will the formulation of stoichiometrically-optimised organic fertilisers and composts to meet specific requirements of the soil–crop complex in question. However, given the high potential for contamination by biosolids, poultry litter and swine manure, these wastes may be optimal for focused nutrient recovery efforts, while comparatively low contaminant-risk wastes may be better-suited for fertiliser production, alone or in combination. In particular, combinations of food waste, crop residues and cattle manure, are likely to provide excellent feed stocks for compost production, due to their high organic C content as well as potentially high nutrient content. Moreover, these compost products can be amended with nutrients recovered from biosolids, poultry and piggery litter, and abattoir waste to enhance mineral nutrient levels where required.

2.3 Generation and properties of key inorganic wastes in Australia

The focus of this report is primarily on wastes of an organic nature; however, there may be several forms of inorganic waste which are relevant to purposes of nutrient recovery and the production of fertilisers and composts. Below two types of inorganic waste (concrete and plasterboard) have been identified as having strong potential for these purposes, due to the volume of their generation and their chemical properties. Critically, both of these wastes constitute part of the Construction and Demolition waste stream, which is increasing in volume nationally (ANWR 2016). Further, they are components of ‘Masonry material’ waste stream, which generates 17 Mt of waste and 5.2 Mt of landfill-fated waste annually, and is the largest of all waste streams in Australia (representing 26.5% of all waste generated; ANWR 2016). Masonry material waste (and C&D waste in general) is increasing nationally as demolition and construction increases due to ongoing urban and industrial development (ANWR 2016). The ANWR 2016 identified the C&I waste stream as the best opportunity for increased resource recovery.

2.3.1 Concrete from building demolition

Smashed concrete from demolition sites is a massive component of C&D waste generation. Concrete can be recycled, however this is usually done so with regard to its physical properties (Construction Materials Recycling Association 2010), and recycling concrete for its chemical value appears to be a largely missed opportunity in Australia. Concrete is the combination of cement, water and aggregates (crushed stone, sand or gravel). Aggregates and may contain useful levels of mineral nutrient, although this will depend on their type and origin. Cement however, being largely the product of limestone and gypsum, contains significant levels of Ca and Mg (Cement Australia 2018). Thus, while levels of N and P are likely to be low or negligible in crushed concrete waste, it seems likely that the crushed concrete waste may be a useful co-amendment for liming (increasing soil pH) in combination with compost or other N- and P-rich organic fertilisers, particularly in acidic soils or when amendments have low pH values. Importantly, use of recycled concrete as a soil amendment would require crushing of the concrete (Construction Materials Recycling Association 2010), an industrial-scale process that would only occur in response to strong economic incentive and economic feasibility.

2.3.2 Plasterboard

It has been claimed that Australia produces in excess of 1 Mt of plasterboard annually for use in building construction (Regyp Pty Ltd 2018). Without recycling efforts, this product is ultimately fated for landfill, and some figures indicate that Sydney alone generates around 20,000 tonnes of landfill-fated plasterboard waste on a yearly basis (Regyp Pty Ltd 2018). Plasterboard is comprised mainly of gypsum ($CaSO_4$) and therefore has obvious potential to increase levels of Ca and S in soil, but also to raise soil pH, thereby increasing P availability in acid soils. Previous research shows that plasterboard (or 'drywall') contains around 21.9% Ca, 18.1% S, 0.22% Mg, 547 ppm Fe, 51.6 ppm P, 9.4 ppm Mn, and 7.3 ppm B (Besnard 2013). Regyp Pty. Ltd. advertises a range of recycled plasterboard products (Regyp 2018), based on plasterboard alone or in combination with mineral nutrients, compost and manures. Importantly, prior research has shown that plasterboard has low levels of heavy metal contaminants, and that application of crushed plasterboard to soil can positively influence crop yields (Edwin and Mark 1993; Munn and Murray 1999; Besnard 2013), and can also enhance soil C sequestration (Besnard 2013). Given these findings, it seems clear that recycled plasterboard waste from construction and demolition activities could be an excellent source of mineral nutrients to be used in combination with other recycled organic wastes, or as a liming agent to improve soil pH in acidic soils.

3. Waste-derived organic fertilisers and soil amendments in Australia: current state, technologies and key challenges

3.1 Background

The intensification of agriculture and associated increase in synthetic fertiliser and pesticide application enabled food supplies to keep pace with the rapid growth of human populations during the 20th century. However, this was also associated with severe environmental and ecological consequences, many of which are ongoing, including contamination of food and soils with highly toxic chemical compounds (e.g. organochlorines and subsequently organophosphates), eutrophication of waterbodies through nutrient runoff, and physical and chemical degradation of soils and landscapes (Carson 1962; Miller and Spoolman 2012). Moreover, the huge demand for nutrients to produce the fertilisers that sustain global agriculture has contributed to the dramatic distortion of the global biogeochemical cycles of N and P (Vitousek et al. 1997; Elser and Bennett 2011; Sardans et al. 2012). Perhaps most importantly, there is an emerging crisis posed by the impending depletion of mineral P rock reserves, from which P fertilisers are produced (Wyant et al. 2013). Some authors suggest that global reserves of rock phosphate could be depleted sometime between the years 2068 and 2118, and many are calling for increased efforts into recovering and retaining P that would otherwise enter the waste stream (Cordell et al. 2009; Ashley et al. 2011; Wyant et al. 2013).

Importantly, the use of organic waste-derived fertilisers was the norm in agriculture in "Western" societies and elsewhere throughout modern pre-history (e.g. Wyant et al. 2013). This only changed at around 1870, when increasing food demand and technological advancement precipitated the 'green revolution', during which the use of organic waste-derived fertilisers and soil amendments quickly gave way to the use of synthetic or industrially-produced (e.g. mined) fertilisers (van Zanden 1991; McGregor and Shepherd 2000; Quilty and Cattle 2011). Thus, in many ways the increasing focus on nutrient recovery and 'recycling' of wastes is not a new idea, but is rather a return to an old concept. However, the numerous problems associated with redirecting waste streams (e.g. risks to human health from heavy metals and pathogens in organic wastes, environmental contamination), along with the huge difference in global food demand between pre-1870 and the present day, means that a return to old practises will not be sufficient or acceptable to address this challenge. Instead, it will be critical to investigate the best possible ways to produce, apply and mitigate the potential disadvantages of waste-derived fertilisers.

The following review marks the initial phase of this research effort, and in doing so describes (a) the main forms of waste-derived fertilisers and soil amendments that are currently available or under development in Australia; (b) some of the main current and emerging technologies that can be used for nutrient recovery and fertiliser production from wastes; and (c) the key challenges associated with recycling of wastes for the purposes of nutrient recovery and fertiliser production.

3.2 Different types of waste-derived fertilisers and soil amendments

Australia has a broad range of waste-derived fertilisers and soil amendments, either commercially available or subject to research and development efforts. Most of them are from the organic waste streams, particularly those detailed in section 2.2 of this scoping report, while there is also a number of soil amendments derived from inorganic waste streams (particularly the construction and demolition stream). Quilty and Cattle (2011) reviewed the main types of organic waste-derived soil fertilisers and amendments available in Australia, and the general application rates and costs of these products are shown in Table 1.15. The major organic waste-derived fertilisers and soil amendments in Australia include the following (based on Quilty and Cattle 2011):

Table 1.15. Application rates and costs of main organic fertiliser or amendment types produced and used in Australia (adapted from Quilty and Cattle 2011).

Organic fertiliser or amendment type	Application rate	Cost
Compost		
Pelletized	0.075–5 t ha^{-1}	\$100–500 per tonne
Non-pelletised	0.5–30 t ha^{-1}	\$7–800 per tonne
Vermicasts / vermicomposts		
Liquids	10–100 L ha^{-1}	\$1–20 per litre
Solids	2–50 t ha^{-1}	\$250–1000 per tonne
Humic substances		
Liquids	1–30 L ha^{-1}	\$4–25 per litre
Solids	0.025–1 t ha^{-1}	\$40–800 per tonne
Meat, blood and bone meal		
Liquids	1–30 L ha^{-1}	\$10–30 per litre
Solids	0.1–1.2 t ha^{-1}	\$800–1200 per tonne
Fish hydrolysate	2–60 L ha^{-1}	\$15–25 per litre
Biochar	10 to > 40 t ha^{-1}	Not widely commercially available

3.2.1 Compost, compost teas and vermicomposts

Compost is the end-result of a (usually) controlled process of decomposition of organic feed stocks (e.g. manure, food waste, plant matter, biosolids; Quilty and Cattle 2011). It is nutrient-rich and has high levels of organic C and humified materials, while the amount of nutrients, C and different functional C forms vary greatly depending on feed stocks and decomposing (or ‘composting’) conditions (duration, temperature, mixing, moisture; Zmora-Nahum et al. 2007). Composts add nutrients to soil in available and organic forms, and the organic matter in compost improves soil structure and moisture characteristics, and biological activity (Hargreaves et al. 2008). Composts are generally applied directly to soil and be mixed into the topsoil. However, they can also be used as a direct growth medium for plants.

Compost teas are essentially the liquid extracts that result from soaking of compost feed stocks in water, often with addition of other additives, and have similar properties to compost but at diluted concentrations. Compost teas can be applied to soil surface or be used as a foliar spray for the purposes of pathogen control (Quilty and Cattle 2011). Vermicomposts are considered as composts produced in the presence of large numbers of earthworms, which consume the feed stocks and excrete ‘casts’, which contain nutrients, organic carbon and potentially beneficial microbial organisms (Arancon et al. 2004, 2005; Gutierrez-Miceli et al. 2007).

3.2.2 Humic substances

Humic substances are a class of heterogeneous organic compounds that are the results of partial decomposition of organic matter. The three main types of humic substances are humin, humic acids, and fulvic acids, which differ essentially in terms of their solubility across a range of pH values (humin being insoluble at all pHs, humic acids being soluble only at low pH, and fulvic acids being soluble at all pH values). Humic substances are found naturally in most soils, while their levels can be increased through compost addition. There are also ‘purified’ humic substances available as soil amendments. These are produced via extraction from composts, and particularly from composts of extremely C-rich substances like peat or brown coal (Brownell et al. 1987). Although not a large source of nutrients compared to other waste-derived soil amendments (e.g. manure, biosolids, or composts), humic substances can improve soil edaphic qualities and have been demonstrated to have positive effects on plant growth (e.g. Brownell et al. 1987; Eyheraguibel et al. 2008).

3.2.3 Meat, blood and bone meal

Meat, blood and bone meal (MBBM) products consist of dried, ground and, in many cases, pelletized animal biomass (e.g. animal carcasses and other waste from abattoirs and hatcheries). These products are extremely rich in nutrients (come from proteins with ca. 17% N), hydroxyapatite (in bone $Ca_{10}(PO_4)_6(OH)_2$), and a variety of other organic molecules (e.g. various elements in lipids, N and Fe in globins, P in nucleic acids; Sterner & Elser 2002). Meat, blood and bone meal amendments are typically applied in solid form directly to the soil surface and subsequently incorporated. Numerous studies have found that MBBM affect soil properties (e.g. increased nutrient availability and microbial activity) and thus likely influence plant performance (Mondini et al. 2008; Nogalska and Zalewska 2013; Stepien and Wojtkowiak 2015).

3.2.4 Manures and sewage by-products (i.e. biosolids)

Manure is the faecal matter of livestock and poultry, and often come combined with bedding materials or ‘litter’ of the animals (particularly poultry). As detailed in section 2, manure is rich in organic C and nutrients but these qualities vary among animals, their feed, and the conditions of manure storage and handling. Manures and manure composts have long been used as plant fertilisers and are still a primary source of fertiliser in many developing areas (Farhad et al. 2009; Dikinya and Mufwanzala 2010). In most cases these products are applied directly to soil as solids and incorporated, and tend to increase soil nutrient concentrations and availability, organic matter content and crop yield (Edmeades 2003).

Sewage is effectively ‘human manure’, and was often applied to crops as fertiliser before an increased understanding in the role of micro-organisms in disease led to concerns about the safety of such practises (Wyant et al. 2013). Concerns over food security, nutrient scarcity and environmentally safe disposal of sewage by-products have shifted attitudes again, and there is an increasing interest in using sewage by-products in a positive and environmentally conscious manner. Like animal manures, sewage is rich in nutrients, with the added benefit of having a huge supply as well as a convenient means of delivery to centralised processing facilities (i.e. the sewer system). Treatment of sewerage results in liquid and solid phases, known as effluent and biosolids respectively. Both of these products have tremendous potential for nutrient recovery and being increasingly applied directly to soils as fertilisers, or being subject to further processing to produce other products such as composts, struvite, slow-release fertilisers (e.g. 'Crystal Green') or other pelletized fertilisers.

3.2.5 Fish hydrolysates

Fish hydrolysates (also referred to as fish emulsions) are produced from the by-products of the seafood industry and are the result of breakdown of fish biomass in a liquid medium through hydrolysis or enzymatic catalysis. The resultant liquid is rich in nutrients, C, carbohydrates and lipids and is applied directly to soil or as a foliar spray, with potential benefits including enhanced plant germination, growth rate and disease resistance (Andarwulan and Shetty 1999; Abbasi et al. 2003; Horii et al. 2007).

3.2.6 Crop residue and 'green manure

The remaining of plant biomass following crop harvest is normally referred to as crop residue, while crops grown with the explicit purpose of cutting and then either leaving on the soil surface or incorporation into soil are termed 'green manure'. Thus, although green manures are often N-fixing crops (e.g. Mandal et al. 2003), these two organic soil amendments are essentially the same thing: undecomposed plant biomass left on top of, or incorporated into, soil. Effects of crop residue or green manure (hereafter both referred to as 'green manure') include increased soil organic C, improved moisture retention, increased soil biological activity and potentially increased soil nutrient levels (Fageria 2007). Many of these effects vary based on the green manure type and application rate (Astier et al. 2006).

3.2.7 Biochar

Biochar is a C-rich material formed via the pyrolysis of organic feed stocks (e.g. wood, peanut shell, manure) under temperatures ranging from 200-1200 ºC. In general, biochar is low in nutrients compared to other organic waste-derived soil amendments, and thus it is more accurately considered as a soil amendment as opposed to a fertiliser *per se*. The key properties of biochar are the large surface area (often with high chemical functionality) and aromatic and extremely porous chemical structures. These properties have stimulated research which has shown that, if applied judiciously, biochar can improve plant yield, expedite soil C sequestration, enhance soil nutrient retention, adsorb heavy metals and help to mitigate soil greenhouse gas emissions (Alburquerque et al. 2013; Esfandbod et al. 2017; Jeffery et al. 2017; Lan et al. 2017).

However, the properties of biochar can be extremely variable, and this likely contributes to the non-trivial degree of scepticism regarding the utility of biochar present in the scientific literature (Atkinson et al. 2010; Jeffery et al. 2017). Nevertheless, while various questions remain about the potential efficacy of biochar for certain purposes, the emerging consensus is that it has considerable potential as a soil amendment if careful consideration is given to the desired outcome and the properties of the biochar and soil—plant system. At present, biochar is not easily commercially available in Australia, due in part to the high cost of production and the residual uncertainty surrounding its benefits.

3.3 Current and emerging technologies for nutrient recovery and organic fertiliser production

There are a range of existing and emerging technologies available for the recovery of nutrients from organic and inorganic waste streams, and for the production of waste-derived fertilisers. Some of these technologies are associated with a specific waste stream or produce specific molecular species, and each is associated with various advantages and disadvantages. Figure 1.8 depicts a generic process flow of fertiliser or soil amendment production (through various technologies) from wastes. A range of current and emerging technologies are described and discussed in the following sections.

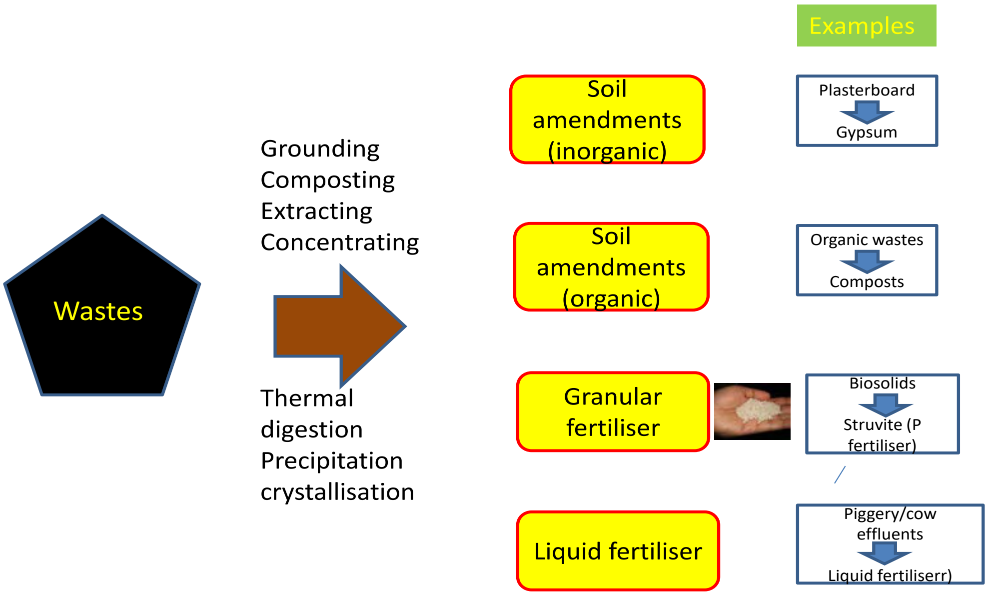


Figure 1.8. Potential technologies for conversion of inorganic and organic wastes into fertilisers and soil amendments.

Table 1. 6 summarises the different technologies associated with respective waste types, the chemical nature of fertilisers produced, the average rates of nutrient recovery from the technologies, and some of the issues associated with the technologies at present. However, in some cases, the method will depend on the nutrient of interest as well as the waste and the waste-derived product's intended use.

Table 1.16. Nutrient recovery or fertiliser manufacture from different sources through different technologies.

Group	Method of nutrient recovery	Product as Fertiliser	Issues and Nutrient Recovery
Watery phase: waste water (treated) or process water (e.g. sludge liquor)	Dissolution followed by precipitation Crystallization	Various, including struvite ($MgNH_4PO_4.6H_2O$) Crystal Green known as "slow release fertiliser"	> 85% of P and 40% of N can be recovered
Dewatered or dried sludge	Wet Chemical Crystallization Thermal digestion	P-loaded pellets reused in the fertiliser industry	30 % P can be recovered
	Wet Chemical	$AlPO_4$ and $Ca_3(PO_2)_2$	

Sewage sludge ash	Thermal digestion	$Ca_5(PO_4)_3Cl$, $Ca_4Mg_5(PO_4)_6$, and Ca $(PO_4)_3$ Cl	Significant reduction (< 90%) of Cd, Cu, Pb, and Zn
Human Urine	Precipitation by adding MgO or $MgCl_2$ at pH ≤ 9	Struvite ($MgNH_4PO_4.6H_2O$)	• P recovery rates: 90-98% • Low in heavy metals and micro-pollutants pollutants • Represents a valuable market fertiliser • Fertilising effect comparable to commercial fertilisers
Biosolid	Thickening: Low-force separation of water and solids by gravity, flotation or centrifugation	Different amount of nutrient - N, P, K, Ca etc.	• Increases solids content by removing water. • Lowers transportation costs
	Digestion (aerobic /anaerobic)		• Reduces biosolids quantity and lowers transportation costs. • Reduces pathogen levels and odours
	Heat drying		•Greatly reduces biosolids volume. • Destroys most pathogen
Manure	Slurry separation (Sedimentation, Centrifugation, Drainage, Pressurised filtration)	Liquid fraction: high N:P ratio, use on farm as N-source Solid fraction: low N:P ratio, transport to farms with low livestock density	•Change of plant nutrient/heavy metal ratio in the biomass (separation process) • pathogens • 60-90% P recovery
Meat and Bone meal	Thermal digestion	• Bone fraction: apatite • Meat fraction: organic P • Slow release fertiliser on acid soils (< pH 5.5)	• Poor agricultural performance • Increase P solubility (e.g. citric acid from 53% to 87%)
Any of the above materials, green waste, food waste, other municipal organic waste	Composting	Compost	• Lowers biological activity • Reduces pathogen loads • Less plant-available nitrogen than other types of biosolids • Increases transportation costs

3.3.1 Composting

Composting, the process by which organic materials are deliberately kept under particular conditions of temperature, moisture and aeration and left to decompose through biological processes, is an ancient practise (e.g. Semple 1928). Thus, there is a diverse range of composting techniques. In general, the initial materials for compost come from a variety of organic waste sources including manures, green waste, food scraps and in some cases animal biomass (i.e. carcasses). These materials are typically mixed in proportions that result in a specific stoichiometric composition (usually with a focus on C:N ratio) to optimise decomposition rates. Materials are then either covered or left uncovered to attain high temperatures to accelerate biological processes, aerated frequently by physical mixing to maintain aerobic conditions, and prevented from desiccation by periodic watering. After a period of weeks or months, the C- and nutrient-rich 'compost' is harvested and usually applied directly to soil.

Composting can occur on a range of scales, from individual gardens to industrial-scale, and this is one of the strengths of composting. Increasingly, industrial-scale composting is taking place in Australia, and there is tremendous potential for designing 'tailor-made' composts with highly targeted applications. These composts might come from a variety of organic (i.e. biosolids, manures, abattoir wastes, green waste) and inorganic (i.e. plasterboard, concrete dust) sources that are widely available in Australia. This potential is increasing as the understanding of the controlling factors of composting processes and compost properties continues to improve.

3.3.2 Dissolution and precipitation

The most common approach for recovery of nutrients (i.e. P) from sewage and manure sludge is the process of dissolution (via application of heat, acid or pressure) of the various forms of the nutrient (e.g. convert organic P forms into PO_4^{3-}) followed by precipitation (in some cases adsorption) of the solubilized nutrient (Sartorius et al. 2011). For example, soluble forms of P (i.e. PO_4^{3-}) can be precipitated with Ca, Mg or Al salts to form struvites, apatites or calcium and aluminium phosphates (De-Bashan and Bashan 2004; Cieslik and Konieczka 2017). This approach has several advantages, including the high quality of end products and their low heavy metal concentration for direct application to crops, and low solubility of most end products which limits potential nutrient pollution in runoff following their application (Cieslik and Konieczka 2017). However, this process is costly (e.g. Weigand et al. 2013), and recovery of P through this process is only around 40% (Cornel and Schaum 2009). The dissolution and precipitation process is also influenced by sludge pH, temperature, and nutrient content (Cieslik and Konieczka 2017).

It may be possible to significantly increase struvite-P recovery by increasing the Mg:P ratio of the sludge (De-Bashan and Bashan 2004). In section 2.3 it was shown that a considerable amount of Mg (as well as Ca) is 'wasted' by the construction and demolition industry during the disposal of plasterboard and concrete. Finding some synergy between the sewage sludge and the construction and demolition industry may thus have unrealised potential to improve P sustainability and economic outcomes from nutrient recovery efforts.

3.3.3 Crystallization

Crystallization is the process wherein the crystallisation of nutrient-containing minerals (such as apatites) is triggered by the addition of specially designed pellets (e.g. calcium-silicate-hydrates) to sludge reactors. This process results in 'P-loaded pellets' and struvites and would also recover up to 40% of N and 85% of P in solution (i.e. the Ostara Pearl^{TM} process). Crystallization has most often been used for nutrient recovery from sewage sludge and urine (Schick et al. 2013).

3.3.4 Slurry separation

Nutrients are typically recovered from manures through a series of physical methods called slurry separation, wherein the solid and liquid fractions are separated and used according to their disparate properties. Slurry separation consists of initial sedimentation (settling of particles), centrifugation, drainage and finally pressurised filtration. The resulting liquid and solid fractions have high and low N:P ratios, respectively (Hjorth et al. 2010; Schick et al. 2013).

3.3.5 Ashing and thermal digestion

The process of thermal digestion may be applied to meat and bone meal and sewage sludge ash. Thermal digestion occurs after meat and bone meal or sewage sludge, biosolids or other mineral nutrient rich materials are converted to ash via combustion in high temperature rotary kilns (e.g. Staroń et al. 2017). Ashes can be applied directly as fertilisers, but may also be digested at high temperature (for example, at 1600 °C in liquid converter slag from steel processing) to enhance various properties relevant to their efficacy as fertilisers (i.e. P solubility; Schick et al. 2013).

3.3.6 Biological (i.e. microbial) digestion

Biological aspects of sewage processes have generally been focused on nutrient removal (from a contamination perspective) rather than recovery. Recently the research focus has shifted to incorporate nutrient recovery to a greater extent. For example, in the face of impending P scarcity, polyphosphate accumulating bacteria (genus *Acinetobacter*, *Microlunatus phosphovorus*, *Accumulibacter phosphatis*, and others) may be particularly useful (Kortstee et al. 1994; Tarayre et al. 2016). Polyphosphates accumulated in these organisms can be extracted from wastes and subsequently converted into P fertilisers (Tarayre et al. 2016). These technologies have the added potential benefit of using the energy (i.e. organic C) in wastes to power the process of nutrient recovery (Chen et al. 2015).

3.3.7 Production of nanofertilisers

The application of nanotechnology to the production of agricultural fertilisers has been proposed as a potential solution to the impending crisis of increasing global food demand in conjunction with decreasing soil health and diminish mineral nutrient (i.e. P) supply (Chhipa 2017a). Nanomaterials in general are materials which are between 1 and 100 nm in size in one or more dimensions, and nanofertilisers (NFs) specifically can be considered as any nanomaterial which supply nutrients to plants or improve crop performance (Liu and Lal 2015). Application of NFs improve yield metrics in various crops (Liu and Lal 2015 and references therein; Jyothi and Hebsur 2017 and references therein).

Macro-nutrient NFs (i.e. those that contain N, P, K, Ca or Mg) include urea-coated zeolite chips, urea-modified hydroxyapatites, apatites, calcites, and various commercial NFs (Delfani et al. 2014; Liu and Lal 2014, 2015; Chhipa 2017b), and have frequently been shown to improve plant performance (Liu and Lal 2015). According to Chhipa (2017b), one of the key strengths of macro-nutrient NFs relative to conventional fertilisers is their low surface area to volume ratio, which leads to their greater efficiency of use by plants. Micro-nutrient NFs are able to supply plants with Mn (via metallic Mn), Fe (via superparamagnetic iron oxides, Fe_3O_4, and other Fe-NPs), Zn (via ZnO), B , Cu (via Cu_2O), Mo (as synthetic Mo nanoparticle NP; Taran et al. 2014) and other micro-nutrients.

The most critical problem of the development of nanoagrochemicals (i.e. NFs and nanopesticides) is the potential for environmental contamination by nanoparticles, and the uncertainty over their safety to environmental, ecological and human health (Kah 2015). For instance, while the small size of NFs convey many of their beneficial characteristics, it can also make them difficult to control as pollutants and may even convey upon them unique properties of toxicity (Seaton et al. 2010). Even so, nanotechnology is likely to remain an important area of research and development for efficient nutrient delivery to plants in agricultural contexts (Singh et al. 2017; Qureshi et al. 2018). Thus, with further research to improve understandings of their respective risks and advantages, there will tremendous potential to combine this novel nanotechnology with the old idea of recycling nutrients from organic ‘waste’ materials.

3.4 Key challenges for use of recycled organic wastes

The use of recycled organic (and potentially inorganic) waste products as fertilisers and soil amendments is made difficult relative to synthetic fertilisers by numerous factors. These factors are largely driven by the biological origin of the organic material and their heterogeneity in space and time. Some of the major challenges include the following:

- **There is a large degree of variability in the chemical characteristics of wastes and waste-derived products** (particularly pH, EC, and C and nutrient content and availability). This problem is evident in many scientific studies with repeated application of the ‘same’ product (e.g. Hargreaves et al. 2009), and would make it technologically difficult, as well as economically unviable, to produce new fertilisers. Section 4 of this report reveals the high degree of variation in the chemical properties of several manures, composts, biosolid sludges and green manures, but also identifies some consistent differences in chemical properties between these products. Further research is needed to understand how wastes can be manipulated or combined to have consistent chemical properties, or to have chemical properties appropriate for a specific, targeted purpose. Similarly, different soils and crop types might vary widely in their appropriateness for or response to, respectively, addition of waste-derived fertilisers or amendments.

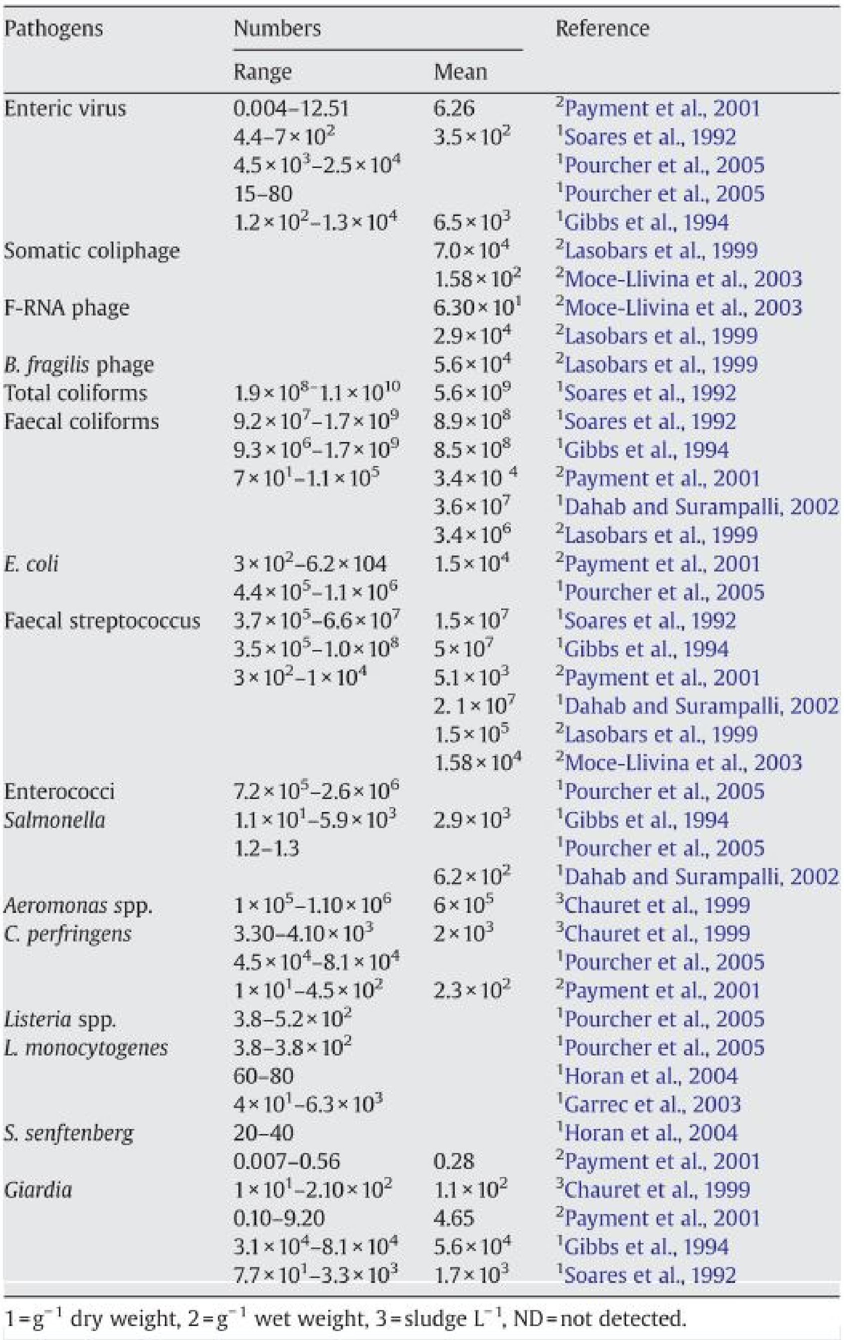
- **Organic waste-derived products engender numerous contamination risks.** The types of contaminants vary between the feedstock and production techniques, and may threaten human health or the health of surrounding ecosystems. Some of the main contamination threats include the following:
    - **Heavy metals**, such as cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), copper (Cu), arsenic (As), and zinc (Zn) can be found in high or harmful amounts in certain organic wastes and waste-derived fertilisers, particularly biosolids, manures, and composts derived thereof (Zhang et al. 2000; Garrido et al. 2005; Petersen et al. 2007). Thus, in many cases the application of organic waste-derived fertilisers can increase available and total levels of heavy metals in soil. In some cases, these increases are reflected in plant tissues (Singh and Agrawal 2010), although this effect varies considerably between studies (Chu and Wong 1987; Zhang et al. 2000; Garrido et al. 2005). Table 1.17 provides several examples of the total concentrations of heavy metals in biosolids, composts, and manures reported in the literature. Interestingly, there may be scope to combine different forms of organic waste-derived products to help mitigate the heavy metal hazard. For instance, biochar may reduce heavy metal availability in biosolid or manure-amended soils, given that biochar cab adsorb some metals, including Ni and Cu (Esfandbod et al. 2017).

Table 1.17. Examples of total heavy metal contents of organic waste-derived fertilisers and soil amendments.

Reference	Fertiliser or amendment	Total metal concentration (ppm)							
		As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Chu and Wong (1987)	Biosolids	-	18.3	-	511	101	-	-	2530
Garrido et al. (2005)	Biosolids	-	3.75	49.2	49.2	-	38.1	-	583.3
Latare et al. (2014)	Biosolids	-	32.3	44.3	186	28.5	54.7	-	161
Singh & Agrawal (2010)	Biosolids	-	154.5	35.5	317.7	186.2	77.2	60	785.3
Evanylo et al. (2005)	Composted biosolids	-	3	-	294	455	73	159	562
Garrido et al. (2005)	Composted biosolids	-	3.5	31	148.1	-	33.7	-	66.2
Chu and Wong (1987)	Composted MSW	-	14.3	-	473	702	-	-	1460
Zhang et al. (2000)	Composted MSW	8	4	261	201	-	67	94	518
Tucker, et al. (2015)	Cow manure	-	-	-	43.8	-	-	-	280
Gunes et al. (2014)	Poultry litter	-	-	-	510	572	-	-	457
Nicholas, et al. (2017)	Poultry litter QLD	13.8	0.2	7.1	139.5	-	5.6	2	479.3
	Poultry litter NSW	10.3	0.1	6.4	107	-	7.3	1.7	495.8
	Poultry litter VIC	11.6	0.1	14.2	94	-	10	3.5	488.8

- **Microbial pathogens** are another widely acknowledged contaminant of biosolids and manures. These pathogens can have environmental impacts (Pell 1997a), but may also have severely adverse impacts for human health if they enter the food supply, including death (Akerman 2018). Biosolids in particular are known to harbour a diverse range of potential human pathogens (Bibby et al. 2010a). Some of the main pathogens in biosolids include *Clostridium*, *Mycobacterium*, *Escherichia coli*, *Salmonella* spp., *Listeria* spp., faecal streptococcus, and a range of viruses (e.g. enteric viruses, somatic coliphages and, F-RNA-phages; Sidhu & Toze 2009; Bibby et al. 2010). Sidhu and Toze (2009) conducted a comprehensive review of apparent pathogen levels in biosolids, and their findings are reproduced in this report (Table 1.18). Pathogen community composition and abundance appears to vary based on treatment (i.e. digestion method) of biosolids (Bibby et al. 2010b). Manures can also carry pathogenic micro-organisms, including various viruses, bacteria (e.g. *Salmonella* spp., *E. coli*, and *Listeria* spp.), and protozoans such as *Giardia* spp. (Mawdsley et al. 1995; Petersen et al. 2007). Swine, poultry and cattle manures may differ in terms of pathogen community composition and abundance. For instance, *Campylobacter jejuni* and *Yersinia enterocolitica* are thought to be more prevalent in swine and poultry litter than in cattle manure (Pell 1997b). The levels of pathogens in biosolids and manures can reportedly be reduced through various treatment methods, including composting, digestion, heat treatment and gamma irradiation, though these methods vary in their effectiveness for different pathogen types (Monteith et al. 1986; Fatunla et al. 2017). Importantly, however, composts may also contain potentially-harmful levels of pathogens and this likely varies based on compost feedstock. It has also been noted that some manures and composts have the potential to carry and spread the seeds of invasive plant species (Quilty and Cattle 2011).

Table 1.18. Table 1 of Sidzu and Toze (2009) summarising the levels of a variety of biosolid-borne pathogens reported in the literature.



Pathogens	Numbers		Reference
	Range	Mean	
Enteric virus	$0.004–12.51$	6.26	[2]Payment et al., 2001
	$4.4–7 \times 10^2$	3.5×10^2	[1]Soares et al., 1992
	$4.5 \times 10^3–2.5 \times 10^4$		[1]Pourcher et al., 2005
	$15–80$		[1]Pourcher et al., 2005
	$1.2 \times 10^2–1.3 \times 10^4$	6.5×10^3	[1]Gibbs et al., 1994
Somatic coliphage		7.0×10^4	[2]Lasobars et al., 1999
		1.58×10^2	[2]Moce-Llivina et al., 2003
F-RNA phage		6.30×10^1	[2]Moce-Llivina et al., 2003
		2.9×10^4	[2]Lasobars et al., 1999
B. fragilis phage		5.6×10^4	[2]Lasobars et al., 1999
Total coliforms	$1.9 \times 10^{8-}1.1 \times 10^{10}$	5.6×10^9	[1]Soares et al., 1992
Faecal coliforms	$9.2 \times 10^7–1.7 \times 10^9$	8.9×10^8	[1]Soares et al., 1992
	$9.3 \times 10^6–1.7 \times 10^9$	8.5×10^8	[1]Gibbs et al., 1994
	$7 \times 10^1–1.1 \times 10^5$	$3.4 \times 10^{\ 4}$	[2]Payment et al., 2001
		3.6×10^7	[1]Dahab and Surampalli, 2002
		3.4×10^6	[2]Lasobars et al., 1999
E. coli	$3 \times 10^2–6.2 \times 104$	1.5×10^4	[2]Payment et al., 2001
	$4.4 \times 10^5–1.1 \times 10^6$		[1]Pourcher et al., 2005
Faecal streptococcus	$3.7 \times 10^5–6.6 \times 10^7$	1.5×10^7	[1]Soares et al., 1992
	$3.5 \times 10^5–1.0 \times 10^8$	5×10^7	[1]Gibbs et al., 1994
	$3 \times 10^2–1 \times 10^4$	5.1×10^3	[2]Payment et al., 2001
		$2.\ 1 \times 10^7$	[1]Dahab and Surampalli, 2002
		1.5×10^5	[2]Lasobars et al., 1999
		1.58×10^4	[2]Moce-Llivina et al., 2003
Enterococci	$7.2 \times 10^5–2.6 \times 10^6$		[1]Pourcher et al., 2005
Salmonella	$1.1 \times 10^1–5.9 \times 10^3$	2.9×10^3	[1]Gibbs et al., 1994
	$1.2–1.3$		[1]Pourcher et al., 2005
		6.2×10^2	[1]Dahab and Surampalli, 2002
Aeromonas spp.	$1 \times 10^5–1.10 \times 10^6$	6×10^5	[3]Chauret et al., 1999
C. perfringens	$3.30–4.10 \times 10^3$	2×10^3	[3]Chauret et al., 1999
	$4.5 \times 10^4–8.1 \times 10^4$		[1]Pourcher et al., 2005
	$1 \times 10^1–4.5 \times 10^2$	2.3×10^2	[2]Payment et al., 2001
Listeria spp.	$3.8–5.2 \times 10^2$		[1]Pourcher et al., 2005
L. monocytogenes	$3.8–3.8 \times 10^2$		[1]Pourcher et al., 2005
	$60–80$		[1]Horan et al., 2004
	$4 \times 10^1–6.3 \times 10^3$		[1]Garrec et al., 2003
S. senftenberg	$20–40$		[1]Horan et al., 2004
	$0.007–0.56$	0.28	[2]Payment et al., 2001
Giardia	$1 \times 10^1–2.10 \times 10^2$	1.1×10^2	[3]Chauret et al., 1999
	$0.10–9.20$	4.65	[2]Payment et al., 2001
	$3.1 \times 10^4–8.1 \times 10^4$	5.6×10^4	[1]Gibbs et al., 1994
	$7.7 \times 10^1–3.3 \times 10^3$	1.7×10^3	[1]Soares et al., 1992

$1 = g^{-1}$ dry weight, $2 = g^{-1}$ wet weight, $3 =$ sludge L^{-1}, ND = not detected.

    - **Pharmaceuticals and toxic organic compounds** are predominantly found in the human waste stream (particularly sewage) and could seriously inhibit its adoption as an organic fertiliser or soil amendment for use on food crops (Mailler et al. 2014; Urbaniak et al. 2017). Jelic et al. (2011) found that sewage sludge (and waste water influents and effluents) consistently contained detectable levels of numerous pharmaceuticals, including Diclofenac, Mefenamic acid, Bezafibrate, Atorvastatin, Diazepam, Lorazepam, Carbamazepine, Furosemide and Hydrochlorthiazide. Further, ZnO and TiO_2 nanoparticles and various polycyclic aromatic hydrocarbons including naphthalene, Benz[a]anthracene, Benzo[b]fluoranthene, Benzo[a]pyrene, and Indeno[1,2,3-cd]pyrene (all of which are considered carcinogenic; Agency for Toxic Substances and Disease Registry 2008) have been detected in sewage sludge (e.g. Oleszczuk 2006; Jośko & Oleszczuk 2013). Finally, Urbaniak et al. (2017) point out that numerous studies have detected polychlorinated dioxins and dibenzofurans, both of which are considered extremely toxic carcinogens and mutagens, in sewage sludge and sludge amended soils (e.g. Molina et al. 2000; Gworek et al. 2013).

- **The production and use of waste-derived fertilisers face numerous logistical issues.** Suitable locations are needed for processing the important and beneficial waste resource. Moreover, facilities must be located with consideration to waste sources as well as end user markets to reduce freight costs and improve economic outcomes.

- **There are competing uses for waste materials and uncertainty over how to optimize waste attributes.** The currently poor characterisation of organic wastes in terms of chemistry and energy density makes it difficult to effectively allocate optimal uses for different waste products. Use of certain nutrient-rich organic waste materials, such as poultry litter, for the generation of energy may compete with nutrient recovery or fertiliser production efforts (RIRDC 2013b). Similarly, it is unclear which wastes are best suited for which purpose out of nutrient recovery and fertiliser (or soil amendment) production, and which crop types will benefit most from which wastes or waste-derived fertilisers.

- **Farmer's understandings and perceptions of organic waste-derived products needs to be improved.** In particular, improving farmer's understandings of soil health as it relates to the role of soil C and soil biota in improving crop yield is critical to establishing sustainable demand for recycled organic products.

- **Without financial viability for end-users, successful adoption of organic waste-derived fertilisers is near to impossible.** Thus, organic waste-derived products will need to cost the same or less than conventional, readily available synthetic fertilisers, and will need to deliver the same if not greater crop yields. This will require significant research efforts to determine which wastes are generated where, what products can be produced from the waste, and which crops are suitable for application of each specific product. Similarly, contamination risks will need to be clearly reduced to levels comparable with synthetic fertilisers to safeguard consumer market confidence in crops grown with waste-derived fertilisers.

Finally, Quilty and Cattle (2011) recognised that an absence of impartial research is a major impediment to uptake of organic waste-derived fertiliser and soil amendments by farmers and land managers. Thus, further research is warranted into this socially- and environmentally-important area.

3.5 Critical research gaps related to recycling of wastes

Some of the critical research gaps in the field of recycling waste for the purposes of nutrient recovery and production of soil fertilisers and amendments include, but are not limited to, the following:

- There is currently limited information on the nutrient content and availability in a variety of inorganic and organic wastes. Moreover, although many waste materials and associated contaminants are highly heterogeneous in nature, there is little understanding of the degree of variability in the chemical, biological and contaminant properties of wastes and waste-derived products.
- Novel and cost-effective technologies (i.e. efficient extraction techniques, nanotechnologies and high efficient composting protocols) will need to be developed to optimise the quality and economic viability of new waste-derived fertilisers and soil amendment products.
- Economic and environmental analyses will be required to assess the viability, technical challenges and environmental risks (including EPA requirements) posed by the recovery and utilisation of nutrients from the inorganic and organic waste streams.
- The specific uses of the various inorganic and organic wastes will need to be optimised in terms of application to particular crops, soil types and geographic regions in order to achieve both productivity and economic benefits.
- It will be critical to identify any potential impediments to (a) the development and manufacturing of the new fertiliser products by the relevant industries, (b) the adoption of waste-derived fertilisers by farmers, and (c) the acceptance of foods grown using waste-derived fertilisers by consumers.

4. Properties of recycled organics and their effectiveness as crop fertilisers: a global-scale meta-analysis

4.1 Introduction

The value of organic waste products (e.g. manure and compost) as fertilisers has long been recognised, and organic fertilisers are used globally to enhance crop yield and remediate soils. While the effect of organic waste fertilisers (hereafter organic fertilisers) on crop yield and plant productivity is typically positive, this is not always the case (e.g. Daniels et al. 2001; Dikinya and Mufwanzala 2010), and it is still unclear which factors drive the positive or negative impact of organic fertilisers on crops. Moreover, while organic fertilisers generally have lower nutrient content than synthetic chemical fertilisers, the higher organic C content of organic fertilisers is thought to improve soil structure (e.g. Agbede et al. 2008), and likely promotes soil microbial activity and microbially-driven nutrient cycling in soil (Senesi 1989; Mandal et al. 2007). Thus, it is unclear whether the positive effects of organic fertilisers on crop yield are enough to make organic fertilisers an economically viable alternative to mineral fertilisers.

A meta-analytical approach will improve the understanding of the properties of organic waste products and fertilisers and their effects on crop yield while comparing them to mineral fertilisers in the same cropping system. To our knowledge, no such meta-analysis has been conducted in previous studies. Thus, a global-scale meta-analysis was performed to address the three following questions: (1) what are the chemical properties of the main types of organic fertilisers in the scientific literature, and how do the different types vary in the chemical properties; (2) how do the main types of organic fertilisers affect the yield of crops; and (3) what factors influence variation in this effect (i.e. crop or fertiliser type, soil or fertiliser properties).

To properly interpret the potential of organic waste products for nutrient recovery and fertiliser production, it is critical to consider the downsides or challenges posed by organic wastes. Contaminants such as heavy metals, pathogenic micro-organisms, organic pollutants, antibiotics, pharmaceuticals, prions, PFAS, PFOS, etc., are important aspects of these challenges. However, the variety of wastes and contaminant types and the fragmented nature of the scientific literature on this topic mean that formal meta-analysis is not ideal for investigating contaminants in organic wastes. Thus, contamination risks have been considered in detail in the previous section (2.2.1), but are discussed in conjunction with the meta-analysis results below where relevant (Section 2.2.3).

4.2 Meta-analysis methods

To perform the meta-analysis, the following terms were searched in Google Scholar on 26th of April 2018:

1. organic waste AND crop yield OR crop productivity
2. cattle manure OR dairy manure OR cow manure AND crop yield OR crop productivity
3. poultry manure OR poultry litter OR chicken manure OR chicken litter AND crop yield OR crop productivity
4. piggery OR swine AND effluent OR sludge OR manure OR litter AND crop yield OR crop productivity
5. abattoir waste AND crop yield OR crop productivity
6. compost AND crop yield OR crop productivity
7. biosolids OR sewage AND crop yield OR crop productivity
8. green manure OR crop residue AND crop yield OR crop productivity

Given the specificity of these search terms (i.e. a specific search for each organic fertiliser type), we conducted a truncated search where only the first 100 search results for each search term were considered for the meta-analysis. This process yielded 253 studies, which were then filtered based on the criterion of (a) applying organic fertilisers or amendments to plants and (b) reporting data on yield relative to an unamended control plot. Because of the Australian focus of this study, we carried out additional searches for studies that were carried out in Australia and included these in the data set. The result of this process was 990 observations of crop yield response to organic fertiliser addition (or comparable addition of mineral fertiliser) coming from 104 studies. These studies were carried out in Australia, the Americas, Africa, Europe, and Asia.

Data on crop yield[1] in response to organic fertiliser addition, soil properties and key chemical properties of the organic fertilisers were extracted from studies. The standardised effect of organic fertiliser addition on yield was calculated as a response ratio (RR; Rosenberg et al. 1999; Harrison 2011; Butler et al. 2018):

$$RR = {}^{\bar{X}_{t_i}}\Big/_{\bar{X}_{c_i}}$$

where $\bar{X}_{t_i}$ = the mean reported yield for the organically-fertilized ‘treatment’ for the i^{th} observation and $\bar{X}_{c_i}$= the mean reported yield for the unfertilized ‘control’ for the i^{th} observation. Response ratios were log transformed and a mean response ratio was calculated using MetaWin 2.1 software (Rosenberg et al. 1999). Confidence intervals (95%) were calculated around mean RR using a bootstrapping procedure with 999 iterations in MetaWin. Observations were weighted during bootstrapping based on the reported level of replication in the original study according to the formula:

$W_{R_i} = (n_{b_i} \times n_{c_i}) / (n_{b_i} + n_{c_i})$

where W_{R_i} = a replicate weighting factor for the i^{th} observation, n_{t_i} = the number of replicates for organically amended ‘treatment’ for the i^{th} observation and n_{c_i} = the number of replicates for the control for the i^{th} observation. Mean RRs and CIs are reported on a percentage basis, and where CIs overlap with zero the effect was not considered significant. The effects of categorical variables (crop type and organic fertiliser type) were analysed by comparing $Q_{between}$ values to a χ^2-distribution following (Rosenberg et al. 1999). The linear relationships between RRs and select soil and organic fertiliser properties were analysed with a weighted least-squares regression in MetaWin.

The main crop types were wheat, rice, maize, ‘other grains’ (including barley, oats and rapeseed), soybean, ‘other legumes’, leafy greens, brassicas, fruit, roots / tubers / bulbs, forage crops and ‘other’. The main organic fertiliser types were biosolids, cattle manure, poultry litter, piggery waste, green manure, ‘other’ manure (including horse, sheep or mixtures of manure), composted manure, and compost. We also collected observations on the response of yield to addition of mineral fertiliser, to compare the effects of organic and mineral fertilisers. Here, only the largest dose of mineral fertiliser was used, as was compared against the same control as were the respective organic fertilisers.

4.3 Results and discussion

4.3.1 Key chemical properties of organic fertilisers

The meta-analysis indicated that the different forms of fertilisers that were derived from organic waste streams are nutrient-rich and vary somewhat in the chemical and stoichiometric properties. Figure 1.9 summarises the reported values of pH, electrical conductivity (EC), total C, N and P and available P values for biosolids, cattle manure, compost, composted manure, green manure, ‘other’ manure, piggery waste and poultry litter.

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[1] Where possible, yield was based on the economically-relevant component of the crop, rather than total productivity of the crop plant. For example, wheat yields were based on grain yield rather than total biomass of wheat plants. Where multiple values of yield were reported for a given crop over time, the average yield across the time period was used, unless several different crops were grown in rotation.

Values of pH are fairly even among the fertiliser types, ranging between 6 and 9, although biosolids display the highest degree of variability and can have pH values as high as 10.6. Electrical conductivities tend to be lower for compost but otherwise range between 0.5 to 19.7 dS m^{-1}. Manures (including biosolids) tended to have higher EC values and composting appeared to reduce EC values for manure.

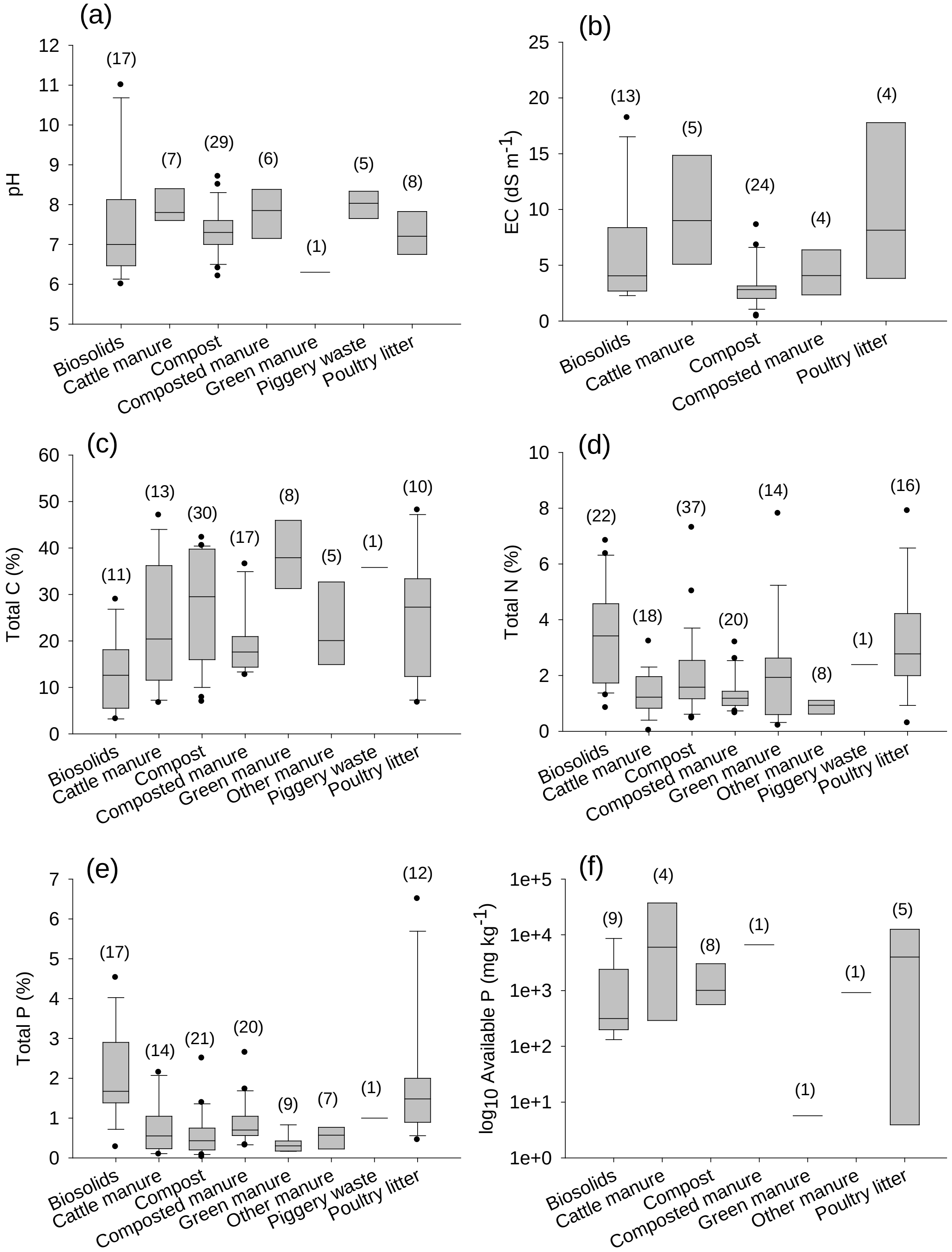

Figure 1.9. Box-and-whisker plots of the key chemical properties of eight types of organic fertilisers derived from the organic waste stream. The number of observations is shown in ellipses above plots for each fertiliser type.

Total C content averaged 24.1% across all waste types, but was typically highest for green manure (mean = 35.5%), and tended to vary greatly in all manures (including biosolids). On the other hand, total N content varied more widely, but also tended to be higher, in biosolids and poultry litter than in other organic fertiliser types. Total N content averaged 2.12% across all fertiliser types, but values as high as 6.83% and 4.69% were reported for biosolids and poultry litter, respectively. Average values of total N content were 3.41% for biosolids, 1.34% for cattle manure, 2.00% for compost, 1.31% for composted manure, 2.04% for green manure, 0.88% for other manure, 2.39% for piggery waste and 3.15% for poultry litter.

A similar pattern was evident for total P content, which averaged 1.05% across all studies and tended to be higher and more varied in biosolids and poultry litter than in other fertiliser types. Total P values reached a maximum of 4.52% in biosolids and 2.06% in poultry litter. Average values of total P content were 2.09% for biosolids, 0.74% for cattle manure, 0.57% for compost, 0.85% for composted manure, 0.34% for green manure, 0.51% for ‘other’ manure, 1.00% for piggery waste and 1.94% for poultry litter. Available P levels were extremely varied and thus presented on a $\log_{10}$ scale. Values of available P in organic fertilisers were lowest for green manure at 5.68 ppm, although there was only one observation. Variation in available P levels was greatest in poultry litter, with reported values ranging between 3 to 14,667 ppm (mean = 5833 ppm). On average, biosolids had 1699 ppm available P, cattle manure 14,513 ppm available P, compost 1745 ppm available P, composted manure 6633 ppm available P and other manure 920 ppm available P.

Biosolids and poultry litter tended to have the lowest C:N ratio values (Fig. 1.10a). These were more constrained than most other fertiliser types, with C:N ratios ranging between 1.89 to 8.81 (mean = 5.09) in biosolids and 0.85 to 13 (mean = 7.27) in poultry litter. The C:N ratios reported for cattle manure, compost and green manure varied widely, ranging between 9.0 to 46.2 (mean= 5.09), 0.94 to 36.5 (mean = 15.6) and 0.88 to 48.4 (mean = 7.27), respectively. The average C:N ratio of composted manure was 15.8 and for ‘other’ manure and piggery wastes the mean C:N ratios were 23.3 and 13.2, respectively. A similar pattern occurred for C:P ratios (Fig. 1.10b), with biosolids and poultry litter, but also composted manure, ‘other’ manure and piggery waste generally having C:P ratios < 50. On average, values of C:P ratio were 8.74 for biosolids, 27.4 for composted manure, 26.0 for ‘other’ manure, 36.8 for piggery waste and 17.8 for poultry litter. Values of C:P ratio ranged more than 15-fold in cattle manure (minimum value = 16.45, maximum value = 253.8; mean = 86.8), and also varied widely in compost and green manure, which had C:P ratio values ranging from 14.7 to 139.1 (mean = 62.3) and 57.2 to 242.9 (mean = 123.8), respectively. Interestingly, N:P ratios tended to be similar between the organic fertiliser types (Fig. 1.10c), averaging of 4.75 overall, and with 85% of values falling between 1 and 15. However, values as high as 52.0 and 27.7 were reported for biosolids and piggery waste respectively, with these two fertiliser types also having a greater degree of variability than other types. Average values of N:P ratio were 7.09 for biosolids, 3.19 for cattle manure, 5.36 for compost, 1.79 for composted manure, 6.89 for green manure, 2.19 for ‘other’ manure, 10.14 for piggery waste and 2.43 for poultry litter. The tendency for low N:P ratios in composed materials likely reflects losses of volatilized N during the composting process, which suggests that compost may be particularly effective for P-intensive and N-fixing crops.

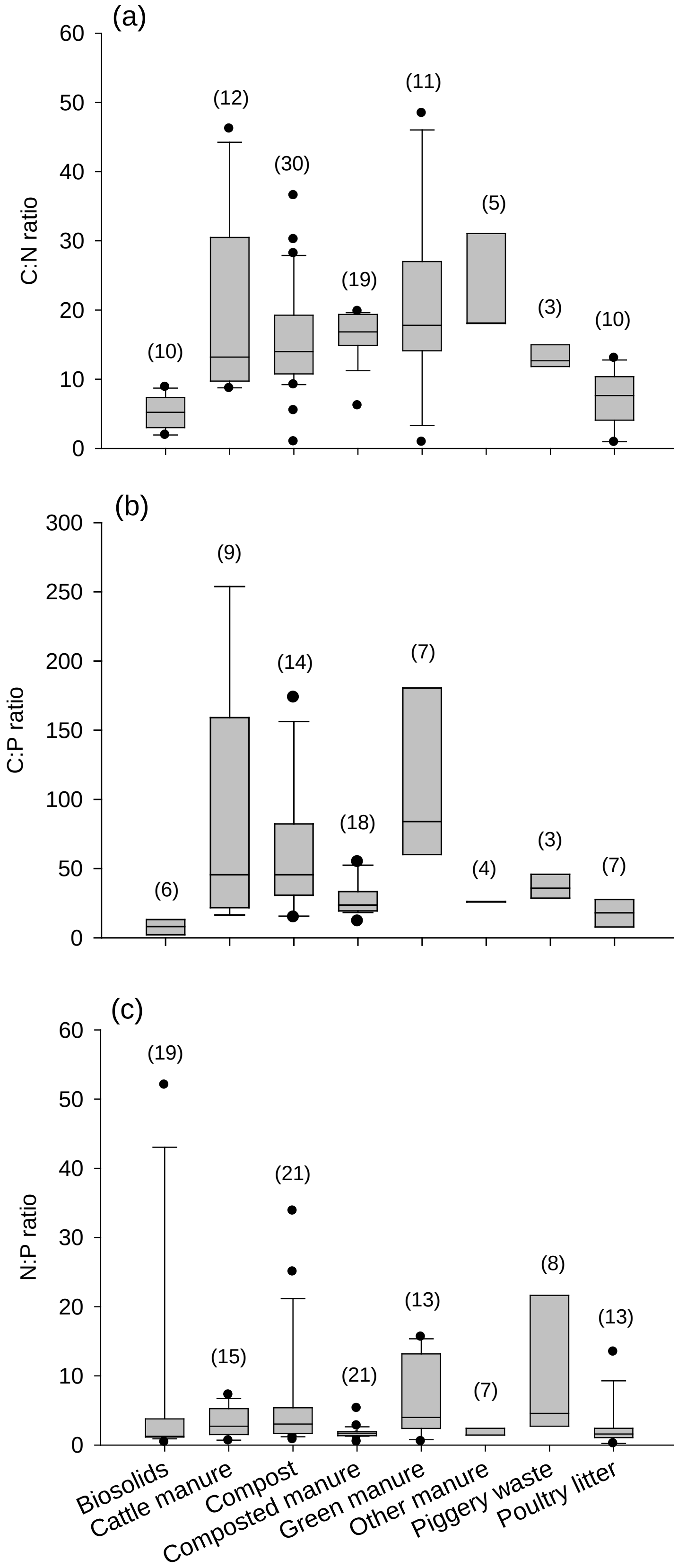

Figure 1.10. Box-and-whisker plots of C:N:P stoichiometric ratios of eight types of organic fertilisers derived from the organic waste stream. The number of observations is shown in ellipses above plots for each fertiliser type.

4.3.2 Effectiveness of organic fertilisers for increasing crop yield

Meta-analysis confirmed that addition of organic fertilisers that were derived from organic waste streams has a consistently positive effect on the 'economically-relevant' yield of food and fibre crops, with the overall mean RR averaging 47.85%, and with 95% bootstrapped CIs ranging from 40.2 to 55.3% (Fig. 11.1). A significant amount of heterogeneity in the dataset was explained by crop type and organic fertiliser type (*P*-values < 0.05).

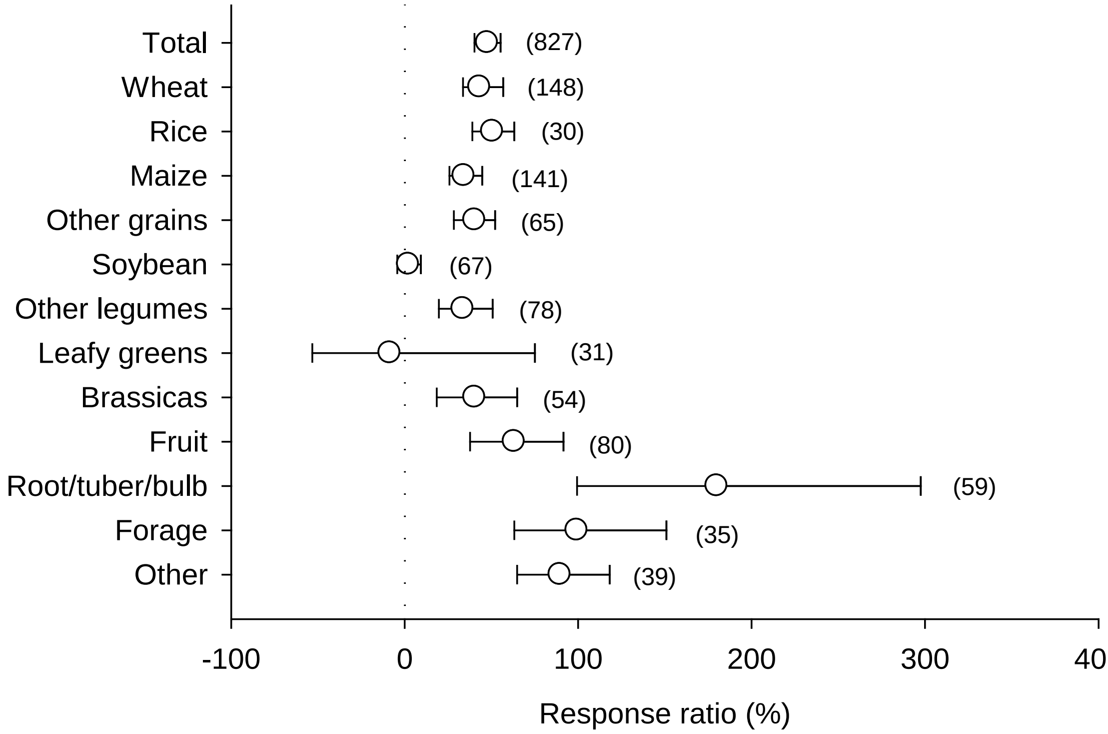

Figure 1.11. Mean response ratios (±95% bootstrapped confidence intervals; CIs) of the effects of organic fertilisers on crop yield (relative to unfertilized controls). The number of observations is shown in ellipses for each category; where CIs do not overlap zero the effect may be considered significant.

The effect of organic fertiliser was similar between grain crops (including maize), and these effects were of similar magnitude to the overall effect size (Fig. 1.12). The effect of organic fertiliser was particularly large for below-ground crops (i.e. root, tuber or bulb crops), for which the RR CIs ranged from 99.4 to 297% (mean = 180%). In contrast, the effects of organic fertilisers on soybean and leafy green crops were not significantly different from zero.

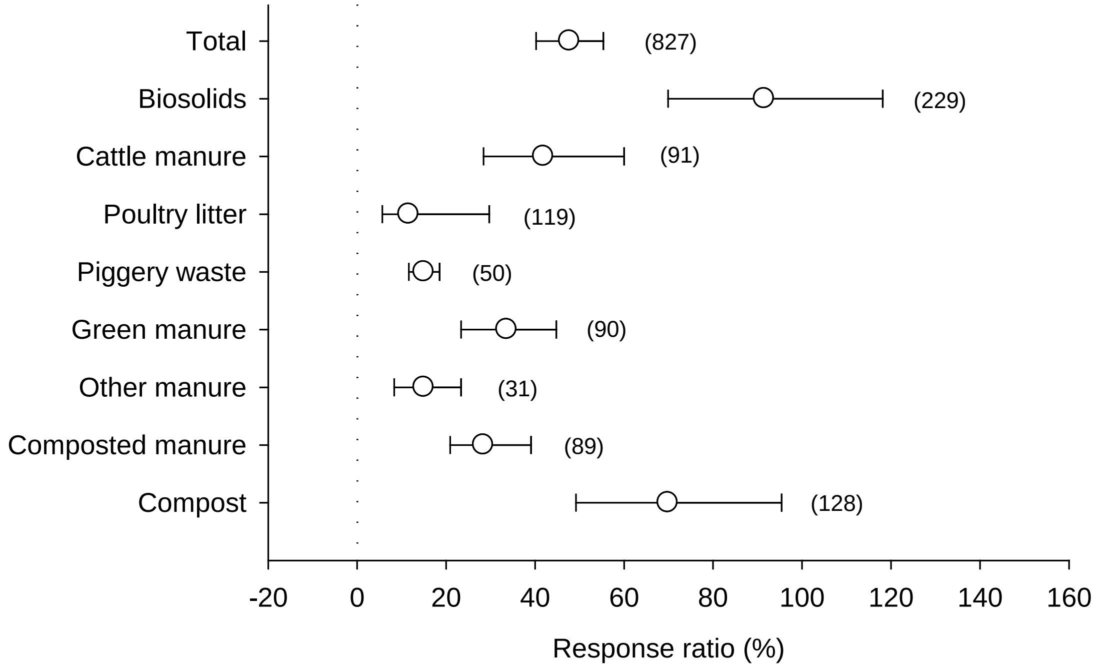

Figure 1.12. Mean response ratios (±95% bootstrapped confidence intervals; CIs) of the effects of organic fertilisers on crop yield (relative to unfertilized controls) for the different organic fertiliser types. The number of observations is shown in ellipses for each category; where CIs do not overlap zero the effect may be considered significant.

Of the eight main types of organic fertilisers used in the meta-analysis, biosolids and compost had particularly marked positive effects on crop yield (Fig. 1.12). Biosolids, with RR CIs ranging from 69.9—118.1% (mean RR = 91.6%), had a significantly greater effect on yield than all fertilisers except for compost, which had RR CIs ranging from 49.2—95.4% (mean = 69.9%). Moreover, compost had a greater effect than all organic fertilisers except for cattle manure. Of the remaining fertiliser types, piggery waste tended to have a weaker positive effect on yield than cattle manure, green manure and composted manure, but all fertilisers had significantly positive RRs.

When only the pool of studies that also reported yield responses to mineral fertilisation (in addition to that which was applied as basal fertilisation in all plots including the controls) was analysed, organic fertiliser type still explained a significant amount of heterogeneity within the dataset (Fig. 13). Importantly, this meta-analysis indicates that the mean RR for mineral fertiliser (mean RR = 50.6%, with bootstrapped CIs ranging from 34.0—69.9%) is not significantly greater than that of organic fertilisers overall (mean RR = 58.5%, with bootstrapped CIs ranging from 47.4—70.6%; Fig. 13). However, mineral fertilisers appeared to have a significantly greater positive effect on crop yield than do poultry litter, piggery waste, and ‘other’ manures, but not biosolids, cattle manure, green manure, composted manure or compost. It is also noted that the response of yield to poultry litter addition was not significantly different from zero in this pool of observations (Fig. 1.13).

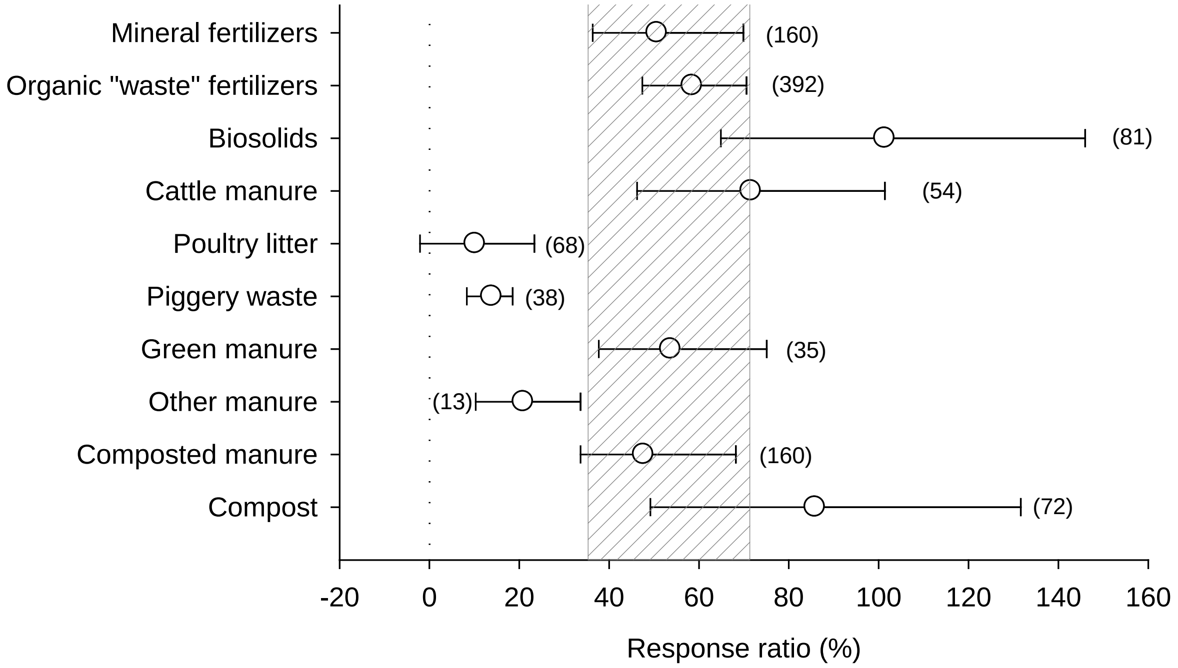

Figure 1.13. Mean response ratios (±95% bootstrapped confidence intervals; CIs) of the effects of organic fertilisers and mineral fertiliser on crop yield (relative to unfertilized controls). The number of observations is shown in ellipses for each category; where CIs do not overlap zero the effect may be considered significant; where organic fertiliser CIs do not overlap the striped area their effect may be considered significantly different from that of mineral fertiliser addition.

Finally, there were several significant linear relationships between RRs and the properties of soil and organic wastes (Table 1.19). In particular, RRs were inversely related to soil total C content and C:N ratios, and soil available P, which indicates that the positive effect of organic fertilisers tend to be greatest in low-fertility soils. At the same time, RRs were inversely related to the EC, total C content, and C:N and C:P ratios of the organic fertilisers, and were positively related to the available P concentration of organic fertilisers.

Table 1.19. **Results of continuous meta-analyses based on least-squares regression of response ratios and properties of soil and organic fertilisers; where Pr(norm) < 0.05 the linear relationship was significant.**

	Slope	Pr(norm)	Intercept	N
Soil properties				
pH	-0.039	0.201	0.674	587
Electrical conductivity	0.145	0.096	0.264	252
Total C	-0.060	**0.004***	0.602	342
Total N	0.085	0.707	0.589	251
Total P	-3.338	0.319	0.760	47
Organic matter	0.014	0.213	0.400	191
Available P	-0.007	**<0.0001***	0.607	433
Clay content	-0.001	0.674	0.336	214
Total C:N	-0.032	**0.0003***	0.858	219
Total C:P	0.010	0.413	0.239	82
Total N:P	-0.015	0.205	0.567	57
Amendment properties				
pH	-0.067	0.257	1.083	317
Electrical conductivity	-0.046	**0.0001***	0.692	162
Total C	-0.009	**0.026***	0.779	282
Total N	0.035	0.115	0.468	496
Total P	-0.041	0.149	0.604	411
Available P	0.000	**0.0002***	0.777	159
Total C:N	-0.021	**<0.0001***	0.928	255
Total C:P	-0.003	**0.034***	0.732	176
Total N:P	-0.005	0.371	0.512	454

Together these results indicate that the level of C in soil and organic fertilisers is a key determinant of the crop yield response, but that the influence is complicated and likely depends on the balance of C with essential nutrients like N and P. For instance, low C:nutrient ratios in organic fertilisers may trigger or exacerbate soil microbial C-limitation, thereby modifying below-ground biogeochemical cycling and, ultimately, leading to a net increase in rates of microbially-driven nutrient mobilisation. Importantly, this effect is strongly influenced by the quality and forms of organic C in the microbial substrate (Eldridge et al. 2013). Further, increases in overall soil C content through addition of organic amendments likely promotes a greater overall abundance of soil micro-organisms or increase in microbial biomass, which would be coupled with enhanced rates of microbial activity in soil.

Overall, these results demonstrate that all of the main components of the organic ‘waste’ stream (i.e. crop residues, manures, biosolids, and municipal solid waste from food) have high potential for both nutrient recovery and production of organic fertilisers. However, different crop types response differently to organic fertilisers. Specifically, organic fertilisers consistently increased the yield of grain crops, legumes other than soybean, brassicas, fruit, and forage crops. Organic fertilisers also had particularly beneficial effects on crops where the economically-relevant component grows below-ground (Fig. 1.11). However, the potential for contamination by soil-borne pathogens by organic fertilisers may impose significant health risks for below-ground crops.

The waste-derived organic fertilisers featured in this meta-analysis vary somewhat in their potentials for the respective applications of nutrient recovery and direct crop application. For instance, biosolids clearly have immense potential for nutrient recovery, fertilization, and compost manufacture, as they have some of the highest nutrient loads and lowest C:nutrient ratios (at least in terms of N and P) and their application has particularly strong positive effects on crop yield. However, biosolids are also associated with particularly high contaminant loads (Pritchard et al. 2010); therefore, management of food and environmental contamination will necessarily be a key aspect of their application as fertilisers for food crops. When contaminants are considered, it seems that nutrient recovery may be a safer use for biosolids than direct application to crops.

Similarly, this meta-analysis revealed that poultry litter and piggery waste had high nutrient loads (Fig. 1.10). However, the effects of poultry litter and piggery waste on crop yields were generally much smaller than that of biosolids according to this meta-analysis, and were smaller than that of the overall average effect of organic fertilisers (Fig. 1.12). Further, meta-analysis indicates that poultry litter has a negligible effect on crop yield compared to mineral fertilisers (Fig. 1.13). Based on these considerations and the potential for contaminants in these organic fertilisers (e.g. Parkinson et al. 1999; RIRDC 2013d), it seems that raw poultry litter and piggery wastes are comparatively poor candidates for production of organic fertiliser, but are ideal candidates for intensive recovery efforts. However, it is noted that poultry litter and piggery wastes were frequently used to produce compost and composted manures (e.g. Abdelhamid et al. 2004), both of which performed equally as well as mineral fertilisers according to the meta-analysis. Further, composting has the potential to reduce pathogenicity of organic waste materials (Quilty and Cattle 2011). Thus, appropriate or improved composting technologies will likely enhance the potential of poultry litter and piggery wastes as organic fertilisers for direct application to crops.

Cattle manure, compost and composted manure all had similar total N and P contents (Fig. 1.10), but the process of composting did appear to influence C:nutrient ratios and N:P ratios, presumably because of losses of volatile C and N during decomposition. The organic wastes, compost in particular, also performed well in terms of crop yield, and had effects that were comparable with mineral fertiliser. From this perspective, it seems that these products are suited for direct application as organic fertilisers, rather than nutrient recovery, particularly given their high organic C contents and lower nutrient content relative to biosolids, poultry litter and piggery waste. If feasible, there may be scope for combining the cattle industry and municipal solid food waste streams to produce high-quality composts.

5. Challenges and opportunities of waste-derived fertilisers for Australian industry and end-users

A series of surveys of waste industries and end-users (farmers, growers) were carried out on the key issues, challenges and opportunities. Results of the surveys are summarised below.

5.1 Industry perspective

5.1.1 Challenges

- Contamination of feedstock
- The machinery cost to separate contaminant from wasted organics
- Cost-effective characterisation and determination of feedstock quality before and after application.
- Lack of proper standardisation method for recycled organics as they currently pass the test as the best product but may have contaminant issue like PFAS or others.
- The market development
- Industry expertise and education
- Technology and adoption

5.1.2 Opportunities

The industry believes that there may be some opportunities in terms of waste-derived fertilisers that better meets industry needs:

Consideration of recycled organics as a value chain

Recycled organics processing must be considered as a complete value chain which is significantly impacted by all stakeholders up and downstream. This requires a common focus and attention to deliver successful outcomes. Success should be outcome-based recovery rates and the value generated by all stakeholders that makes the entire process sustainable. The value may be contributed in terms of economic, social and environment that is to be placed on community and environmental benefits. Also, the government must contribute to this chain by support of waste levy.

Quality checking at the source

While the Australian soils being renowned for their poor quality, it is imperative that we make use of the resources we have. In Australia the organics make up 50% of all landfill on average. It is termed food waste and green waste but in actual fact it is a beneficial resource that is being wasted. If we can separate the organics at the source, they are contaminant free, we can then turn them into high quality composts and soil amendments at a reasonable cost that can then be used on Australian farms to improve soil health, increase yields and help satiate the demand of the global food bowl.

5.2 Farmer and end-user perspective

5.2.1 Challenges

- Access to cheap and contaminant-free products
- Lack of information on regional resources
- Lack of information on application rate of waste-derived fertiliser
- Lack of information on impact of waste-derived fertiliser on soil health and soil productivity
- Engineering solution for subsoil application of recycled organics
- Biosecurity risks of bringing manure on farm
- Off-site impact of recycled organics on water quality and the Great Barrier Reefs

5.2.2 Opportunities

Subsurface application

Subsurface application presents a promising opportunity for farmers and growers to further improve their crop yield and soil fertility. There is an opportunity to investigate the effects of subsurface application of recycled organics. Some questions that need answering include:

- What is the optimum depth of application (surface, 200 mm, 500 mm, deeper?)
- What is the optimum rate at depth?
- How can this product be applied at depth? (will require engineering solution)
- What is the soil health benefit of applying this product at depth, and how long does it last?

Product integrity

Integrated approaches and co-composting of different feedstock materials may be used to address the various issues in terms of quality of organic products. There is an opportunity to find the alternative mixed products that can provide greater benefits than single product, such as mill mud compost. Mill mud can be used as a base for compost to see if it can significantly improve soil performance over mill mud or not.

Characterisation and cost effective processing of resources

The current waste resources and products can be identified on the basis of quantity, quality, value and their issues in terms of limitation and contaminations. All information relating to group, region and resource will help to find market opportunity, and a cost effective method can be developed on basis of need priority which brings benefit to both industry and end-users (farmer and grower). It will help to produce a product around what they need. A cost effective method for fertiliser delivery out of recycled organics does not have just a nutrient value in it but also bring $ to the farmers and growers through productivity. This can deliver what farmers can see and feel for future soil health and food production.

5.2.3 Current applications

Many farmers and growers apply some recycled organics as soil amendments that can enhance soil organic matters, nutrient management, soil structure and pH. These products are mostly mill mud, mill ash, biosolid, piggery waste, chicken sheds waste and cattle feedlot manure.

6. Conclusions and recommendations for future research and investment

The following key the research opportunities are identified and recommendations are made for the future research investment for new, targeted and high performance fertiliser products.

a) **In-depth characterisation of wastes on regional scales for optimum use**. Regional-scale quantification and characterisation of various solid (e.g., biosolids, manures, composts) and liquid (recycled water, daily effluent, piggery effluent) wastes produced in Australia for economic and effective application for specific soil type, crop type and climate condition. Much more fine-scale research is needed to fully understand the different types and available quantities of organic and inorganic wastes in a given region that can be effectively converted into the waste-derived fertilisers. This research will require consideration of physical and chemical properties of wastes, controls on their generation, logistic and geographic contexts of waste generation and subsequent fertiliser production and application as well as economic feasibility and even socio-psychological aspects from farmers to consumers.

b) **Matching sources of organic fertilisers to plant and soil type.** It is necessary to understand why different waste derived fertilisers influence crop yield and soil properties differently, and why some plants seem to respond in a different way than others. For instance, meta-analysis indicates that application of biosolids and compost improve yield to a far greater extent than most other amendment types, and that crops with below-ground marketable yield components (i.e. root, tuber or bulb crops) response particularly well to organic fertilisers and soil amendments. The reasons are unclear, but may be related to differences in organic waste chemical properties, phytotoxic contaminant loads, changes in soil physical properties or stoichiometric mechanisms.

c) **Improved understanding of roles of organic C functionalities for increasing crop yield.** While prior research and the meta-analysis in section 4 have clearly indicated that some of the beneficial effects of organic-waste derived soil fertilisers and amendments are driven by changes in soil C content, much remains unknown regarding its underlying mechanism. In particular, it is unclear how waste-derived products differ in terms of organic C functionality and what potential roles this functionality plays in nutrient retention, stimulation of biological and biochemical processes and adsorption of heavy metals and other contaminants.

d) **Optimising existing technologies to recover nutrients efficiently for maximising profitability.** There are numerous techniques available for recovering nutrients from wastes and subsequently producing fertilisers and soil amendments. However, it is still unclear how to optimise these existing and emerging technologies to meet environmental (in particular, reduction of ‘waste’ and nutrient pollution to zero, improved soil health and C sequestration and retention of scarce nutrients like P) and economic goals (i.e. meeting or improving on current standards of yield for equal or lower cost to farmers). Some important avenues for future research in this context include investigation of potential synergies between waste streams to enhance recovery or fertiliser efficacy, such as addition of waste plasterboard (for its Mg content) to sewage sludge to enhance P recover, and the potential for production of nanofertilisers from the organic and inorganic waste streams.

e) **Synergistic and antagonistic effects and economic viability** of co-utilization of waste-derived fertiliser products with commercially available inorganic fertilisers

f) **Developing sound strategies for minimising environmental risks.** Development of strategies for managing the potential risks to human health and surrounding environments, posed by the manufacturing and application of the waste-derived fertiliser products by the relevant industries, will be essential to their successful adoption by farmers and acceptance by consumers.

PART II: DEVELOPMENT OF NEW, TARGETED AND LOW RESIDUAL PESTICIDE/HERBICIDE DELIVERY SYSTEMS

By Dr Md Nuruzzaman, Dr Yanju Liu and Professor Ravi Naidu, Global Centre for Environmental Remediation (GCER), University of Newcastle

Executive Summary

Increasing world population and food demand has triggered increasing pressure on agricultural productivity, which depends on utilization of large amount of pesticide/herbicides. However, a major issue regarding agricultural application of pesticide/herbicide is the residue effect of pesticide/herbicide which pose risks to environment and human health. Thus cost-effectively application and management of insects and weeds is critical for growing in productivity. This project report focus on the utilization of various materials for pesticides/herbicide delivery which help reduces loss, residue, targeted release and sustainable release. The information summarized covered background information on application of controlled releasing pesticide/herbicide system, key materials being investigated for the delivery, limitations of different materials and future considerations for development of cost-effective and environmental friendly pesticide/herbicide delivery systems.

Abbreviations

2,4-D	2,4, dichlorophenoxy acetic acid
AIs	active ingredients
CRFs	controlled release formulations
EMB	emamectin-benzoate
HNT	halloysite nanotube
INT	imogolite nanotube
IPM	integrated pest management
SCF	supercritical fluid
APVMA	Australian Pesticide and Veterinary Medicine Authority
ECs	emulsifiable concentrates
RTU	ready-to-use low concentrate solutions
ULV	ultralow-volume concentrates
SC	suspension concentrates
SL	soluble concentrates
ME	microencapsulates
SP or WSP	soluble powders
WP	wettable powders
WG	water-dispersible granules (),
D	dusts
PE	pellets

GR	granules
TA	tablets
BA	baits
GE	gels
DF	dry flowables
A	aerosol
CRFs	controlled release pesticide formulations
PEG	polyethylene glycol
PCL	poly-ε –caprolactone
PLGA	poly(lactic-co-glycolic) acid
PLA	polylactic acid
PGA	polyglycolic acid
PEG–PBA–PEG	polyethylene glycol–polybutyleneadipate–polyethylene glycol
MSNs	mesoporous silica nanoparticles
PHSNs or HSNs	porous hollow silica nanoparticles
SFDL	supercritical fluid drug loading
HNT	halloysite nanotube
LDHs	layer double hydroxides
INT	imogolite nanotube

1. Background

1.1. Application of Pesticide in Agriculture

Maximising agricultural productivity is crucial to meet increasing demands for food globally. Agro-chemicals play a vital role in improving productivity, in particular to reduce yield loss due to insect pest, plant pathogens and weeds [1]. Thus, agricultural practices involve usage of large amount of pesticides including herbicide that can reduce grain loss by 30–40% through protecting the crop from insects, plant pathogens and weeds [1-3]. The food crops are competing with up to 30,000 species of weeds, 3,000 species of nematodes (microscopic worms) and 10,000 species of plant-eating insects, as well as viruses, fungi, mites and mice in the current world (https://www.croplife.org.au/topics/why-do-we-even-need-pesticides/). Whereas increasing global population rate has put pressure to farmers for increasing crop productivity to meet up the food demand. The food production must be more than double to avoid truly widespread hunger and malnutrition for the expected world's population near to 10 million by 2050. In addition, climate change, depletion of natural resources and diminishing arable land, the world's farmers face increasing challenges that leads them to utilize pesticide.

Globally in 2006 and 2007, approximately ~2.36 million tons of pesticide were used (worth of US$35.8 billion in 2006 and US$39.4 billion in 2007) [4]. Where the utilization of pesticide increased gradually and in 2012 the amount of global pesticide usage reached to ~2.9 million ton with expense of US$56 billion [5]. Similarly utilisation of pesticides increase Australian crop yield by about 40% each year, which increase the value of food production by $13 billion [6]. It has been reported that the total Australian market for pesticides and other products regulated by Australian Pesticide and Veterinary Medicine Authority (APVMA) was AUS$ 1648.81 million in 2006/07 [6]. This indicated significance of pesticide to the Australian agro-economy.

Generally, natural or chemical substances or mixtures of substances used for preventing, destroying, or controlling any pests are commonly known as pesticide. However, the term "pesticide" covers a vast area and includes various types depends on its classification (Appendix A). Among them, insecticides, fungicides and the herbicides are the major types of pesticide used in agricultural practices to control insects, fungus and weeds respectively. Worldwide, the usages of herbicides are dominating over other the pesticides followed by insecticide and fungicide [5]. So far various types of pesticide formulations are commercially available in the market including: emulsifiable concentrates (ECs), ready-to-use low concentrate solutions (RTU) and ultralow-volume concentrates (ULV), suspension concentrates (SC), soluble concentrates (SL), microencapsulates (ME), soluble powders (SP or WSP), wettable powders (WP), water-dispersible granules (WG), dusts (D), pellets (PE), granules (GR), tablets (TA), baits (BA), gels (GE), dry flowables (DF), aerosol (A), etc. [7]. These pesticide formulations are a mixture of different materials including active ingredients (AIs). In a pesticide formulation, only the AIs are responsible chemical or substance used to kill, repel, attract, mitigate or control target pest while they may not be effective in their raw or unformulated condition even not suitable for application. The materials other than AIs are used collectively known as inert ingredients to make the AIs effective and useful. Generally, most of the AIs are organic compounds with poor water solubility. Therefore, special considerations should be made when handling or storing them. Thus, the manufacturers add other ingredients such as solvents, surface-active ingredients, stabilizers etc. to formulate the pesticide in to final product to maintain their solubility, improve storage ability, handling, safety, application, or effectiveness. On the basis of the nature and properties of these formulations, they are applied directly or processed as a solution, suspension, or emulsion prior to their application. However, a successful modern crop protection chemical should have several properties [8], including:

(1) the ability to remain active or survive in the spray environment (sun, heat, rain);
(2) to be taken up into the target organism (e.g., fungus, insect) effectively;

(3) to resist the defence of the pest and pathogen;
(4) to remain benign to plants, humans, and other mammals;
(5) to preferably possess a new mode of action;
(6) to provide economic returns

Most of the conventional pesticides and biocides applied in agricultural fields are unable to maintain such properties and even cause serious problems not only to human beings but also to the total environment.

1.2. Issues of Pesticide Application

Though the pesticide application is essential to increase the crop productivity, however, most of the commonly used pesticides are greatly limited in their application due to a number of problems. It was reported that more than 90% of applied pesticides are either lost in the environment or unable to reach the target area required for effective pest control [9]. Van den Berg et al. reported that up to 20-30% of the applied pesticides are lost through emissions [10]. This may reach up to 50% depending on a number of factors, including the application technique, physicochemical properties of the pesticides and environmental conditions (e.g. wind speed, humidity, and temperature) that influence the extent of the loss during application [10, 11]. Most often the pesticide formulations are failed to deposit properly over leaf surface. Consequently, the pesticides are further lost through leaching, evaporation, deposition, wash away and degradation by photolysis, hydrolysis and by microbial activity [12]. Figure 2.1 demonstrated the pathways of pesticide degradation in the environment.

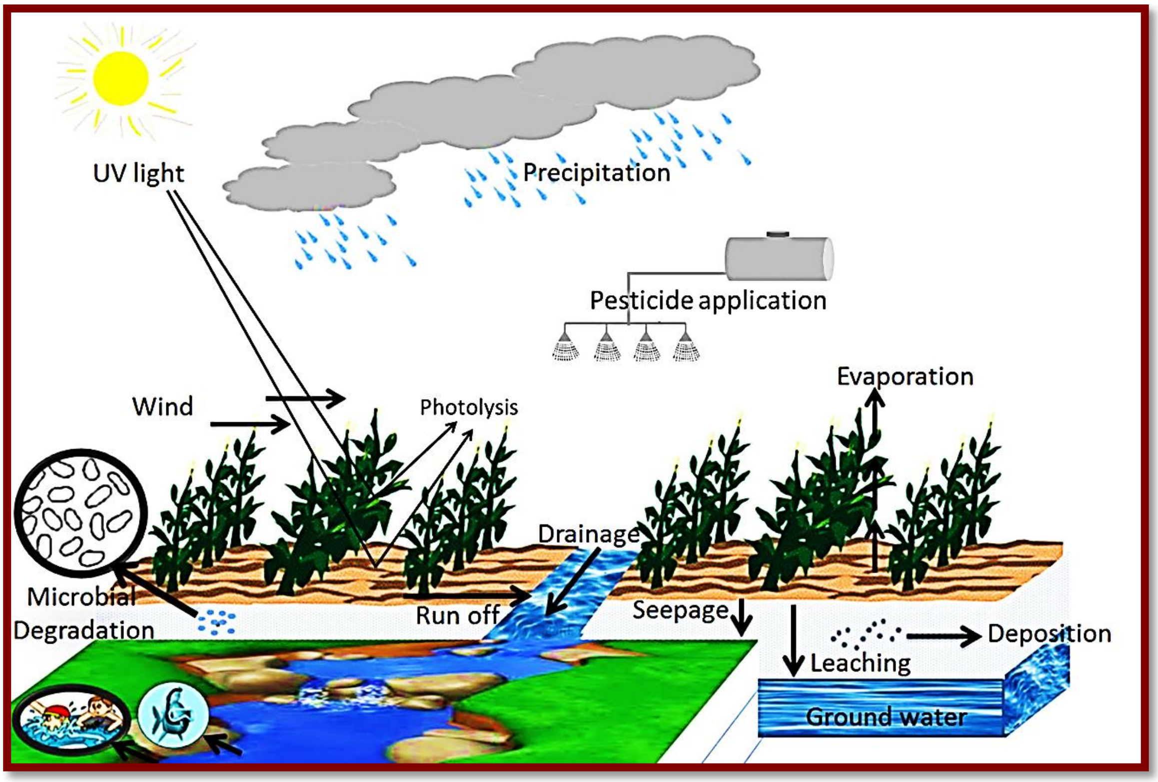

Figure 2.1. Pesticide losses and degradation pathways (adapted and modified from [13]).

As a result of these losses, the active ingredients in the pesticide are removed prior to performing their action, and therefore the concentration at the target area is well below the minimum effective concentration required (Figure 2.2).

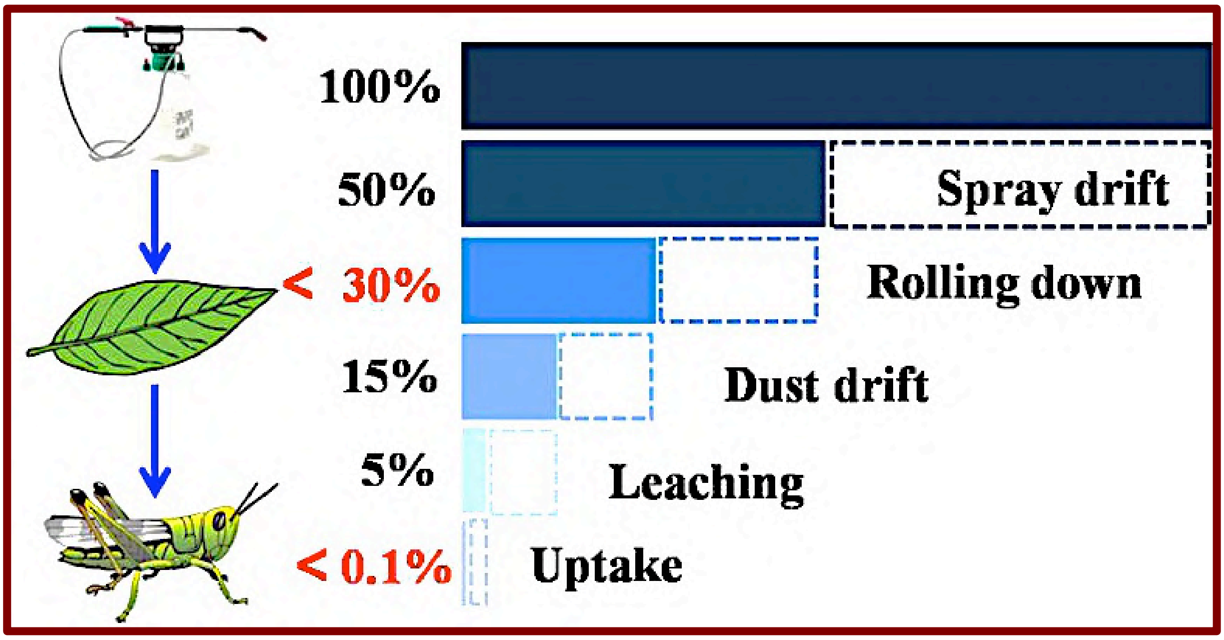

Figure 2.2 Low efficiency of conventional pesticide formulations.

Therefore, nonspecific and periodic application of pesticide is required to achieve the desired biological response in terms of pest control within a given period [14]. In this way, the amount of applied pesticides greatly exceed the amount actually required to control the target pests [9]. As a result, not only the cost of treatment increases; such usage results in unfavourable effects either to plants or to the environment including soil and water pollution, which ultimately becomes hazardous to public health [12, 14]. The repeated and indiscriminate usages of pesticide increases pest and pathogen resistance, reduces soil biodiversity and nitrogen fixation, raises bioaccumulation of pesticides, kills predators and pollinators, destroys habitats and feed of birds [15]. Increasing knowledge of the negative effects of agrochemicals (especially pesticides) on public health and wildlife has resulted in increasingly stringent controls on their use. Coelho reported that the European Parliament approved new regulations on pesticide registration in 13th January 2009 [16]. According to the legislation, pesticides are considered as potentially harmful and will not get any license until proven that they are safe for human health and to the environment [17].

Moreover, market dominancy as well as continuous exposure of a certain pesticide may also cause environmental problems. For instance, amongst the pesticides, neonicotinoids have been the fastest growing in the global market compared to other insecticides such as carbamates, organophosphates and pyrethroids for the last two decades [18]. Neonicotinoids are registered in more than 120 countries for commercial use to control a wide range of sucking and chewing insect pests in both agricultural and household scenarios [18]. The first neonicotinoid insecticide, namely, imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine) was introduced in the market in 1991 and is the representative of neonicotinoid insecticides [19]. In the meantime, imidacloprid has become the most successful, efficacious and best-selling insecticide worldwide due to its unique chemical and biological properties [20]. Imidacloprid processes a broad-spectrum insecticidal activity with low application rates, excellent systemic characteristics related to plant uptake and translocation as well as adaptability to various application methods. The application methods include, for example, irrigation systems, in furrow application, granular application or seed treatment, etc. [20].

More importantly, its mode of action and selective toxicity towards insects has generated much attention regarding the safety profile of insecticides [21]. Imidacloprid mainly acts on the central nervous system (CNS) of insects through binding with nicotinic acetylcholine receptors (nAChRs) blocking the nicotinergic neuronal pathway. Imidacloprid shows high binding affinity to insect nAChRs compared to mammals, and consequently is more toxic to insects than mammals [20, 21]. Thus, the application of imidacloprid is not limited to agricultural crop fields but extends to widespread applications to controlling household and garden pests (e.g., termites, cockroaches, aphids, thrips, turf beetles, etc.) and even to controlling fleas on domestic animals [18]. However, their massive application and physico-chemical properties related to solubility and stability have made them a potential contaminant of surface and ground water especially via leaching [22].

It was observed that global contamination of surface water with neonicotinoids has been very evident during the last decade and among the neonicotinoids, imidacloprid was the most widely existing contaminant found in Australia, Canada, Germany, Spain and the United States [23]. Thus, this pesticide can become a major threat to aquatic organisms. Recent studies have documented the toxic effects of imidacloprid and its metabolites on aquatic organisms such as algae, crustaceans, invertebrates, fish, etc. [24-29].

Similarly, glyphosate, the best-selling herbicide throughout the world was reported showing resistance to weeds. In Australia, rigid ryegrass (*Lolium rigidum)* has already become resistant to this herbicide [30]. Another widely used anionic herbicide, namely, 2,4-D (2,4, dichlorophenoxy acetic acid) is prone to loss via leaching.

1.3. Improvement of Pesticide Formulations

In agriculture, the development of new plant protection product or formulation is always desired to increase their efficacy as well as to overcome the problems associated with them [13]. People always require safer and more convenient pesticide formulations. In earlier 90s, Seaman reviewed the trend of pesticide formulations and noted that WP and EC were major conventional pesticide formulations; however, these formulations were less favoured by farmers as well as registration authorities [31]. In general, WP is a dry and finely ground powder pesticide formulation composed of pesticide AIs, inert fillers, and other additives. The particles also do not dissolve in water thus settle down quickly in sprayer during application. In addition, this formulation is easily drift and runoff into the environment. Whereas EC is a liquid pesticide formulation that is formulate by dissolving the AIs in the solvent, added with an emulsifier, and then diluted into water to form a stable emulsion. However, mostly the toxic solvents such as xylene, toluene are used that directly leach and leak into the environment. Ultimately, causes serious pollution in soil and water systems and chemical residues in crops and food products and is a potential threat to human health. Alternative to WP and EC, the other formulations such as SL had attracted much attention. Additionally, water dispersible granules and emulsions in water were found as promising formulations of capsule suspensions and polymeric surfactants that work more effectively and safely in favourable condition. These formulations were deemed to lead towards the formation of microencapsulated pesticide formulations for the controlled release of AIs. In fact, the development of controlled release pesticide formulation was introduced at middle of 60s [32]. Because of the requirement of a huge amount of fund for developing a new pesticide or bioactive agent, recent studies are focusing more to improve the delivery system especially through preparing controlled release formulations (CRFs).

Controlled release formulations of pesticides are considered as the depositories of AIs from where the active constituents are released in a controlled way into their release environment over a defined period of time [32]. The main advantage of CRFs is that they reduce the amount of pesticide much less than conventional pesticide while retain similar period of activity by regulating the supply and release of AIs [33]. Figure 2.3 depicts the ability of CRFs in reduction of amount of pesticide over conventional pesticide. In most cases, the performance of conventional pesticides is reduced by environmental forces that remove the excess amount of pesticide before they can perform their function. The rate of pesticide removal at any time is directly proportional to the amount present in the environment at that time. Thus, periodic application is required for conventional pesticide to maintain the effective concentration. Conversely, an ideal CRF reduces the number of applications as well as relevant cost and time.

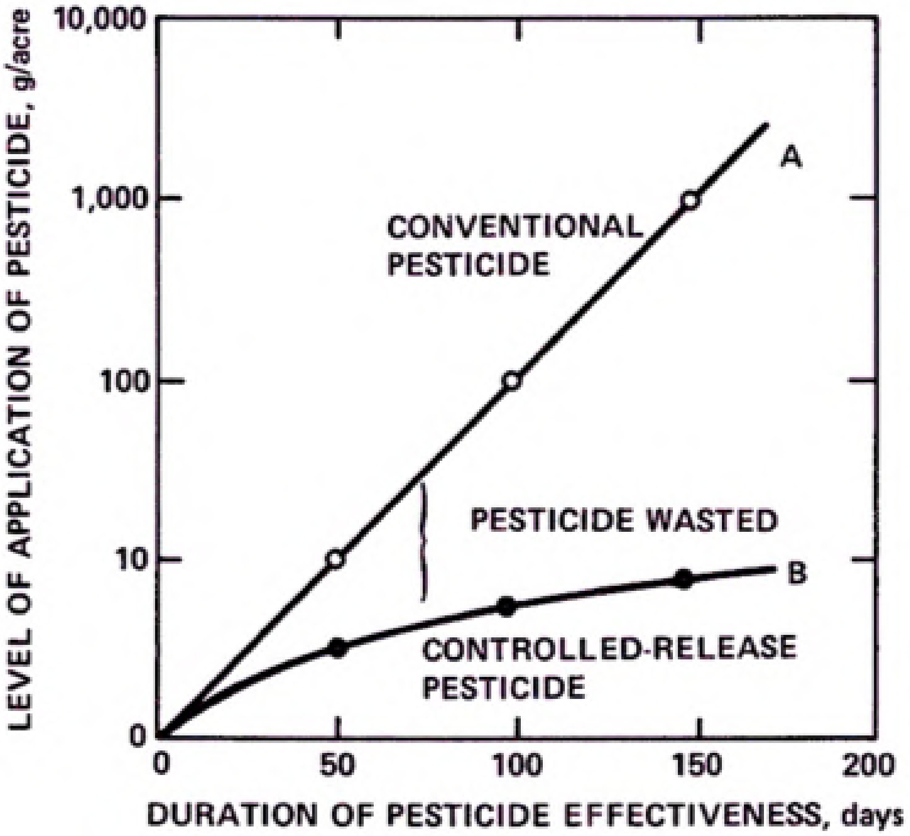

Figure 2.3. Relationships between the level of application and the duration of action for conventional and controlled release formulations (adapted from [33]).

However, preparation of an ideal CRF is not only challenging but also an active area during the past decades. At the beginning, the CRFs were prepared by incorporating the AIs to polymeric matrix to obtain a sustained release profile of the active agents. In this system, release of AIs occurs for an extended period of time maintaining their constant exposure. The rate of exposure may decrease due to general loss of AIs or increase due to rupture of the protective barriers. Later on, the concept of CRFs was completely changed though the principal of sustained release or controlled release is same even sometime overlap with each other but mechanism of release is significantly different. A controlled release formulation may exhibit a fast release or a slow release or a constant or a changing release pattern of the AIs depending on the design of the formulation. Thus, release rate may categorized as three types, (1) “zero-order release” where the release rate remains constant until the carrier is exhausted of active agent, (2) “first-order release” where the release rate is proportional to the amount of active agent within the reservoir and declines exponentially with time as the reservoir approaches to exhaustion, and (3) “square-root-of-time” release where the release rate is linear with the reciprocal of the square root of time. The release rate remains finite as the carrier advance towards exhaustion [34].

Some promising concepts on developing CRFs were firstly, preparation of polymeric capsules filled with a solid or liquid pesticide or with a suspension or solution of the agent in a fluid, in which the release of pesticide is controlled by Fickian diffusion through the capsule walls or through micropores in the capsule walls; secondly, preparation of a solid biodegradable or non-biodegradable polymeric matrix with a heterogeneous dispersed pesticide particles or droplets from where the release of agent occurs via diffusion through the matrix, erosion of the matrix, or a combination of both diffusion and erosion; and lastly, chemical bonding of a pesticide to a natural or synthetic polymeric material, as by pendant anhydride or ester linkages, or formation of macromolecules of pesticides via ionic or covalent linkages, which control the release of the agent by hydrolysis, thermodynamic dissociation, microbial degradation, or some other retrograde chemical reaction of the linkages. The structural properties of the CRFs also significantly affect the release and releasing principals (Table 2.1).

Table 2.1. Structural principals of physically incorporated polymeric CRFs

Structure of the CRFs	Release controlling system	Release mechanisms
Capsules (Microcapsule, Macrocapsule)	Release control by membrane	Diffusion
Hollow fibre	Capillary forces	Dissolution, diffusion
Porous polymeric substances	Capillary forces	Dissolution, diffusion
Polymeric gels		Dissolution, diffusion
Semipermeable membrane coating	Release control by membrane pores	Osmotic pump
Layer (film) structured polymers	Laminate system (membrane controlled)	Diffusion
Polymeric matrix (non-porous)	Monolithic system	Matrix erosion, diffusion

Nevertheless, among various polymeric CRFs, microencapsulates have already emerged as one of the promising commercial pesticide formulations. So far, various synthesis techniques have advanced the progress of microencapsulate formulation. For instances, preparation of the emamectin-benzoate (EMB) embedded slow-release microspheres by emulsion polymerization technique has illustrated in Figure 2.4.

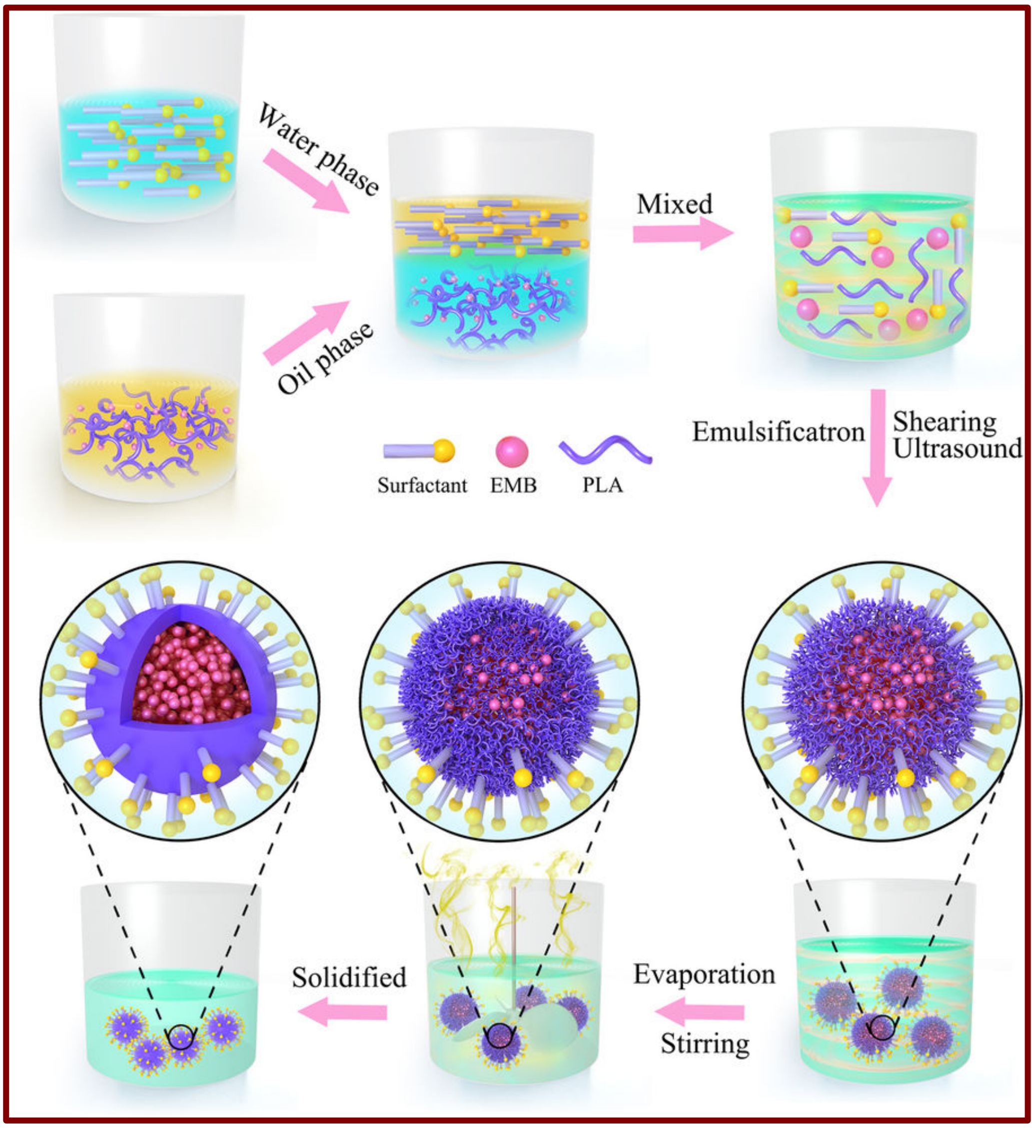

Figure 2.4. Schematic description of preparing the emamectin-benzoate (EMB) slow-release microspheres (adapted from ref. [35]).

Recently, a market survey based company **MarketsandMarkets™ Research Private Ltd.** estimated that the microencapsulated pesticides market was to reach USD 312.5 Million in 2017, and is projected to reach 539.5 Million by 2022, at a cumulative annual growth rate of 11.54% from 2017 to 2022 (https://www.marketsandmarkets.com/PressReleases/microencapsulated-pesticide.asp). This is because of the requirement of limited amount of AIs for an effective action against the targeted pests, able to protect AIs from volatilization, reduces the loss from the application site, less phytotoxic to plants and expected to reduce environmental and health risks to the applicators. MarketsandMarkets™ also reported that the market for insecticide formulations was the largest, by type, in 2016 and the interfacial polymerization technique is most suitable for the preparation of microcapsules. This technique is also less expensive and suited to large-scale production. Additionally, the Europe is the leading region due to the declining trend for emulsifiable concentrate (EC) formulations for its harmful effect on the environment and the increasing application of integrated pest management (IPM). Some of the world's leading pesticide companies such as BASF (Germany), Bayer AG (Germany), Syngenta (Switzerland), Monsanto (US), ADAMA (Israel), and FMC Corporation (US) have already launched their product in the market. For an example, microencapsulated methyl parathion has commercialized as Penncap-M by Mosanto Agr. Prod. Co. However, microencapsulated pesticide formulations may retain some major drawback. Microencapsulated pesticides often tend to poor stability after dilution and the controlled release is affected by their wide shell thickness.

In this consequence, nanotechnology is considered as one of the latest and advanced technologies emerged for agricultural practices to improve productivity and product quality, including development of more effective and non-persistent pesticides and new techniques of application including CRFs. Over the last decade, the intensified research growth and promising application aspects of nanotechnology in agriculture specifically in pesticide delivery indicate its ability to revolutionized pesticide sector formulating controlled release nanopesticide formulations along with the existing microencapsulated pesticide.

2. Project aims and objectives

This part of the *Scoping Study* aimed to undertake a review of the potential technologies those are able to efficiently deliver pesticide to the agricultural fields with low residue effects. In this report, a broad techniques and materials that are currently investigated for their pesticide delivery process are summarized, with a particular focus on nano-porous materials for pesticide delivery.

The specific objectives include:

- To summarize technologies for pesticide delivery
- To explore the potential nano-porous materials that can be applied for pesticide delivery
- To identify future research areas based on conclusions of review

This report outlines the main findings from the review, commissioned by the Soil CRC, to identify key areas, technologies to develop existing pesticide formulations for pesticide delivery of particular interest to CRC members and participants, through research, consultations, and a survey. The overall findings present a valuable resource to inform the development of projects across the CRC and target specific areas of industry and community engagement.

3. Pesticide delivery and the role of nanotechnology

Utilization of nanotechnology in agricultural practices is considered as one of the most promising practices in recent years. It is the design, fabrication and utilization of materials, structures, devices and systems through control of nanometer length scale (1-100 nm) and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale in at least one dimension [36]. There are investigations found in the literature related to utilization of nanotechnology in various agricultural practices such as seed treatment, germination, plant growth and development, pest control, pesticide delivery, fertiliser delivery, genetic material delivery, toxic agro-chemical detection, pathogen detection, etc. [9, 13, 14, 37-42]. In terms of pest management, nanomaterial at their nanoscale size have novel properties that can increase the agrochemicals' (e.g., pesticide, fertiliser, growth hormone et.) efficiency and make the delivery system "smart" [14]. In pest management, using the smart delivery system the pesticides could be delivered in a controlled and targeted manner that is so far postulated in drug delivery to human [43]. From the available literature, it is notable that various nanomaterials have exhibited their potential as carriers for pesticide delivery. Moreover, some nanoparticles are also capable to control agricultural pest.

3.1. Nanopesticide

Considering the definition of nanotechnology, the addition of the prefix "nano" with pesticide may differentiate them with conventional pesticide on the basis of size and structure in a simplistic way. According to Bergeson, very small size particles of active ingredients or other small-engineered structures having the properties to prevent, destroy, repel or mitigate pests will be considered as nanopesticides [44]. However, based on the purpose of nanomaterial utilization the nanopesticides could be categorized as follows:

- Nanocide
- Nano-delivered pesticide

3.1.1. Nanocide

Nano-scale materials or nanoparticles having the pesticidal effect, thus act as active ingredients are known as nanocide such as nano-metal and metal oxides, non-metal and their oxides [37, 45-47].

3.1.2. Nano-delivered pesticide

Nanomaterials utilize as carrier material for the delivery of conventional pesticide. In this phenomena, the nanomaterials provide support to the conventional pesticide AIs for preparation nanostructured pesticide formulations through adsorption, ligand mediated attachment, entrapment and encapsulation [9]. Nanomaterials such as nano-encapsulates, nano-containers and nano-cages used for pesticide delivery and utilization of these nanomaterials are good techniques for the preparation of controlled release pesticide formulations (CRFs). These nanomaterials also protect the active ingredients from premature degradation, increase the stability and pest control efficacy as well as reduces the amount of pesticide application [13]. In some cases, nanomaterials are introduced in composite materials such as polymeric matrix to enhance the efficacy of the system as a carrier for pesticide delivery. In recent days, emulsion based pesticide formulation have been formulated more effectively with beneficial aspect of nanotechnology. Utilizing this technology, emulsions such as microemulsion and nanoemulsion are prepared where the droplet sizes are maintained below 100 nm. Thus, microemulsions and nanoemulsion based pesticide formulations show better stability over conventional emulsion based formulations.

In spite of pest control efficiency of various nanoparticles, the main aspect of this report is improving the conventional pesticide formulation with the help of nanotechnology. Hence, this report mainly focused on the potential application of nano-delivered pesticide.

3.2. Goals of nanopesticide

The nanopesticide formulations are prepared by loading the AIs to nano-carriers or nanoencapsulation materials for enhancing the bioavailability of active substances and reduce toxicity, improving the timed release of active substances and enabling the precise targeting of active substances [48]. Nanoencapsulation technology has been introduced in crop protection chemicals to achieve either of these outcomes, or being nanosized, which reduces the amount being applied due to the high surface area of the nanomaterials.

The utilization of novel techniques aims to achieve the following effects:

- increasing the apparent solubility of poorly soluble active ingredients
- releasing active ingredients in a slow/targeted manner
- protecting the active ingredient against premature degradation
- reduce the amount of pesticide application
- Increasing the stability of the pesticide.

4. Nano-porous materials for pesticide delivery

The application of nanotechnology in pesticide delivery involves the use of nanomaterial. Before going to investigate the potentialities of different nano-porous materials, it is important to clarify about the various types of nanomaterial that have been discussed in this report. Most often, the terms related to nanomaterial found in the literature are conflicting with each other. Generally, nanomaterial is a generic term indicates material with any external dimension in the nanoscale or having internal structure in the nanoscale. Accordingly, the nanomaterials could be grouped as firstly, nanostructure material and secondly, nano-object. Material having internal nanostructure or surface nanostructure indicates the composition of interrelated constituent parts, in which one or more of those parts within nano-scale region are considered as nanostructured material. In contrast, if at least one external dimension of a nanostructured material within nano-range is known as nano-object. Furthermore, depending on the external dimensions of the nano-objects they are further known as nanoparticle, nanorod, nanotube, nanoplate, nanofibre etc. (Fig.2.5).

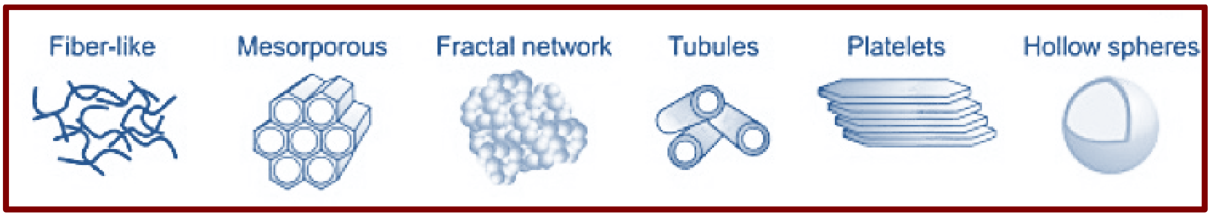

Figure 2.5. Different types of nano-objects.

From this scenario, one can get information about the formation and structure of a wide range of nano-porous materials. The materials can be built with either organic or inorganic framework. The nano-porous materials can be classified into two groups such as bulk materials or membranes. For example, zeolites are the true representative of natural bulk nano-porous material whereas cell membranes are the example of nanoporous membranes. Thus, a wide range of natural and synthetic organic or inorganic based bulk nano-porous material as well as polymer or polymeric membrane based materials could be utilized as an encapsulation or carrier material for the effective delivery of pesticide (Table-2). Depending on the pore size IUPAC has classified the nano-porous materials as microporous materials (pore size 0.2–2 nm), mesoporous materials (pore size 2–50 nm) and macroporous materials (pore size >50 nm). In terms of controlled release formulation preparation pore size is very important because of their significant influence on pesticide loading and releasing behaviour. Currently, the nano-porous materials investigated for pesticide delivery are summarised in the following sections.

4.1. Organic Nano-Porous Materials

4.1.1. Polymer-based nanomaterials

Different polymeric nanomaterials so far exhibited their potential to be utilized in a wide range of applications as a carrier for bioactive molecule delivery such as drug delivery to human. In case of pesticide delivery the nano-delivered pesticide formulations were first introduced through the preparation of nano-size polymeric vesicles where the pesticide AIs were coated with biodegradable polymers. So far various polymeric nanomaterials have been utilized to deliver pesticide such as nanocapsules, nanospheres, polymeric micelles, nanogels etc. (Figure 2.6).

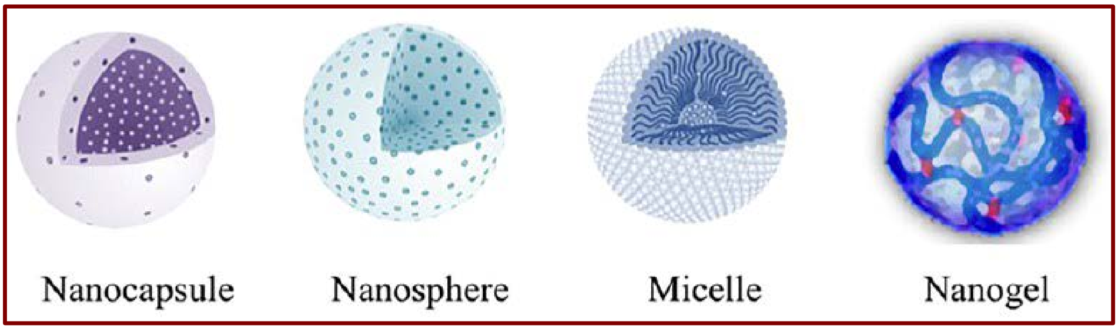

Figure 2.6. Different morphological forms of polymeric nano-delivered pesticides (adapted from ref. [13]).

However, these polymer-coated nanopesticides suffer from various limitations such as poor thermal and chemical stability, rapid elimination by the plant enzyme system, and degradation of some polymers, resulting in the formation of acidic monomers and decreased pH value within the polymer matrix [49]. Currently, their utilization is increasing gradually due to a number of available sources, easy to modify surfaces, and simpler synthesis techniques, such as the self-assembly properties of amphiphilic block copolymers.

Among the polymer-based nanocarrier nanocapsules are most commonly used vehicles investigated for pesticide delivery. Nanocapsules are known as vesicular systems that are made up of a polymeric membrane encapsulating the active compounds as an inner core at the nanoscale level [50, 51]. Hence, the nanocapsule structure is built with a core−shell arrangement of pesticide active compounds and a polymeric membrane or coating respectively. The active ingredients are arranged in the core in various ways. The active substances are usually dissolved in the solvent act as inner liquid core and solidified evaporating the solvent. The inner core is also structured with pesticide formulations or polymeric matrix. Sometime the polymeric shell may absorb the AIs as well. In this way the active substances are encapsulated by nanocapsules spontaneously during the formation of nanocapsules. Polymeric nanocapsules are widely applied and, subsequently, intensified research studies have been conducted for their effective synthesis. The availability of different polymers and their inherent properties have given researchers the option for synthesizing nanocapsules through different methods. The most commonly developed strategies are

- Nanoprecipitation
- Emulsion diffusion
- Solvent evaporation
- Double emulsification
- Emulsification coacervation, and
- Layer-by-layer deposition

Nevertheless, various other methods were found in the literature along with modifications of the above-mentioned methods, such as

- Melt dispersion
- Emulsion polymerization
- Interfacial polymerization
- Interfacial deposition method
- Solvent displacement technique
- Emulsion evaporation

To date, a wide range of synthetic and natural polymers have utilized for the synthesis of nanocapsules. For instance, Yang et al. synthesized nanocapsules using polyethylene glycol (PEG) loaded with garlic essential oil [52]. In another study, PEG-400 was utilized to encapsulate a neurotoxic organophosphate pesticide, namely, acephate [53]. A polymer such as poly-ε –caprolactone (PCL) is considered to be a good synthesis material for preparing nanocapsules due to their water insolubility and slow degradation process while remaining harmless to the environment. In their study, Grillo et al. prepared nanocapsules using PCL for encapsulating herbicides such as ametryn, atrazine, and simazine by employing the interfacial deposition method [54, 55]. The nanoencapsulated herbicides could control the target species, and the formulation was safe for non-target species. This formulation also remained stable over time and reduced the mobility of atrazine [55]. Such properties exhibited the potential utilization of nanotechnology in agriculture.

Considering the environmental benefit utilization of natural polysaccharides such as chitosan, sodium alginate, and starch has become more popular due to their nontoxic, biodegradable, and biocompatible properties [56]. The neonicitinoid pesticide namely, imidacloprid was successfully loaded in alginate based nanocapsules [57, 58]. The ability of different polymer for the formation of amphiphilic block copolymers also facilitated the synthesis of nanocapsule. The amphiphilic copolymers are able to form nanosize micelles in aqueous solution that allow them to entrap the pesticide in the interior region of the micelles. A diblock copolymer namely, chitosan−poly(lactide) (chitosan-co-PLA) was used to encapsulate imidacloprid via formation of nanocapsules [59]. Similarly, organophosphate pesticide chlorpyrifos was encapsulated into the nanocapsules synthesized using amphiphilic chitosan copolymer (chitosan-co-PLA-DPPE) [60]. In another study, the readily available copolymer known as poly(lactic-co-glycolic) acid (PLGA) originated from polylactic acid (PLA) and polyglycolic acid (PGA) was used for the first time as a nanocarrier material in a plant protection system [60].

The amphiphilic triblock copolymers have also received special attention for synthesizing polymeric nanocapsules. Memrizadeh et al. (2014) prepared amphiphilic ABA tri-block linear dendritic copolymers composed of poly(citric acid) (PCA) as block A and PEG as block B. They encapsulated the pesticide imidacloprid using the copolymers' self-assembling ability [61]. The triblock copolymer polyethylene glycol–polybutyleneadipate–polyethylene glycol (PEG–PBA–PEG) also exhibited their efficacy to encase the plant extract in the form of nanocapsules [62]. The miceclles of the block copolymers also could be used as vehicles for pesticide delivery. Generally, direct dissolution and film casting methods are employed for the micelle formation polymer's weight as well as CMC influence on radius of gyration. So far, a number of studies have tried to encapsulate commercial and biological pesticides into nanomicellar aggregates using PEG-originated amphiphilic block copolymers [63-69]. The micellar characteristics depend on the nature of the block copolymers and structures of the hydrophilic block. The radius of gyration increased when the size of the hydrophilic segment was increased.

Copolymer of chitosan in conjugation with polylactide, namely, chitosan-co-(D, L-lactide) or chitosan−PLA. This copolymer was designed to achieve the amphiphilic nature of the polymer so that the micelle structure could be easily formed in aqueous media. The pesticide imidacloprid was encapsulated within the core of the micelle via the nanoprecipitation method [59]. Feng and Peng (2012) prepared another amphiphilic chitosan derivative, namely, 6-O-carboxymethylated chitosan with ricinoleic acid (R-CM-chitosan), to encapsulate biocides such as azadirachtin. The particle size of the encapsulated azadirachtin−(R-CM-chitosan) was reported to be 200-500 nm with a loading efficiency up to 56%.

The other polymeric nanocarriers such as nanospheres and nanogels also could be utilized as carrier for pesticide delivery. In nanospheres the AIs are uniformly distributed to polymeric matrix [50, 70]. Synthesis processes of nanospheres are similar to nanocapsule systhesis e.g., emulsion or interfacial polymerization. Whereas nanogels are aqueous dispersions of hydrogel particles formed by physically or chemically crosslinked polymer networks in the nanoscale size. Nanogels are formed through the controlled aggregation of interactive polymers due to their self-assembly properties in aqueous media. The polymers are hydrophobically modified to generate self-assembly properties. The nanogels remain in a swollen condition due to the presence of an ample amount of water, which facilitates loading of active compounds spontaneously through electrostatic, van der Waals, and/or hydrophobic interaction between active compounds and the polymer matrix. In this way, the active compounds are trapped in the polymer matrix while stable nanogel particles are formed.

Employing nanogels as a media to deliver pesticide is a very recent phenomenon and only a few studies have been published on it. From the available literature, it was observed that nanogels were synthesized from natural polymers, which is a very good sign for establishing an eco-friendly approach to pest control with the help of nanotechnology. Abreu et al. (2012) synthesized nanogels from a mixture of chitosan and cashew gum to encapsulate *Lippia sidoides* oil. The essential oil was loaded into the nanogels via the spray-drying method [71]. In another analysis, nanogels were prepared from a myristic acid and chitosan mixture to encapsulate the *Carum copticum* oil [72]. The oil-loaded nanogels exhibited more fumigant toxicity than the free oil over a longer period of time. To increase the sustained release of pheromones for longer periods, nanogels were prepared from a low molecular mass gelator [73].

4.1.2. Lipid-based nanomaterials

In addition to polymeric vehicles, lipid-based nanocarriers could be potential delivery systems for bioactive substances with better encapsulating efficiency and low toxicity [74, 75]. The lipid-based nanocarriers are able to encapsulate both the hydrophilic and hydrophobic or lipophilic active ingredients. For instance, nanoliposomes are vesicles consisting of a bilayer lipid with a watery interior at nanoscale level. Colloidal structures are formed by the arrangement of lipids, most commonly phospholipids in an aqueous solution [76]. Generally, a high-energy input is required to form bilayer vesicle otherwise they may form flat membrane like layer structure [77]. Most often the cholesterols are incorporated into the phospholipid membrane to increase the shape stability of the liposomal vesicles by modulating the fluidity of the lipid bilayer. The impregnated cholesterol prevents the crystallization of the acyl chains of phospholipids as well as provides steric hindrance to their movement, hence, reduces the permeability of lipid membrane to the solutes. The cholesterol also prevents peroxidation and acyl-ester hydrolysis of the liposome membrane by drying the lipid−water interface [78, 79]. In the absence of stabilizing agents the liposomes' or nanoliposomes' structures are not stable due to their geometrical constraints. So far, various methods have been investigated to stabilize the nano-sized liposomes to prolong their shelf life. These include lyophilization /freeze-drying, spray-drying and supercritical fluid (SCF) technology where lyophilization proved to be the best one used for stabilization [80-83]. The phase transition can be avoided by adding lyoprotectants [84]. Sugars such as monosaccharides, disaccharides, polysaccharides, or even synthetic saccharides can be used as lyoprotectants, however, among the disaccharides, trehalose proved to be the most effective [85].

Along with other applications, nanoliposomes are considered to be very efficient in encapsulating and delivering bioactive substances to targets of biological, biochemical, pharmacological, and agricultural interest [87]. In terms of pesticide loading nanoliposomes are flexible in nature and able to encapsulate hydrophilic (or water soluble) molecules during vesicle formation trapping along with aqueous media in the inner core of vesicles and hydrophobic or lipophilic molecules are incorporated into liposomal bilayers. It is notable that due to the lipophilic characteristic of the nanoliposomes, they are potential carriers for contact insecticide and allow the bioactive compounds absorb through the cuticle of the insect body. They also regularly facilitate the dispersion of hydrophobic AIs in aqueous solutions. Thus, both the water-soluble and -insoluble active ingredients can be delivered simultaneously. This may facilitate the application of multi-pesticide application (both contact and systemic), which will combat a wide range of agricultural pests.

However, high costs, low payload, and comparatively faster release of active ingredients are the disadvantages of this carrier material [75]. To delay the release, the coatings with polymers and various parameters in the synthesis process can significantly affect size, surface charge, dispersibility and even encapsulation efficacy. For instance, Bang et al. utilized lecithin (phosphatidylcholine) and cholesterol for the synthesis nanosized liposomes to encapsulate the pesticide etofenprox [88]. The size of prepared liposomes was reduced (up to 150 nm) by elevating the ratio of lecithin and extending homogenization time (2−6 min). The surface charge was positive (10.3 mV), whereas the low molecular weight chitosan (0.1%, w/v) coated nanoliposomes had a lower absolute value of zeta potential compared to the high molecular weight chitosan (0.1%, w/v) coated nanoliposomes. The surface charges changed from positive to negative due to a secondary coating with alginic acid (−21.8 mV). The size also changed remarkably in the ± 30 nm ranges after a secondary coating with alginic acid (0.1, 0.3, and 0.5%, w/v). However, their pesticide encapsulation efficacy declined slightly with a larger concentration of chitosan (0.1−0.5%, w/v) [88]. In another study, Hwang et al. reported that the nanoliposomes' size varied with the ratio and molecular weight of coating materials (chitosan) [89]. Recently, other vesicles namely, niosome was introduced that have similar structure to liposomes but is able to avoid the limitations related to stability and complexity of liposome. Niosomes are vesicles consisting of a bilayer of non-ionic surfactant and cholesterol with a watery interior. Alkyl or dialkyl polyglycerol ether based non-ionic surfactants are mainly used and could be a prospective alternative of nanoliposomes in pesticide delivery.

Other than lipid-based vesicles, non-porous solid lipid nano-matrix or nanoparticles (SLNs) were reported as being a superior carrier material relative to other nanocarrier materials such as polymeric nanoparticles, liposomes/nanoliposomes, nanoemulsions, and nanosuspensions in colloidal system [90-93]. It has been reported that SLNs can retain the beneficial properties of other colloidal carriers and have no disadvantages in terms of physical and chemical storage stability, toxicity, loading capacity, production scale, target-oriented releasing properties, feasibility, etc. [90]. Thus, SLNs are considered to be a promising colloidal carrier material in controlled-delivery systems. The SLNs may be either semicrystalline or crystalline, solid lipid spherical nanostructure substances, which are stabilized by surfactants. However, the main requirements of SLNs synthesis are lipids that are solid at room and physiological temperatures, surfactant(s)/emulsifier(s) and water. The lipid includes triglycerides, partial glycerides, fatty acids, steroids, and waxes. The choice of emulsifiers or surfactants needed to stabilize the aqueous lipid dispersion depends on the type of lipid utilized for the synthesis of SLNs. Various emulsifiers that differ in terms of charge and molecular weight can be used, but phospholipids may be one of the best choices, for example, soybean lecithin or egg lecithin. Various methods have already been developed for the synthesis of SLNs such as high-pressure homogenization microemulsion, and nanoprecipitation. High-pressure homogenization is most commonly used technique for large-scale production where this process involves either hot homogenization or cold homogenization.

Achieving physical stability in colloidal suspension of SLNs requires specific surface charge as well as storage at low temperatures [94]. The charged nanoparticles are prevented from being aggregated due to electric repulsion. Steric stability with a zeta-potential value of >8−9 mV is required for their proper stabilization. However, the application of SLNs in pesticide delivery is not well managed and still in its infancy. Only a few studies were found in which the pesticidal active ingredients were successfully loaded into the SLNs. For example, Lai et al. prepared SLN-based pesticide formulations by applying the high-pressure homogenization technique. The ecological pesticide *Artemisia* *arborescens* L essential oils were loaded into lipid as Compritol 888 ATO and stabilized by surfactants such as Poloxamer 188 or Miranol Ultra C32 [95].

4.2. Inorganic Nano-Porous Materials

Synthesis of inorganic porous nanomaterials with interesting hierarchical morphologies as well as their utilization has attracted much attention to enhance the sustainability of nano-delivered pesticide system. Along with the biodegradable polymer and lipid based nanocarriers, various inorganic nanomaterials have also offered a nontoxic, biocompatible, and stable alternative and have been used for controlled-release applications. Additionally, various inorganic nanoparticles also exhibited their competence as AIs for controlling a wide range of agricultural and stored grain pest. However, the available literature revealed that of the various inorganic nano/macron sized materials, nano-porous materials are highly significant for the preparation of CRFs of pesticide. So far various nano-porous materials have been synthesized whereas in terms of pesticide delivery silica-based porous nanomaterials as well as calcium carbonate nanospheres were found as the promising inorganic nano-porous carriers. These nanomaterials also have beneficial aspects on agricultural applications providing support to the plant against abiotic stress and soil amendments.

4.2.1. Silica-based porous nanomaterial

The synthesis of different porous silica has advanced rapidly for active ingredients delivery due to their controllable morphologies, mesostructures, and porosities, high level of biocompatibility, and ease of functionalization [96]. Depending on their surface structure and interior design, porous silica nanoparticles are grouped as mesoporous silica nanoparticles (MSNs) and porous hollow silica nanoparticles (PHSNs or HSNs). The pesticides are encapsulated by the MSNs or HSNs without forming any non-covalent binding between the active compounds and silica (SiO_2) nanoparticles. This process involves either adsorption of active compounds within the mesopores of silica nanoparticles or entrapment within the capillary pores. To deliver the pesticide as part of this process, the synthesis of porous silica is first required. Both MSNs and HSNs have exhibited their potential as carrier for pesticide delivery. Nonetheless, the efficacy of these materials varies according to their structural properties such as pore size, particle size, morphologies, porous structure and so on. Generally, sol-gel process is most commonly used for the synthesis of silica nanoparticles. In case of MSNs, the amphiphilic surfactants play the vital role, which provides basic structure. In contrast, for HSNs synthesis a template is required which is mainly responsible for hollow space.

The synthesis of silica-based porous materials began with the successful production of mesoporous silica nanoparticles (MSNs), known as “MCM-41”. Over the last two decades synthesis of various types of MSNs has fortified the utilization of MSNs as a vehicle for pesticide delivery. Depending on the morphology, structural arrangement, pore size, channel structure the MSNs denoted differently such as MCM-41, MCM-48, IBN-1, SBA-1, SBA-3, SBA-15, SBA-16, FDU-12, HMS and so on. The properties of different MSNs have been summarized in Table 2.2.

Table 2.2. **Pore size and structure of MSNs**.

Mesoporous silica	Space group	Pore diameter (nm)	Channel structure
MCM-41	P6mm	2-50	Hexagonal 1D/2D
MCM-48	Ia3d	2-5	Bicontinuous/cubic 3D
IBN-1		2	Cubic 3D
SBA-1	Pm3n	2-4	Cubic 3D
SBA-3	P6mm	2-4	Hexagonal 2D
SBA-15	P6mm	5-10	Hexagonal 1D/2D
SBA-16	Im3m	Min 1-6; max. 4-9	Body centred arrangement of cages
FDU-12	Fm3m	Min 4-9; max 10-12	Face centred cubic arrangement of cages
HMS	P6mm	2-5	Hexagonal

Whereas the porous structure of various MSNs have presented in Figure 2.7.

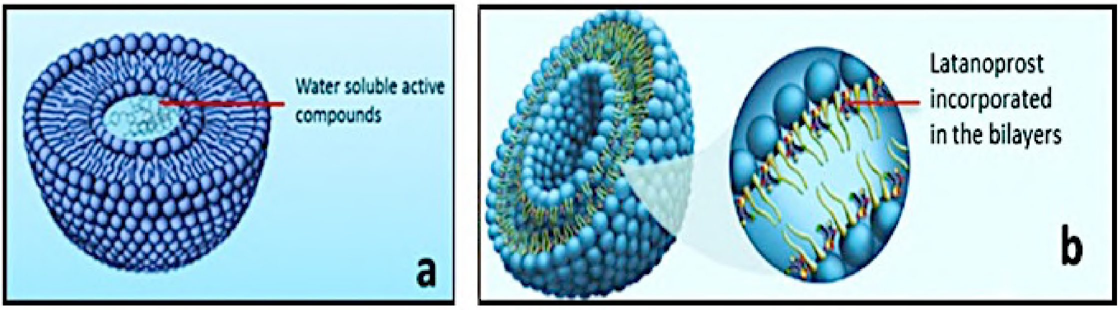

Figure 2.7. Schematic representation of (a) water-soluble active compounds at the inner core of liposomes and (b) liposomes with the drug latanoprost incorporated into the lipid bilayer (adapted from ref. [86]).

Thus, it is apparent that the pesticide loading capacity of the MSNs will be significantly different with each other (Table 2.3).

Table 2.3. Pesticide loading efficacy of different MSNs.

Mesoporous silica	Target pesticide	Particle size (nm)	Surface area (m^{2}g^{-1})	Pore diameter (nm)	Pore volume (cm^{3}g^{-1})	Loading method	Loading/ adsorption capacity (mg g^{-1})	Ref.
MCM-41		150	1020.00	2.40	1.03	Adsorption		[96]
MCM-41 (Imi)	Imidacloprid		754.00	2.00	0.50	(Diffusion)	3	
MCM-48		120	1250.00	2.00	1.35			
MCM-48 (Imi)	Imidacloprid		650.00	1.80	0.50		16	
SBA-15		200 (dia)	505.00	6.50	0.84			
SBA-15 (Imi)	Imidacloprid		415.00	5.10	0.75		4	
IBN-1		100	919.00	11.00	0.86			
IBN-1 (Imi)	Imidacloprid		700.00	10.20	0.70		7	
MSN		~160	810.00	3.20	0.67	Solvent		[97]
RMSN	Metalaxyl	~162	766.00	2.90	0.58	Evaporation	14%	
MSNs		288	1138.73	3.73	1.28			[98]
Py@MSNs	Pyraclostrobin	--	543.45	3.48	0.59		26.7%	
Py@MSNs-HTCC	Pyraclostrobin	299	29.02	59.79	0.22		28.5-41.6%	
Py@MSNs-HTCC (calcined)	-		960.17	3.88	1.14			
MSNs	--	200-300	808.90					[99]
Py-MSNs	Pyrimethanil		9.47			Simple immersion	29.77% (toluene)	
P-MSN	--		1356.00	3.75	1.65		1.5%	[100]
MSN-TA			956.40	2.31	0.59			
2,4-D@MSN-TA	2,4-D		454.80	--	0.03		21.7%	

TA-Trimethyl ammonium

The structural differences of MSNs have also significant effect on releasing behaviour of pesticide. For instance, Popat et al. observed that 40% imidacloprid was released from all the experimental MSNs into water within few hours but MCM-41 and SBA-15 showed a slightly slower releasing pattern due to their 2D channel structure compared to MCM-48 and IBN-1 those were structured with 3D channel. The initial burst release was observed due to diffusion of imidacloprid from hydrophilic mesopores and dissolution silica in the medium (water) [96]. In their study, Wanyika found that 76% free metalaxyl was released into soil whereas only 11.5% metalaxyl was released from MSNs into soil over 30 days. The release of metalaxyl from MSNs in water was faster than soil and around 47% metalaxyl was released over 30 days. Adsorption-desorption isotherms showed hysteresis (H=3.059) [97]. The release rate of AIs from MSNs can also be made faster with surface modification. It was observed that less than 40% free pyraclostrobin was released into 30% aqueous methanol solution containing 0.5% Tween-80 emulsifier over 10 h. In contrast, 55% pyraclostrobin was released from bare MSNs whereas 72% pyraclostrobin was released from chitosan-caped MSNs within 2 h. This is due to the changes of crystalline structure of pyraclostrobin whereas chitosan was adsorbed water that also made the AIs ready to release [98]. The condition of the release medium such as pH, temperature, ionic strength can also affect the release rate. It was observed that 56% pyrimethanil was released into phosphate buffer solution having pH 6.13, 6.93 and 8.06 over 30 h. After 30 h, release of pyrimethanil was faster in low pH (6.13) condition and around 99% pyrimethanil was released over 60 h. In contrast, 93% and 91% pyrimethanil was released with pH values of 6.93 and 8.06 respectively over 80 h [99]. Similarly, pH of the releasing medium significantly affected the releasing behavior of 2,4-D from trimethyl ammonium modified MSNs (MSN-TA). 16% pesticide was released into water with pH 3.0 within first 2 h while 43% pesticide was released at pH 10.0. Ionic strength of the releasing medium enhanced the releasing rate of 2,4-D. Around neutral pH 40% pesticide was released from 2,4-D@MSN-TA while in presence of 0.1 M NaCl 90% pesticide was released over 5 h. Temperature dependent release of 2,4-D was also observed from 2,4-D@MSN-TA. 96%, 75% and 52% pesticide was released at 40, 30 and 20 °C respectively over 900 min [100].

HSNs act as carrier materials for both oil-soluble and water-soluble pesticides, and loading efficiency depends on their morphological features. In their study, Chen et al. loaded both oil-soluble and water-soluble pesticides, namely avermectin and validamycin, respectively, in HSNs [2, 101]. However, pesticide-loading efficacy often is controlled by pore size that can be increased by improving the loading methods. For instance, the pesticide avermectin was loaded into the HSNs employing the simple immersion method and the amount of pesticide loading reached 58.3% (w/w) [2]. Pesticide loading by simple immersion takes longer to reach the point of adsorption saturation; for example, for avermectin this process took 2 weeks due to the tiny nanosized pores (around 5 nm) in the shell of silica nanoparticles. It is expected that the open pore network and hollow interior of PHSNs will facilitate the transport of vapors and gases through the entire volume of the material, and pressure can be an important variable that will enhance the adsorption [102]. On the basis of this mechanism, Liu et al. loaded the pesticide validamycin using the supercritical fluid drug loading (SFDL) process. It was observed that this process improved the loading capacity and decreased the adsorption saturation period compared to the simple immersion method. At a weight ratio of validamycin to PHSNs of 2:1, ~ 36% wt of validamycin was loaded within 9 h via SFDL, whereas 14 days was required to load only 25% wt with the simple immersing method [101].

The pesticidal active compounds can also be encapsulated by the porous silica nanoparticles during synthesis of HSNs. Different soft templates including emulsion droplets are utilized to decorate the porous silica with a hollow structure. Generally, the pesticides are dissolved into the water phase or oil phase during synthesis and then directly encapsulated into the hollow interior during synthesis. Qian et al. encapsulated tebuconazole (fungicide) into the porous hollow silica nanospheres during synthesis through the formation of miniemulsion, where the emulsion droplets functioned as a soft template for the synthesis of HSNs. Furthermore surface functionalization of HSNs can be an effective tool for improving adsorption capacity, where the active compounds are absorbed by the surface of silica nanoparticles [103]. However, in pre-synthesis loading process the release of AIs is controlled by shell thickness of HSNs whereas the release is controlled by pore diameter while pesticides are loaded to HSNs after synthesis [104].

4.2.2. Porous calcium carbonate nanospheres

Calcium carbonate ($CaCO_3$) is considered as one of the most abundant inorganic biominerals. The utilization of this nanomaterial as carrier for biomolecule delivery is attracting more and more attention because it possesses the advantages of low cost, environmental friendliness, and high stability. Its application in drug delivery to human furthermore ensures its biocompatibility [105]. The application of nano-$CaCO_3$ is not limited to drug delivery however, this nanomaterial at their porous structure has exhibited as potential nanocarrier for pesticide deliver as well, where the pesticide could be loaded easily via electrostatic interaction as well as hydrogen bonding interaction [106-108]. Hua et al. reported that $CaCO_3$ nanoparticle not only provides nutrient to plants but also enhance its pest tolerance ability [109].

4.3. Natural Nano-Porous Materials

In search of nano-porous materials as carrier for pesticide delivery those are crucial for the development of new, targeted and low residual delivery system, some nature based porous mineral materials are considered to be ready to go due to their world-wide natural deposits, low cost, availability and biocompatibility.

4.3.1. Nanoclays

The application of clay materials has a long pedigree records even before their structure was determined and understood. Their utilization as carrier for pesticide delivery is considered as one of the most suited environmental benign approaches due to their natural sources. It is expected that clays will not add extra threat to the environment. The physicochemical properties of clays such as biocompatibility, thermal stability, natural abundance, low cost and other environment friendly characteristics have made them excellent candidate for the carriers for pesticide.

Nanoclays belongs to the wider group of minerals which are commonly described as aluminium silicates or hydrous silicates with sheet-like structures. The sheet-structured hydrous silicates are generally termed as phyllosilicates, which are very important because they build the structure of individual clay minerals [110]. The phyllosilicates constituted a layered structure of two types of sheets, specifically tetrahedral silicate and octahedral alumina. The diversity of clay minerals depends on the arrangement of these sheets in the layer, including 1:1 type of clay (e.g., kaolinite), 2:1 type of clay (e.g., montmorillonite), and 2:1:1 type of clay (e.g., chlorite).

The thickness of the layers of primary clay particles is in the nanometer range, and consequently clay and clay minerals may be regarded as nanomaterials of geological and pedological origins, although their length varies in the millimetre range [111]. For instance, the thickness of the elementary layers of smectites can vary from 0.96 to 1.50 nm but by a few tenths to hundreds of nanometers in length and width [112]. However, the thickness of the elementary layers varies from clay to clay minerals. The clay layers are attracted by each other and may be joined together in a clay crystallite due to van der Waals force, interlayer cations, electrostatic force or hydrogen bonding [113] leaving an interlayer space which is known as the gallery (Figure 2.8).

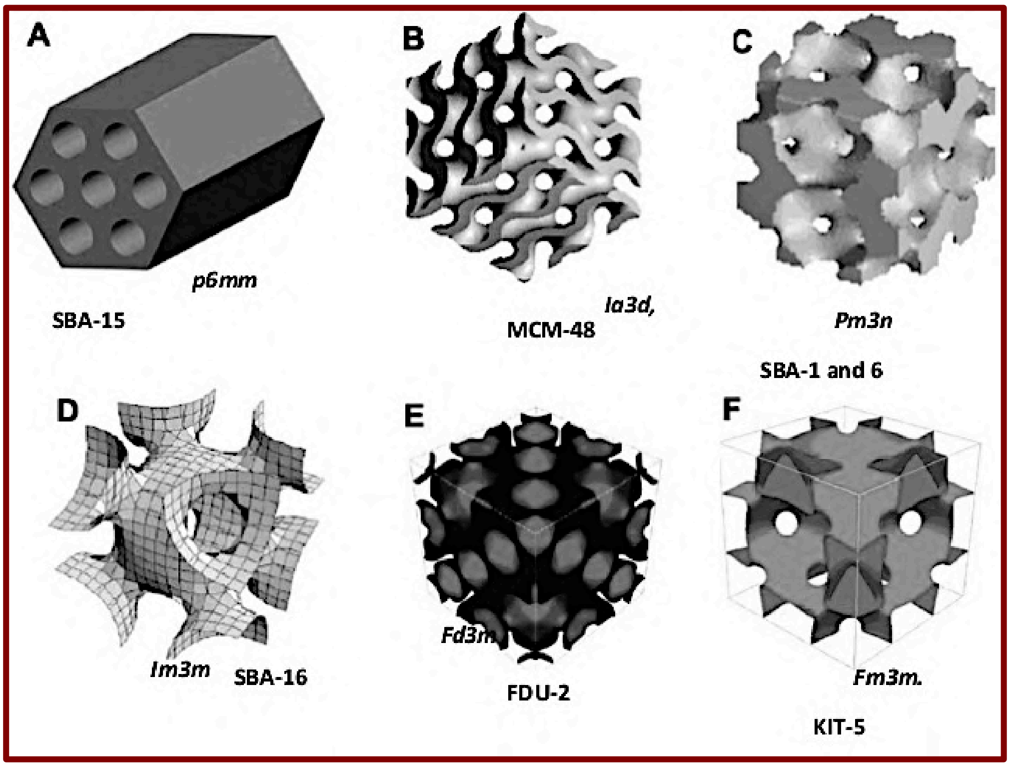

Figure 2.8. Structure of several ordered mesoporous silica.

The active compounds are mainly encapsulated into this interlayer space or gallery. The penetration of active compounds into the interlayer space is also denoted as intercalation [114].

The clay or organoclay minerals can be modified with polymers forming polymer−clay nanocomposites. Depending on the state of layered silicates, polymer−clay nanocomposites are formed as conventional nanocomposites, intercalated nanocomposites, and exfoliated nanocomposites. The formation of polymer−clay nanocomposites is influenced by their preparation methods. Chen et al. reported that exfoliated nanocomposites are mainly synthesized via the in situ polymerization and solution method, whereas it is easier to synthesize intercalated nanocomposites with the melt processing method. For instance, a molten low-polar polymer like polystyrene can be directly intercalated into the alkyl-ammonium modified smectites [115]. The coexistence of exfoliated and intercalated nanocomposites can also be observed. Some other methods of polymer-clay nanocomposite formation may be co-vulcanization, solid state intercalation, sol-gel, emulsion, supercritical CO_2 fluid methods and others [116]. When the polymers originate from a natural source such as starch, cellulose, or their derivatives, such as chitosan and gelatin, the composites are termed bio-nanocomposites. The biopolymers are considered to be eco-friendly polymers and can be used as an alternative to conventional polymers for environmental application. They are able to synthesize the nanocomposites similarly to a conventional polymer. For example, Chevillard et al. prepared new pesticide formulations combining Ethofumesate (model pesticide) and polymer−clay nanocomposites via the bi-vis extrusion process. The nanocomposites were designed with wheat gluten and three montmorillonites (MMT), that is, unmodified MMT (HPS) and two surfactant-modified MMTs (C30B and D72T). In their investigation, well-dispersed nanoclays were observed, which indicated that wheat gluten was able to interact with modified and unmodified MMT, and a well-intercalated−exfoliated nanocomposite structure was formed [117].

The hydrophilic properties of the clay minerals' surface can be achieved through hydration of exchangeable cations and in the presence of Si−OH clay mineral groups. When water is absent, the clay minerals have a higher affinity to the hydrophobic compounds [118]. The hydrophilic surface of the clay minerals can become hydrophobic during the modification of clay minerals as "pillared clay" with a suitable pillaring agent. Both the inorganic and organic compounds can be used as a pillar. The pillared clays can be prepared according to a simple procedure of replacing exchangeable cations (Ca^{2+} or Na^+) into the interlayer space with large polyoxocations of a multivalent metal such as Al, Si, Cr, or Zr in which hydroxy-oxides pillars separate the platelets from each other. In this way, the pillared clays possess a porous structure with a high surface area [119]. In their analysis, Gerstl et al. prepared pillared clay modifying the sodium-montmorillonite with $Al(OH)_x$ and the herbicide alachlor was successfully loaded into the interlayer of pillared clays. The clay materials can also be modified with heat treatment or acid treatment. In their analysis, Bojemueller et al. investigated the morphology of thermally modified bentonite and its interaction with pesticide. They found that the mesopore (diameter = 2−50 nm) volume of calcinated bentonite rose above 450 °C, whereas the micropore volume decreased. They also noted that pesticide molecules interact with aluminum ions or oligomeric hydroxoaluminum cations, which enriched at the edges of the silicates due to the heat treatment [120].

4.3.2. Layered double hydroxides

Utilization of layer double hydroxides (LDHs) has attracted much attention for the preparation of controlled/slow release pesticide formulations due to their high buffering capacity, high water retention ability, acid neutralizing potentials, and high affinity to ubiquitous carbonate ions, which may facilitate the preparation of complete and controlled release pesticide formulations through intercalation of the pesticide molecules. Generally, LDHs are anionic lamellar compounds made up of positively charged brucite ($Mg(OH)_2$) type layers of mixed metal hydroxides (Figure 2.9).

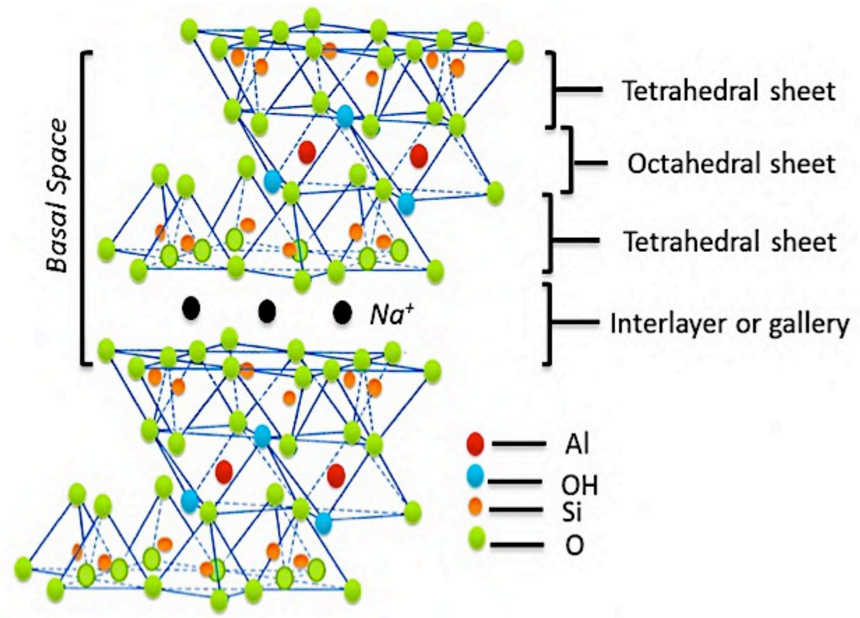

Figure 2.9. Structure of sodium montmorillonite (2:1 type) of clay minerals (adapted from ref. [13]).

The brucite layer mainly consists of shared octahedron of hexacoordinated of Mg^{2+} cation with hydroxide groups, thus, play the key role of forming infinite two-dimensional nanosheets. The thickness of the nanosheets is around 1 nm and a lateral size ranging from sub-micrometer to several tens of micrometers. In the octahedron, the hydroxide ions remain at the vertexes position whereas the metal cations occupy the central position. However, LDHs are produced due to partial isomorphic substitution of Mg^{2+} ions by a trivalent cation having a similar ionic radius, such as Al^{3+}. The positive charge in LDHs also generates due to this substitution. To compensate the positive layer charge, the anions occupy the interlayer positions. The generic formula of LDHs has been represented in the literature as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$, where M^{2+} and M^{3+} denote as divalent and trivalent metal cations respectively, such as M^{2+}= Mg^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+} or Ni^{2+} and M^{3+}= Al^{3+}, Ga^{3+}, Fe^{3+}, or Mn^{3+}; A^{n-} is the non-framework charge compensating inorganic or organic anions. The most commonly anions present in the interlayer are CO_3^{2-}, NO_3^{-}, Cl^{-}, SO_4^{2-}, or could be replaced by RCO^{2-} along with water in hydrated form; and x is the mole fraction of M^{3+} normally ranges between 0.2-0.4. For instance, hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$), a naturally occurring layered mineral is the true representative of carbonate phase of MgAl-LDH where the ratio of M^{2+}: M^{3+} is 3:1 (Figure 2.10). Thus, the divalent and trivalent metals cationic ratio significantly affects on charge density of LDHs.

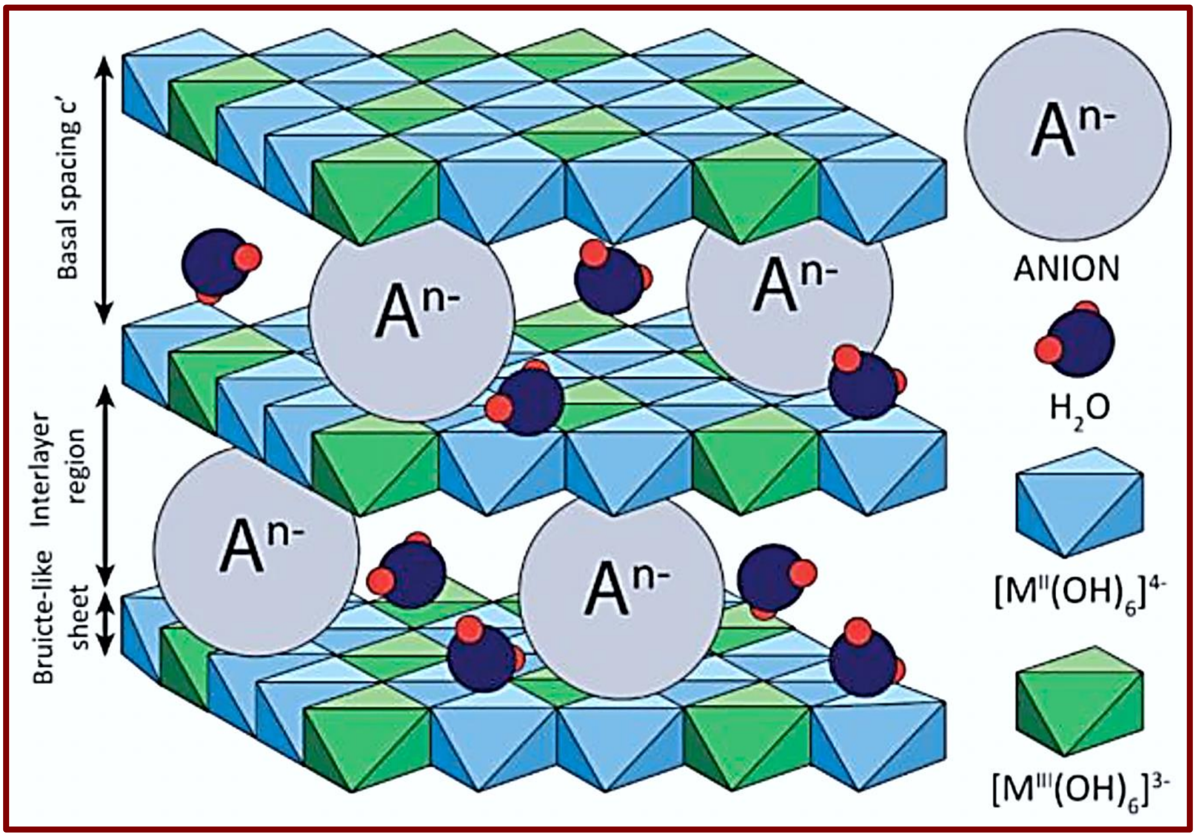

Figure 2.10. **Schematic representation of the LDH (hydrotalcite) structure (adapted and modified from [121]).**

Thus, LDHs are good carrier for anionic pesticide. In their investigation, Cardoso et al. (2006) intercalated anionic herbicides 2,4-D, MCPA, and picloram into MgAl-LDH where LDHs were found to be effective for encapsulating the natural bioactive compound [122]. Whereas Park et al. (2010) evaluated the potential of LDHs as an encapsulated material for a natural antibiotic, cinnamate, which also serves as a fungicide. Cinnamate was intercalated using the co-precipitation method, where the intercalated amount was 42 wt% [123].

4.3.3. Clay nanotubes

In addition to layered structured clays and LDHs, the hollow tubular structured clays such as halloysite clay have added a new dimension to utilize natural clays as carrier for pesticide delivery. Halloysite nanoclay is considered as natural wonder and true representative of nature-based nanomaterial not only for their nano-size diameter but also having nano-sized lumen structure. The halloysite is mainly an aluminosilicate clay mineral having an external diameter ~50 nm and inner diameter ~10-15 nm but varies in length from to [124]. Due to their nano-sized tubular structure, halloysite clay is known as halloysite nanotube (HNT) [125]. It has a similar structure to kaolinite but process a significant difference in presence of an additional water monolayer between the adjacent clay layers. The chemical formula of halloysite nanotube is $Al_2SiO_5(OH)_4$.nH2O where ‘n’ indicates the presence or absence of water. The space between the inner and outer layer of aluminum hydroxide is 10 Å in the hydrated form (n=2) and 7 Å in the anhydrous form (n=0) [126]. The external surface of HNT consists of mainly siloxane group (Si−O−Si) whereas the inner lumen is structured with aluminol group (Al−OH). The Al-OH and Si-OH can also be found at the edges and in defects of the aluminosilicate layers. Normally, pure halloysite is white in colour but those obtain from natural deposits varies from yellowish to brown and some greenish colour due to the presence of different impurities. The size, diameter, pore size, surface area and morphology also vary on their natural sources. In some natural deposit platy and spheroidal structured halloysite was also found. However, the hollow tubular structured halloysite nanoclay is the most attractive form that is using in current research because of their large surface area, low density, mechanical and thermal stability and surface permeability [127].

So far, the application of halloysite nanotube as a carrier material has been investigated for delivery of a wide range of chemicals and bioactive agents [129]. Recently, the application of HNTs as a carrier for pesticide delivery was also observed in the literature (Figure 2.11) [128, 130, 131].

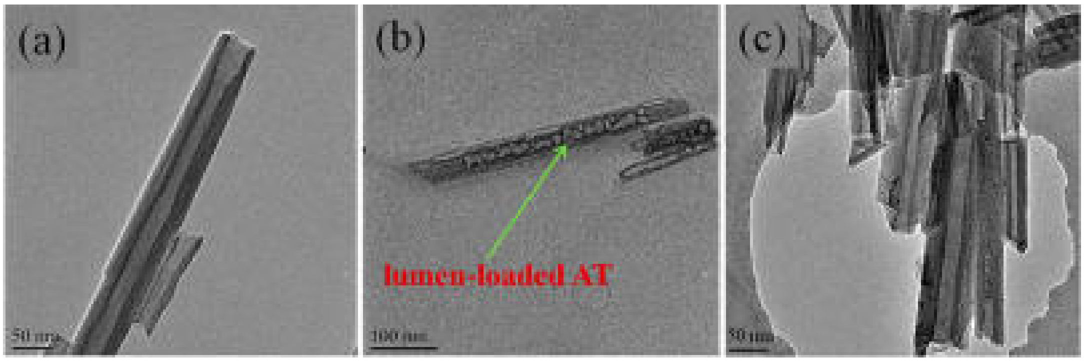

Figure 2.11. TEM images of (a) pristine HNTs; (b) HNTs-AT before the deloading of AT; and (c) HNTs-AT after the deloading of AT [128].

In a comparison study, HNT showed better loading efficiency for the herbicide namely, amitrol compared to kaolinite. The loading capacity in HNT also enhanced by surface modification with methoxy due to expansion of coiled interlayer space. However, the herbicide releasing behavior was much slower in surface modified kaolinite than HNT because of the less amount intercalated herbicide in HNT than kaolinite [131]. Additionally, In comparison with other tubular nanomaterial such as carbon nanotube, halloysite nanotube is also considerably cheaper and bears an ecofriendly application prospective [124].

Similarly, the tubular structured other clay nanomaterials such as imogolite nanotube (INT) and chrysotile nanotube and antigorite nanotube could be used as carrier for pesticide delivery. However, the lumen diameter of imogolite nanotube is around 1-5 nm; thus, only suitable for smaller pesticide molecules whereas environmental application of chrysotile nanotube and antigorite nanotube is controversial.

4.3.4. Zeolite

Natural zeolites are considered as one of the bestowed materials of nature. Naturally, zeolites are formed in the areas of volcanic rocks and ash layers those are react with alkaline ground water. In respect to their widespread applications, researchers and mineralogists have referred them as ‘the magic rock’ [132]. So far their massive applications have been observed in chemistry, biotechnology, environmental pollution control and pesticide and medical industry because of their attractive physical and chemical properties especially high cation exchange capacity, hydration-rehydration features and catalytic activities [132]. In agriculture, zeolites are used as soil enhancers, soil conditioners, livestock feed additives, pesticide active ingredients, hydroponic growing media and so on [133, 134]. They are also used to serve the purpose of fertiliser management, mycotoxin control, and environmental pollution control [133]. Zeolites are similar to other clay minerals structured with tectosilicate aluminosilicates instead of phyllosilicates. In plant protection, zeolite itself exhibited pest control efficacy over a wide range of agricultural pests including fungus and various insect pests [135, 136].

The zeolite structure may be represented by the formula, $M_{x/n}[(AlO_2)_x\,.\,(SiO_2)_y]$. wH_2O; where M is an alkali or alkaline-earth cation (Na^+, K^+, Li^+ and/or Ca^{2+}, Mg^{2+}, Ba, Sr), n is the cation charge, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell and the ratio y/x usually has values ranging from 1 to∞ [137]. According to Valtchev and Tosheva, '*zeolite is a crystalline aluminosilicate built of oxygen-linked tetrahedral silicon and aluminum atoms that form a three-dimensional microporous structure comprising channels and voids occupied by alkali or alkali-earth cations and water molecules'* [138]. From this definition, it is considered that the basic building unit (BBUs) or primary-building unit (PBU) of zeolite consisted of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra commonly denoted as TO_4 (T is mainly tetrahedrally coordinated Si or Al) [137]. Thus, framework of zeolite is built by interlinked tetrahedra. In this case, each tetrahedron is connected with four neighbours by sharing the vertex O atoms and forms the three-dimensional framework. Zeolites framework is complex because of the wide arrangement abilities of the BBUs among them that lead to the formation of chain or layer like structure known as secondary building unit (SBU). A more complex building unit termed as composite building unit (CBU) further structured with different combination of BBUs that usually reflects the characteristic of zeolite framework. Every zeolite is generally classified based on the CBU type. The structural commission of international zeolite association (IZA-SC) has assigned a three lowercase letter to each of these CBU. CBUs are interconnected with each other leaving cage and cavities/supercages (Figure 2.12) in zeolite framework which is the most important phenomena of zeolite in relation to pesticide delivery those accommodate the guest molecules i.e., pesticide AIs.

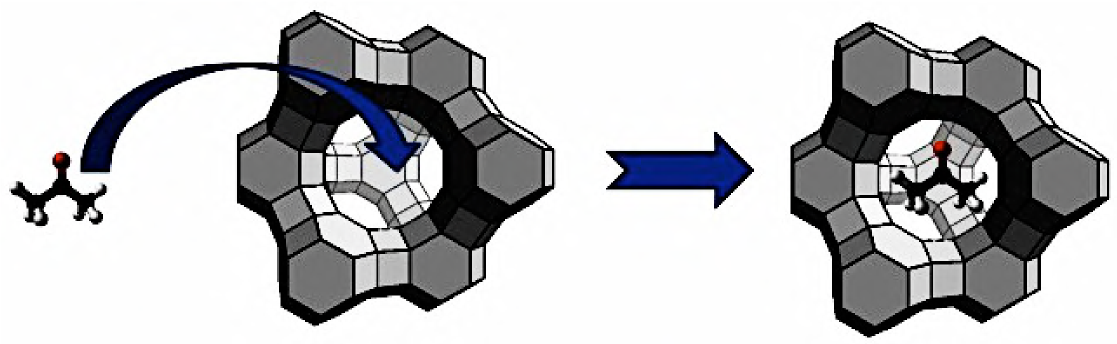

Figure 2.12. Adsorption of an acetone molecule into a zeolite Y supercage (window 7.4 Å, cage 13.2 Å) (adapted from ref. [139]).

The application of zeolite as a carrier for pesticide delivery is promising due to their porous structure but only limited work has been observed in the literature [140]. The available literature also reported that most often the pore size (<2 nm) of zeolite is too small to penetrate the large pesticide molecule when the AIs are larger than 20 °A. Zhang et al. prepared controlled release formulations of paraquat by loading them into surface modified zeolite Y (Carbide, LZY-52) [140]. Paraquat was loaded to zeolite via adsorption following ion exchange process. It was assumed that paraquat (13.4 X 6.4 X 3.4 °A) would easily ion exchanged to zeolite Y through its super-cages (13 °A diameter) only [140]. In spite of pore size limitations, the physicochemical properties of zeolite mentioned earlier made them an excellent adsorbent to remove pesticide from aqueous solution and the research works have been maximized in this area. Surface modification with polymers, surfactants or different silylation agents was found as promising approaches to enhance the sorption capacity. Surface modifications or functionalization also delay the release of AIs from pesticide-adsorbed zeolite through creating film-barrier. In this case, the pesticides are released via diffusion process has two different steps; firstly, intrazeolitic diffusion of ions within zeolite framework and secondly, out of the surface modified zeolite framework [140]. However, layered structured montmorillonite clay showed higher 2,4-D sorption capacity compared to zeolite (clinoptilolite and zeolite Y), whereas in zeolite Y exhibited higher sorption capacity than clinoptilolite [141]. Thus, it could be assumed that structural differences of zeolites including pore size are influential factors on their sorption capacity.

Owing to the potential application of zeolite, synthesis of zeolites has received much attention. Till to date, 235 zeolites framework have been described by IZA-SC including more than 40 natural zeolites (http://www.iza-structure.org/databases/). Different zeolite frameworks have been presented in Figure 2.13.

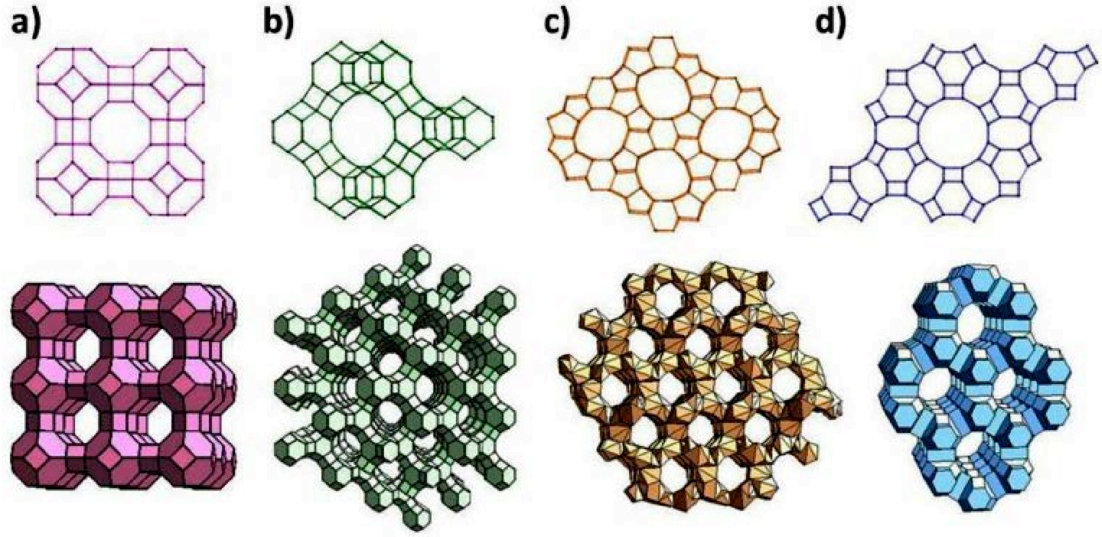

Figure 2.13. Representative zeolite frameworks, (with sodalite pore openings). (a) zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) Zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) D—dimensions of channel system (adapted from ref. [139]).

Synthesis of micro-mesoporous zeolites, micro-macroporous structured zeolites and micro-meso-macroporous structured zeolites are the promising aspect of recent studies for enhancing the mass transport properties of zeolites [142]. For an example, Ramos et al., reported the synthesis of mesoporous zeolite (pore diameter >50 nm) while evaluated their potentialities as a carrier for insect pheromone namely, rhychophorol [143]. Synthesis of nanocrystalline zeolites also supposed to be an effective approach to receive the benefits of nano scale material [144]. For instance, a nanocrystalline zeolite with a crystal size of 50 nm has an external surface area of >100 m^2 g^{-1} whereas a 500 nm zeolite crystal has less than 10 m^2 g^{-1} of external surface area. Various green synthesis routes of zeolite enhanced its possible ecofriendly application [145, 146].

4.4. Other Nano-Porous Materials

Some other nano-porous materials that could be promising for controlled release pesticide delivery include

- Carbon nanotube
- Carbon nanosphere
- Dendrimers
- Porous calcium carbonate nanoparticles
- Polymerosomes
- Nanostructured lipid

5. Summary and recommendations

Nanomaterials have the potential to act as guard for pesticides, biocide and biopesticide. In terms of agrochemical (pesticides, fertilisers, growth hormones, etc.) delivery, nanoscale particles have novel properties that can increase the agrochemicals' efficiency and make the delivery system "smart". Through a smart delivery system, chemicals can be delivered in a controlled and targeted manner that is similar to nanodrug delivery to human.

Cost of processing of nano-based pesticide formulations should be low and safe to the environment as well as to the users. They should not have environmental hazards due to degradation and additives in response to hydrolysis, oxidation, solar radiation, heat and biological agents. The size and dissolubility of nanocarriers should be addressed carefully. Through studies are required to evaluate biotransformation of nanocarriers to the environment. Regulatory framework and guidelines for application of nanomaterials to the environment need to be established/developed.

It is expected that nanoencapsulated pesticide will use the similar pathways of commercial pesticide, i.e., direct and indirect contact with nanoencapsulated pesticides such as dermal adsorption, direct inhalation of nanoencapsulated pesticides or air contaminated with nanoencapsulated pesticides and exposure through the food chain, that is, eating food and drinking water contaminated with nanoencapsulated pesticides. Therefore, utilization nano-sized carrier materials are the major concern related to their human toxicity and eco-toxicity which depends on their properties as below:

- Size and size distribution
- Shape and aspect ratio
- Specific surface area
- Solubility
- Surface chemistry
- Surface charge
- Elemental and chemical composition
- Aggregation and agglomeration
- Degradation process and by-products

Thus, before application to environment their toxicological aspect must be evaluated. However, the utilization of nanocarrier materials in cosmetics and personal care products as well as carriers for drug delivery to human ensures their potential future application near future.

In this contrast, natural polymer based nanocarriers are preferred because of their natural sources, biodegradability, availability and low cost. Starch, chitosan, gelatin, dextran, albumin, lignin, chitin, cellulose, and alginic acid can be used as natural polymers in controlled release formulations. Other biopolymers like PLA (polylactic acid) or block copolymers such as PLGA (poly lactide-co-glycocide) attracted much interest. Water insoluble biodegradable synthetic polymer such as poly-ε–caprolactone (PCL) could be a good choice for developing more efficacious controlled release pesticide formulation. Where block copolymers are the best choice for the preparation of polymeric nanocarriers. In addition, lipid based nanocarriers are best suited for the delivery of contact insecticide rather than systemic.

Among natural nanoporous materials nanoclays are mostly suited for more hydrophobic and cationic pesticide while they are also able to interact with pesticide molecules via cation exchange process, hydrogen-bonding interaction thus establishes controlled release mechanism. In contrast, LDHs and halloysite nanotubes are mostly suited for anionic pesticide such as 2,4-D. However, HNTs are suited to all types of pesticide because of their larger inner tube diameter. Zeolites are generally possessed crystalline frameworks and ordered networks of micropores (typically 0.25–1.5 nm), have been widely used in agricultural application including pest control. While their application as carriers for pesticide delivery is limited as most of the organic pesticide compounds are too large to penetrate the zeolite framework or to the inner cavity through the micropores. Their high adsorption capacity make it possible to utilize them for the preparation of controlled release pesticide formulations through controlling the rate of diffusion of pesticide molecules present at inner and outer side of the micropores. Zeolites with hierarchically porous structures have garnered much attention due to their highly attractive properties. Hierarchically structured zeolites integrate at least two levels of porosity and present the advantages associated with each level of porosity, from selectivity to mass transport.

Lastly, the inorganic based nano-porous materials are able to provide protection of active ingredients from degradation and transformation. However, their environmental fate and toxicological aspect must be evaluated before application.

APPENDIX A

Definition of Pesticide

Pesticide may represents as natural or synthetic chemicals or agents those have the ability of -

- Destroying, stupefying, repelling, inhibiting the feeding of, or preventing infestation by or attacks of, any pest in relation to a plant, a place or a thing; or
- Destroying a target plant; or
- Modifying the physiology of a plant or pest so as to alter its natural development, productivity, quality or reproductive capacity; or
- Modifying an effect of another agricultural chemical product; or
- Attracting a pest for the purpose of destroying it.

Types of Pesticide

On the basis of target pests the pesticides are generally categorized as follows:

- Insecticides: Used to kill or control insect pests.
- Acaricides (or miticides): Used to kill or control fleas, ticks and mites
- Fungicide: Used to kill or control plant pathogenic fungus.
- Nematicide: Used to kill or control nematodes.
- Bactericides: Used to kill or control harmful bacteria.
- Algicides: Used to kill or control or slow the growth of algae.
- Rodenticides: Used to kill or control rodents like mice, rats, and gophers.
- Molluscicides: Used to kill or control slugs, snails and other molluscs.
- Piscicides: used to kill fish to eliminate a dominant species of fish in a body of water, as the first step in attempting to populate the body of water with a different fish. They are also used to combat parasitic and invasive species of fish.
- Avicides: Used to kill or control crop-destroying birds.
- Herbicides: Used to kill or control weeds/unwanted plants where they grow. e.g., ryegrass

On the basis of function the pesticides are categorized as follows:

- Contact or non-systemic: Non-systemic pesticides are generally controls a pest or disease as a result of direct contact with the causal organisms via inhibiting their growth.
- Systemic: Systemic pesticides are taken up by the roots and transported throughout the plant. Thus, systemic pesticide either controls weed directly or causal organisms when they are administrated orally.
- Repellents: These pesticides are designed to repel unwanted pests, often by taste or smell.
- Fumigants: Produce gas or vapour intended to destroy pests in buildings or soil.
- Disinfectants: Used to control germs and microbes such as bacteria and viruses.
- Attractants: Attract pests (for example, to lure an insect or rodent to a trap)
- Pheromones: Biochemicals used to disrupt the mating behaviour of insects
- Insect growth regulators: used to disrupt normal growth of insects.

On the basis of chemical moieties the insecticides are categorized as follows:

- Organochlorine: These are mainly chlorine containing synthetic organic compounds act on act on the nervous system of insects. They include substances such as DDT, dieldrin, chlordane, heptachlor, endosulphan etc.

- Organocarbamate: These are mainly organic compound derived from carbamic acid such as aldicarb, carbofuran, carbaryl, ethienocarb, fenobucarb, oxamyl, methomyl etc.
- Organophosphate: These are synthetic organic pesticides that are manufactured from carbon chemicals and also contain phosphorus. They include chlorpyrifos, dichlorvos, malathion, diazinon, temephos etc.
- Synthetic pyrithroids: These are insecticides that have been chemically manufactured (man-made) to work like naturally occurring pyrethrins. Chemicals belongs to this group are generally low in toxicity to humans, but are very effective against a wide variety of insect pests. Some of the examples are bifenthrin, permethrin, bioresmethrin, tetramethrin, deltamethrin etc.
- Neonicotinoid: These are a class of neuro-active insecticides chemically similar to nicotine. Some of the neonicotinoid pesticides are imidacloprid.

APPENDIX B

Table A2. List of nano-porous materials and their efficacy in pesticide delivery.

Sl. No.	Pesticide/ Biocide	Encapsulation material	Nano-porous carriers	Improved features achieved due to nanoencapsulation	References
Commercial pesticides					
	2,4-D	Silica nanospheres	MSNs	Slower release of the active ingredient was achieved up to 26 days	[147]
	AI	Poly-(ε-caprolactone) (PCL)	Nanospheres	Better stability of nanospheres was obtained in an aqueous suspension over two months	[148]
	Acephate	PEG originated block copolymers	Nanocapsules	Nanoencapsulated acephate was more efficacious than commercial formulations where retained greater functional integrity over time	[149]
	Amitrol	Halloysite nanotube	HNTs	Loading capacity was increased form 17.5% to 30.5% in methoxy modified HNTs compared to pristine HNTs and slow releasing properties were observed.	[131]
	Atrazine	Halloysite nanotube	HNTs	AT loaded in nanotubes displayed much slower release from PVA/ST film in water than free AT; for example, the total release amount of AT from PVA/ ST film with loaded AT was only 61% after 96 h, while this value reached 97% in PVA/ST film with free AT.	[128]
	β-cyfluthrin	PEG originated block copolymers	Nano-micelles	Slow release of the AI compared to commercial pesticide formulations and application rate of β-cyfluthrin can be optimised to achieve insect control at the desired level and period.	[66]
	Carbofuran	PEG originated block copolymers	Nano-micelles	Applications of the AI can be optimised to achieve insect control for the desired period depending on the matrix of the polymer used	[69]
	Carbofuran	PEG originated block copolymers	Nano-micelles	Under field conditions, developed CR formulations of carbofuran more effective managed pests than the commercial formulation	[67]

Carbofuran	Bentonite, kaolinite and fuller’s earth with polymer	Nanocomposites	Adding clay particles in the formulations reduced the release of active ingredients	[150]
Deltamethrin	Chitosan coated beeswax (solid lipid)	Solid lipid nanoparticles (SLNs)	Chitosan-SLNs demonstrated ability to protect deltamethrin against photodegradation	[151]
Deltamethrin	Corn oil (liquid lipid) and beeswax (solid lipid)	Nanostructured lipid carriers	Higher payload, slower release rate and higher photo-protection was obtained due to incorporation of corn oil compared to SLN	[152, 153]
Emamectin benzoate	Polyacrylate (PAL)	Nanoparticle conjugation	Photostability and insecticidal effects of the novel emamectin benzoate formulation increased than those of the commercial pesticide formulation	[154]
Entofenprox	Chitosan coated lipid	Liposomes	Better pest control efficacy was observed for a longer period	[89]
Ethofumesate	Montmorillonites and wheat gluten	Nanocomposites	Slow releasing properties were achieved due to clay/ pesticide interactions	[117]
Gamma-cyhalothrin	Compritol 888 (lipid)	SLNs	Reduced toxicity to aquatic fish (*Brachydanio rerio*) and daphnia (*Daphnia magna*) by a factor 10 and 63, respectively, compared to the traditional emulsifiable concentrate	[155]
Imidacloprid	PEG originated block copolymers	Nano-micelles	The developed CR formulations slowly released in water the AIs than commercial formulations	[63]
Imidacloprid	Poly-ethylene glycol originated block copolymers	Nano-micelles	CR formulations of imidacloprid exhibited significantly better pest control efficacy compared to its commercial formulations	[156]
Imidacloprid	Chitosan -co-(D,L-lactide)	Nano-micelles	Sustained release of imidacloprid was achieved	[60]
Imidacloprid	PCA–PEG–PCA triblock copolymers	Nanocapsules	Due to nanoencapsulation of imidacloprid, dosage of pesticide and their environmental risk significantly decreased	[61]
Imidacloprid	Sodium alginate	Nanocapsules	Retained better pest efficacy over uncoated imidacloprid and exhibited less cytotoxicity towards….	[57]
Imidacloprid	Silica nanosphere	MSNs	Release of imidacloprid from these nanoparticles was found to be controlled over 48 hours	[96]

	Metalaxyl	Silica nanosphere	MSNs	Slower release of metalaxyl was exhibited from mesoporous silica nanospheres in soil than the free metalaxyl	[97]
	Methomyl	Biocopolymers of Az and CMC-chitosan	Nanocapsules	The insecticidal activity of methomyl-loaded nanocapsules against the armyworm larvae was significantly superior to the original, even 100% over 7 days	[157]
	Paraquat	Alginate/chitosan	Nanopaticles	The release profile of the herbicide was altered and its interaction with the soil, indicating this system could effectively minimise the problems caused by paraquat.	[158]
	Picloram	Mesoporous silica nanospheres	MSNs	Slower release of the active ingredient was achieved up to 30 days	[147]
	Tebuconazole	Porous hollow silica nanospheres	HSNs	Slower release of the active ingredient was noticed in water under different conditions	[106]
	Thiram	PEG originated block copolymers	Nano-micelles	Slow releasing properties have been achieved due to encapsulation and their applications can be optimised to achieve disease control for the desired period	[67]
	Thiamethoxam	PEG originated block copolymers	Nano-micelles	More time is required for releasing 50% of the active ingredients in sandy loam soil than commercial formulations	[68]
Bio pesticides					
1.					
	Artemisia arborescens L essential oil	Compritol 888 ATO (lipid)	Solid lipid nanoparticles (SLNs)	Physical stability was obtained as the solid lipid nanoparticles reduced the rapid evaporation of essential oils	[95]
	Avermectin	Porous hollow silica nanoparticles	HSNs	Release of avermectin can be controlled by adjusting pH and temperature; UV-shielding properties were improved when shell thickness was adjusted	[2, 159]
	Azadirachtin-A	Poly-ethylene glycol	Nano-micelles	In water, the rate of release of encapsulated azadirachtin-A from nano- micellar aggregates was reduced by increasing the molecular weight of PEG which controlled half release time ($t_{1/2}$) of 3.05 to 42.80 days	[65]
	Azadirachtin	Amphiphilic chitosan derivatives	Nano-micelles	Azadirachtin was protected by the carriers from rapid degradation and released over the course of 11 days into the environment	[160]

	Carum copticum oil	Myristic acid and chitosan	Nanogels	Nanogels exhibited more fumigant toxicity than the free oil over a longer period of time to control store grain pest	[72]
	Cinnamate	LDHs	Nanohybrid of C-LDHs	Considered to be a green pesticide due to its controlled release and nature compatibility properties	[123]
	Garlic essential oil	Poly-ethylene glycol	Nanocapsules	The encapsulation materials reduced volatilisation of essential oils and retained 80% pest control efficacy over 5 months	[52]
	Lansiumamide B	Poly-ethylene glycol	Nanocapsules	In pot experiment, nanoencapsulated lansiumamide B showed higher nematicidal activity compared to only lansiumamide B where LC_{50} values were observed 2.1407 mg L^{-1} and 19.3608 mg L^{-1}, respectively, after 24 h treatment	[161]
	Lippia sidoides oil	Chitosan and cashew gum	Nanogels	Slower and sustained release of *Lippia sidoides* oil was noticed in vitro release profiles while more effective larvicide efficacies were obtained compared to the pure *L. sidoides* oil.	[71]
	Methyl eugenol (Pheromone)	Gelator	Nanogels	The evaporation of pheromone significantly slowed down and remained stable in open ambient conditions	[73]
	Rotenone	Amphiphilic chitosan derivatives	Nano-micelles	The solubility of rotenone increased (up to 26.0 mg mL^{-1}) which was about 13000 times greater than free rotenone in water (about 0.002 mg mL^{-1})	[162]
	Validamycin	Porous hollow silica nanoparticles	PHSNs	Controlled release formulations were prepared	[101]

PART III: MICROBIAL CARRIERS FOR SOIL HEALTH AND MOISTURE RETENTION

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Executive summary

Agricultural sustainability practices mainly focus on the development of environmentally friendly fertilisers and pesticides for maintaining soil health and fertility. A promising method to sustain and improve soil health is to use microbial inoculants or beneficial plant growth promoting micro-organisms (PGPM) as fertilisers. Although several microbes have been identified as potential candidates as microbial inoculants, Rhizobium, in particular, is well-studied and proven as microbial inoculants suitable under various field conditions. To deliver microorganisms from lab to field always require a suitable carrier (substrate) to sustain viability and healthy microbial population. Among the various organic and inorganic carriers studied, peat remains as the carrier of choice for many years (commercial microbial inoculant producers). However, the major limitation in using peat is its availability and accessibility. Therefore, the exploration of alternative microbial carriers with low cost and reliable consistency under the field conditions is highly warranted. In addition, one of the most important bottlenecks in microbial inoculant production is the desiccation of microbes during storage conditions which subsequently reduces the efficiency under field conditions. Therefore, this study focused on addressing the gaps in microbial carrier technology to develop an alternative carrier material with strong capacity of moisture retention and water activity for microorganisms as a sustainable, economical and ecofriendly alternative to peat. In addition, attempts will be made to explore microbial inoculants with potential ability to tackle abiotic stress conditions such as drought, salinity, soil non-wettability, inorganic and organic pollutants.

1. Introduction

Soil plays a pivotal role in supporting and maintaining life by controlling ecological balance, maintaining biodiversity and agriculture. To accommodate ever-increasing global human population, urbanization and deforestation have led to the degradation of the soil health worldwide (Banwart, 2011). Continuous and excessive use of chemical fertilisers and pesticides over the years resulted in the serious impacts to terrestrial and aquatic ecosystems such as reduction in soil fertility and biodiversity, and also eutrophication (Mulvaney et al., 2009). Therefore, for judicious utilization of natural resources, it is crucial to develop novel soil fertilization and soil protection strategies to reduce the input of the chemical fertilisers and pesticides and their adverse impacts on the agro-ecosystems. A promising alternative method to maintain the soil health and to promote plant growth and development is the addition of beneficial micro-organisms to the soil as inoculants commonly referred as “biofertilisers” (Bashan, 1998). Microbes added to a supporting material/carrier, and additives are termed as microbial inoculants that are applied for enhancing soil health. The microbial inoculants are efficient and viable microorganisms that are applied to seed, plant surfaces or soil (rhizosphere-region surrounding the root) to promote plant growth and development.

Microbes are the key components of the soil-plant continuum, involved in a framework of soil-plant-microbe interactions and have a significant role in plant growth and development with antagonistic effects on pests and diseases. Microorganisms convert the complex organic matter present in the soil to the simple compounds and provide essential nutrients to plants, enhances soil fertility, maintains the natural soil microbial population and thereby improving crop yield (Jha and Prasad, 2006). The plant growth promoting microorganisms (PGPMs) *Rhizobium*, *Azotobacter*, *Azospirillum* and blue-green algae and phosphate solubilizing bacteria like *Pseudomonas* and *Bacillus* are proven its significant role in various agricultural systems (Wu et al., 2005). However, except rhizobia, there is little or no evidence of these group of organisms and its effectiveness as commercial inoculations under field conditions.

Research reports suggest that the international biofertiliser market share might expect to cross US$ 3 billion by 2024 (Global Market Insights Inc). Also, to satisfy the expanding market development, inoculants producing companies are required to be aware of product quality, and the awareness on the importance and usage of bio-fertilisers (Kannaiyan, 2003; Husen et al., 2016).

The major limitation of the microbial inoculant technology is the poor survival rate and the establishment of the microbial strains in field conditions. The success of microbial inoculants that are applied to seeds and soil mainly depends on the moisture content of the formulations. Therefore, retaining moisture content in the formulation is crucial and requires further research for formulation developments. Also, the functional success and failure of the microbial inoculants depend on the type of carrier material used during the production. Regardless, the microbial inoculants produced through optimal production techniques with suitable carriers and active microbial load when delivered in the field at the right amount results in multiple advantages both in terms of soil and plant health.

Numerous studies have established the importance of inoculation of plants with the microorganisms however research on the carrier delivery systems are still limited. This review provides comprehensive insights on the importance of microbial inoculants including the (1) need for microbial inoculants in Australia; (2) information on the types of carrier materials that are available to date; (3) Advantages and disadvantages of the existing carrier materials and, (4) research for developing and testing suitable microbial carrier with the ability to retain moisture.

2. Need for microbial inoculant formulations in Australia

2.1 Nutrient solubilisation

Phosphorus (P) and potassium (K) are the primary nutrients required for the crop growth and development. However, the availability of P and K to plants from the soil is minimum as the most substantial proportion of P and K in the soil are insoluble rocks, minerals and other deposits (Goldstein, 1995). The major concern in the Australian soils is the low availability of phosphorus to plants from soil for their growth and development. Plants may use only 10-30% of phosphorus in a year from the applied fertilisers, and remaining amount of the phosphorus is locked up in the soil and not available for plant use (Holford, 1997).

The mechanism involved in the solubilization potential for organically bound phosphates and inorganic phosphorus by some bacterial species were determined by the ability of the microbes to release metabolites in particular organic acids such as gluconate, ketogluconate, acetate, lactate, oxalate, tartrate, succinate, citrate and gluconate (Stella and Halimi, 2015). In addition, the endophytic bacterial population from wheat, rice, maize, peanut, legumes, and sunflower can solubilize phosphates from the soil. Also, the larger number of PGPB belonging to genera *Azotobacter, Citrobacter Burkholderia*, *Enterobacter*, *Erwinia*, *Flavobacterium*, *Paenibacillus*, *Pseudomonas*, *Rhizobium,* and *Serratia* were reported with the phosphate solubilizing property (Sharma et al., 2017). In Australia, the only phosphate solubilizing microbial strain *Penicillium bilaii* was sold commercially with scientific evidence that supports the label survival rate of the strain by the manufacturer Novozyme Biologicals (Karamanos et al., 2010). It is, therefore, necessary to have phosphorus and potassium solubilizing microbial inoculants to promote soil fertility.

2.2 Soil moisture retention

The soil wettability is the dynamic surface property of the soil that is interlinked with many other physical, chemical, and biological soil properties. Based on the equilibrium contact angle between water and soil surface in the soil, the soil wettability they are classified as 1) spontaneous wetting, 2) partial wetting and 3) subcritical soil water repellency (SWR). Over 50 countries in the world have been recorded with SWR under various soil types, climates and land use scenarios (Dekker et al., 2005). In Australia, particularly in the south-western parts, the soil water repellency is the major problem in which the soils have the incapability of retaining moisture in much of the year, leading to infertility of soils. Even though many researchers focused on the soil water repellency as their major objective to determine the evolution of soil water repellency but the understanding on the cause of SWR is still more need to be understood (Roper et al., 2015). Many direct approaches such as slow-release nitrogen fertiliser, liming, fungicides, stimulation of earthworms, and irrigation and indirect approaches such as application of surfactants, claying soil aeration, and compaction were formulated to rectify the problems caused by SWR and each of the approaches has different degree of pros and cons (Müller and Deurer, 2011). Among the various approaches, the biological approach using microbes for rectifying SWR was considered as an effective method based on the understanding that the SWR was caused by waxy coating of soil particles (Doerr et al., 2000). A number of wax degrading bacteria such as *Actinobacter* sp., *Mycobacterium* sp., *Rhodococcus* sp. and, *Streptomyces* sp., producing biosurfactants were isolated and tested in lab conditions for their efficiency to improve SWR conditions (Roper, 2004). In Western Australia, the *Rhodococcus* spp. were found to be the most effective bacteria in reducing the water repellency in field conditions.

3. Microbial carriers

Carriers act as a delivery vehicle of live and potential soil improving microorganisms from lab to field conditions (Bashan, 1998). Carriers were designed to provide a suitable microenvironment for the inoculant viability with adequate shelf life. Based on the weight and volume carriers occupy a major portion of the inoculant formulation. The carriers were either solid based or liquid-based and can be either sterile or non-sterile. The sterile carriers have marked advantage over the non-sterile carrier by delivering right number viable microorganisms in good physical conditions.

3.1 Characteristics of ideal carriers

According to Bashan (1998), the major essential characteristics of all microbial carriers are as follows,

1) *Support growth of microorganisms:*

The main characteristic of the ideal carrier is to provide suitable microenvironment to the target microorganisms and to deliver a right number of the viable microbial cells in good physical conditions.

2) *High stability*

A good carrier should have sufficient shelf-life and stable for at least 2-3 months at room temperature. Also, they should adhere well to seeds and the soil and allow the controlled release of the micro-organisms in the rhizosphere of plants.

3) *Optimal physicochemical properties*

The ideal carrier should be physically and chemically uniform, ability to maintain good water holding capacity, permits gas exchange, high organic matter, good pH buffering capacity with readily adjustable pH, should be free from any lump forming materials and are compatible with the nutrient and adjuvants addition (Ferreira and Castro, 2005).

4) *Ease of manufacture and handling*

The inoculants must be manufactured easily with the suitable available with cheap raw materials and should allow the addition of the additives. Also, the microbial inoculants should be easy to handle with suitable technology to deliver high-quality inoculants with specialized machinery (Date, 2001).

5) *Eco-friendly*

The carrier should be free of toxic materials and thrive well in all types of environmental conditions (Ferreira and Castro, 2005). They should be consistently available in good quality. They should be biodegradable without causing any harm to the environment. (Stephens and Rask, 2000).

6) *Successful acceptance by end users*

The microbial carriers should be compatible with the already available farm equipments.

3.2 Types of Microbial carriers

Carriers are usually commercialized as liquid carriers and solid carriers. The solid carriers are further divided based on their origins which includes organic, inorganic, and polymeric carriers (Malusá et al., 2012). The selection of carriers mainly based on the microorganisms and hence there is no universal carrier as a single solution for all the microorganisms. The inorganic materials include vermiculite, talc, active carbon filters, torrefied grass fibers, pelite, and kaolin. The polymeric materials include alginate, chitosan, cornstarch, carboxymethyl cellulose and ethyl cellulose. The common organic materials include peat, coal, sawdust, wheat bran, peat supplemented with chitin containing materials. Among the earlier used organic carriers, peat moss was reported as the well served carrier for rhizobium (Smith, 1992). Often, other alternative organic carriers that are developed were tested in comparison with peat moss (Albareda et al., 2008). In recent years biochars, have become most appealing inoculum carriers, and are advocated as a soil amendments for improving soil fertility, and also mitigating global climate change.

The selection of carriers mainly depends on the nature of microorganisms, and hence there is no universal carrier as a single solution for all the microorganisms. Therefore, earlier studies formulated carriers from different origins which includes organic, inorganic, or synthetic carriers (Malusá et al., 2012).

3.2.1 Liquid carrier

Liquid carriers are generally aqueous based mineral or organic oils, oil-in-water suspensions or polymer-based suspensions (Malusá et al., 2012). Essentially, the liquid carriers are the liquid suspensions amended with the substances that improve stickiness, stabilization, and surfactant dispersal abilities (Singleton et al., 2002). The liquid carriers allow the producers to add sufficient amount of nutrients, cell protectants, and growth enhancers.

The major drawback in the liquid formulations is their poor shelf-life, which could be due to the osmotic imbalance and lack of oxygen. The liquid carriers were produced in the larger volumes, and therefore they occupy larger storage space. Even though, the use of concentrated microbial emulsion and suspensions considerably reduce the size of the storage space and transport but then the steps involved in the processing of liquid formulations entail high production cost (Singleton et al., 2002). Also, contamination exists in liquid carriers even in emulsions. In order to overcome the problems related to contaminants antimicrobial agents were added to the emulsions nevertheless they negatively affect the survival of microbial inoculants. In addition, more viable microbial biomass was needed for the liquid carriers as the mortality of cells were higher due the longer adaptation period (John et al., 2011).

3.2.1.1 Amendments made in liquid carriers

In order to rectify the drawback of liquid carrier’s additives such as sucrose, carboxymethyl cellulose (CMC), gum arabic, polyvinyl polymers (PVP) were used to improve the survival of the micro-organisms in the liquid inoculants (Figure 3.1).

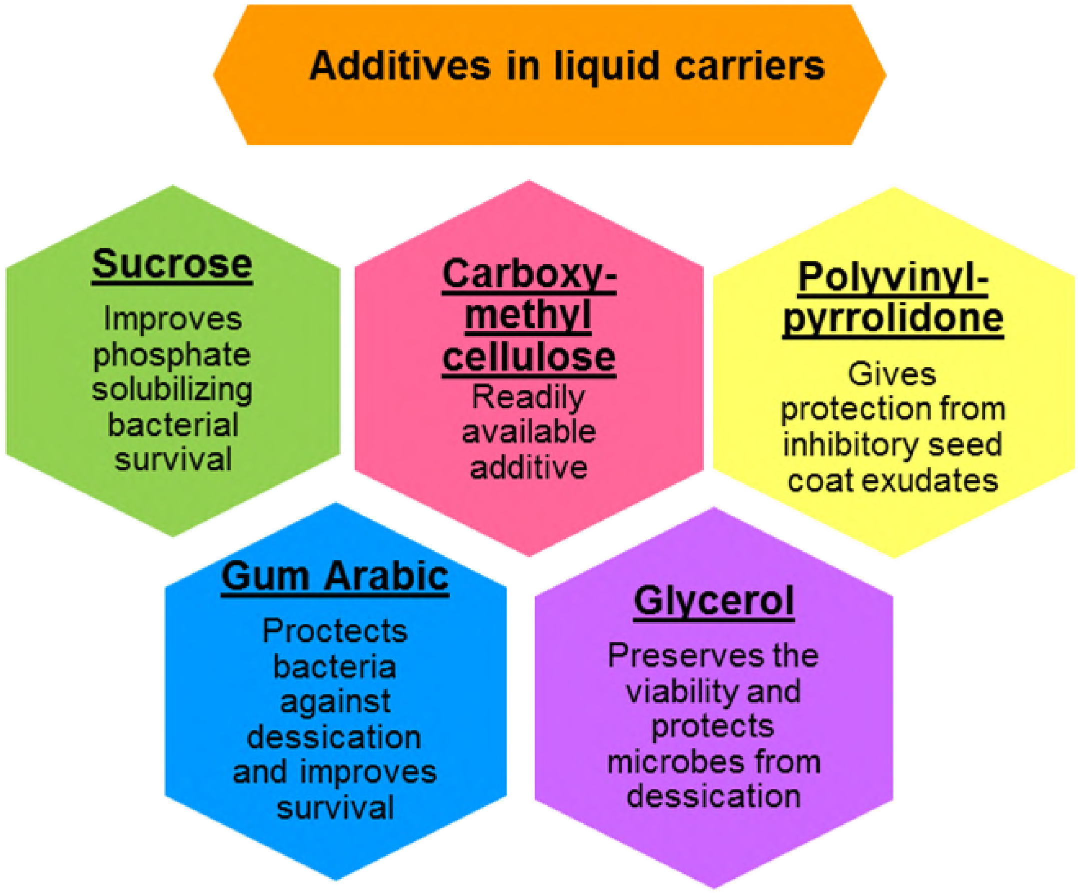

Figure 3.1. Amendments made to enhance the ability of the liquid carrier.

Addition of sucrose to culture medium improved the survival rate of rhizobia and *Pantoea* sp. – a phosphate solubilizing bacteria (PSB) (Taurian et al., 2010). Glycerol addition has become common amendment in liquid formulations as it prevents the microbial cells from desiccation which is considered as the main drawback in the production of microbial formulations (Singleton et al., 2002). The CMC is a readily available common additive, which protects microbes against pathogens. Also, greater results with the addition of CMC can be obtained even at the lower concentration (Dal Bello et al., 2002). The gum arabic and PVP aids in the survival of the microbes by protecting them from desiccation and also both the additives have additional protection against inhibitory seed coat exudates that are detrimental to the rhizobia (Deaker et al., 2011).

3.2.2 Solid carriers

The solid based carriers are most commonly used carrier due to its wide availability and can be produced from different origins such as organic, inorganic and polymeric materials. The usefulness of the solid carrier-based microbial inoculants was demonstrated in various agricultural and horticultural crops against the pest, diseases, and nematodes under controlled growth conditions as well as field conditions (Saravanakumar et al., 2007; Saravanakumar et al., 2009). Also, this type of microbial inoculant formulations benefits the growth and development of plants by solubilizing soil nutrients.

The shelf life of the microbes during the storage period and field application were poor, mainly due to the desiccation particularly in case of the inorganic carriers. This issue can be rectified by using advanced formulation technology such as encapsulating microbial gel in a polymeric matrix. Also, the limited availability of the raw materials is the major disadvantage in the solid carriers. In developing countries, most of the solid carriers such as peat, compost, clay pellets and vermiculite are used without sterilization, and this invites the larger contamination than the liquid carriers (Amer and Utkhede, 2000; Van Nieuwenhove et al., 2000). However, In Australia, all the peat used for rhizobia inoculants were sterilized prior to preparing rhizobial inoculant formulations. Every batch of inoculant formulation was independently quality checked by the Australian Inoculants Research Group (AIRG) (GRDC, 2016).

3.2.3 Organic carriers

The organic carriers are developed using materials such as peat, coir dust or coco peat, vermicompost, charcoal, sawdust, lignin, wheat or oat bran bagasse poultry manure and wastewater sludge. Among the organic carriers, peat remains as the carrier of choice for the wider range of micro-organisms (Bashan et al., 2014). Peat is generally made of partially decayed vegetation that is accumulated over the years. Peat provides growth and nutritive environment for the growth of an extensive range of the microorganisms (Herrmann and Lesueur, 2013). The peat is available locally at a reasonable rate and has high organic matter content and water holding capacity (GRDC, 2016). Usually, the quality and performance of all the other proposed carriers were compared with the standard of peat. However, despite the long and successful history of peat as a potential carrier of PGPB, there was growing interest for the development of alternative carrier due to the limited availability, higher investments for processing and release of toxic substances during sterilization. An extensive review has been done on the pros and cons of peat as microbial carrier materials (Herrmann and Lesueur, 2013; Bashan et al., 2014).

In order to overcome the limitations of peat, alternative carriers with the ability to maintain good microbial shelf life, non-toxic, easy handling and minimum processing and handling steps were needed (John et al., 2010). As an alternative to peat, the organic carriers such as charcoal, compost, coir and coco peat, bagasse vermicomposting and wastewater sludge gained importance with different degree of advantage. However, most of the carrier were considered as inferior to peat (Bashan, 1998; Singleton et al., 2002). In recent years, it was demonstrated that the wastewater sludge from the municipal and industries could serve as the sole raw material for the growth of rhizobia (Cheng et al., 2018). The sterile sludge supported the growth of both fast and slow growing rhizobia. Even though the composition of the sludge affected the generation time, cell yield and nodulation index but the acid and alkaline pre-treatments minimized the generation time of bacteria. Nevertheless, transport and treatment cost limit the use of wastewater sludge as a microbial carrier (Rebah et al., 2007).

The coir dust, compost, and coco peat had great potential as good carriers for several rhizobia and PGPB and demonstrated with high moisture holding a capacity of 500 - 600% (Prabhu and Thomas, 2002). Because of their high moisture holding capacity, the carriers were used for the application of nitrogen-fixing *Cyanobacteria* in larger field scales (Malliga et al., 1996). The earlier research evaluated four non-sterile organic carrier’s charcoal, saw dust, sand and sugarcane bagasse for *Rhizobium leguminosarum* and *Pseudomonas fluorescens* as the alternate carrier for peat. Out of the four carriers the saw dust remains as the best carrier in maintaining the bacterial population (Arora et al., 2008). Similarly, del Carmen Rivera-Cruz et al. (2008) demonstrated that the performance of P- solubilizing bacteria *Azospirillum* and *Azotobacter* in banana plants were considerably improved when poultry manure and banana waste was used as their carrier.

Another potential organic carrier is biochar which is defined as the product that is produced through thermal degradation process (pyrolysis) of biomass under elevated temperature with limited oxygen supply (Roberts et al., 2009). Many earlier types of research have demonstrated on the progressive influence of biochar on the soil quality (Chan et al., 2008; Xu et al., 2012). Application of biochar enhances soil organic matter content and consequently improves soil fertility by increasing the availability of phosphorus and potassium to plants (Xu et al., 2012). Also, biochar has a positive effect on the moisture retention due to its high total porosity and retaining water molecules in their small pores and thereby increasing soil water holding capacity. Moreover, biochar allows the percolation of water from the top soil into deeper layers through their larger pores (Asai et al., 2009). Furthermore, the porous structure of the biochar provides suitable habitat for many micro-organisms by protecting them from predators, desiccation and supplying bacteria with nutrients (Table 3.1). The bacterial colonization in the biochar pores could protect the bacteria better from the grazers and native competitors.

The use of biochar not always enhances the agricultural productivity, but there are potential drawbacks of using biochar in soil which includes, 1) excessive supply of nutrients except those produced from wood and municipal green waste, 2) increases soil pH and EC, 3) releases toxic materials like heavy metals and polycyclic aromatic hydrocarbons that could present in the biochar, 4) differential response of microbial groups with the addition of biochars, 5) Biochar may contain some of the phytotoxic compounds that have negative impact on the seed germination (Khodadad et al., 2011; Rogovska et al., 2012) and, 6) the absorption ability of organic compounds may block the micropores of the biochar and reduce their absorption efficiency (Uchimiya and Bannon, 2013). Further, ecotoxicological impacts of biochar remain largely unexplored.

Table 3.1. Types of biochars used for producing inoculants of PGPB.

Biochar	Bacteria	Amendments	Advantage	Reference
Agricultural waste	*Bacillus* sp. strain A30, *Burkholderia* sp. strain L2	Fly ash addition	Increased the viability of bacteria for a period of 240 days of storage	(Kumar et al., 2017)
Pinewood	*Enterobacter cloacae* UW 5	Nil	Supported the growth and survival of bacteria which was in comparison to peat	(Hale et al., 2015)
Hydrochar from maize silage	*Bradyrhizobium* sp.	Nil	Improved bacterial survival even under the drought conditions.	(Egamberdieva et al., 2017)
Pine wood biochar	*Pseudomonas putida* UW4	Luria–Bertani broth and Earth worm casting extract	Maintained high population density in the plant rhizosphere.	(Sun et al., 2016)
Softwood feed stock	*Bradyrhizobium Japonicum* 532C	Guar gum addition	Supported the bacterial viability	(Głodowska et al., 2017)
Acacia wood, coconut shell	*Azospirillum lipoferum*	Nil	Retained moisture and retained maximum bacterial population	(Saranya et al., 2011)
Cotton Stalks	*Bacillus subtilis SL-13*	Nil	Biochar provides a beneficial micro-environment for the slow release and prolonged survival of bacteria	(Tao et al., 2018)

3.2.4 Inorganic carriers

The carriers are made of the inorganic materials, natural polymers or synthetic materials. Inorganic carriers were an older version of developing microbial inoculants. The inorganic carriers include clay pellets, perlite, talc, turf, activated carbon filters, kaolin, and vermiculite. Among the inorganic carriers, clays were used largely in several agricultural formulations and can be applied as granules, suspensions, and powders (Anandham et al., 2007).

Numerous advantages related to inorganic materials were reported with their efficiency in protecting the agricultural and horticultural crops against pest and diseases (Bharathi et al., 2004; Saravanakumar et al., 2009). However, the formulations that are prepared from the inorganic carriers suffer from lower performances in field conditions, greater contamination compared to other carrier types and poor performances under the field conditions (Saravanakumar et al., 2009). Also, most of the inorganic microbial carriers are not used as the microbial carriers. The only inorganic inoculant formulation that is sold in the Australian market is granular clay pellets manufactured by Alosca Pty Ltd.

3.2.5 Polymeric carriers

The polymeric beads are formed by bioencapsulation of microorganisms in the polymeric matrix. The basic principle of the bioencapsulation technique is to maintain the viability of micro-organisms, to protect the microorganisms from soil environments, microbial competitors and to ensure a gradual release of desired microbial strains colonizing root zone (Kim et al., 2012; Bashan et al., 2014). Both the natural and synthetic polymers are used for the encapsulation of the microbes. The natural polymers such as alginate, carrageenan, agar-agar, agarose are formed by polymerization or cross-linking. Besides, the synthetic polymers such as polyacrylamides, polystyrenes, polyurethane were also used as microbial carriers (Cassidy et al., 1996). Among the natural and synthetic polymers, polyacrylamide and alginate are the most commonly used polymers for microbial encapsulation. Nevertheless, alginate is the material of choice and the most promising encapsulation material tested so far (Date, 2001). Alginate is a natural, non-toxic, and eco-friendly polymer which forms a three-dimensional porous gel when mixed with the multivalent cations (Ca^{2+}) (Yabur et al., 2007; Malusá et al., 2012). Alginate beads are capable of entrapping the highest number of the bacterial cells with the cell density of 10^{11} CFU g^{-1} of the bead (Bashan et al., 2002). The main advantages of polymeric beads are they are easy to produce, store and handle during the industrial operations. The entrapped micro-organisms were slowly liberated in the soil when the polymer starts to degrade slowly, thereby releasing PGPB –rhizobia in the rhizosphere region (BASHAN, 2016). The encapsulation of the bacterial cells was of two types which include macro and microencapsulation (Figure 3.2).

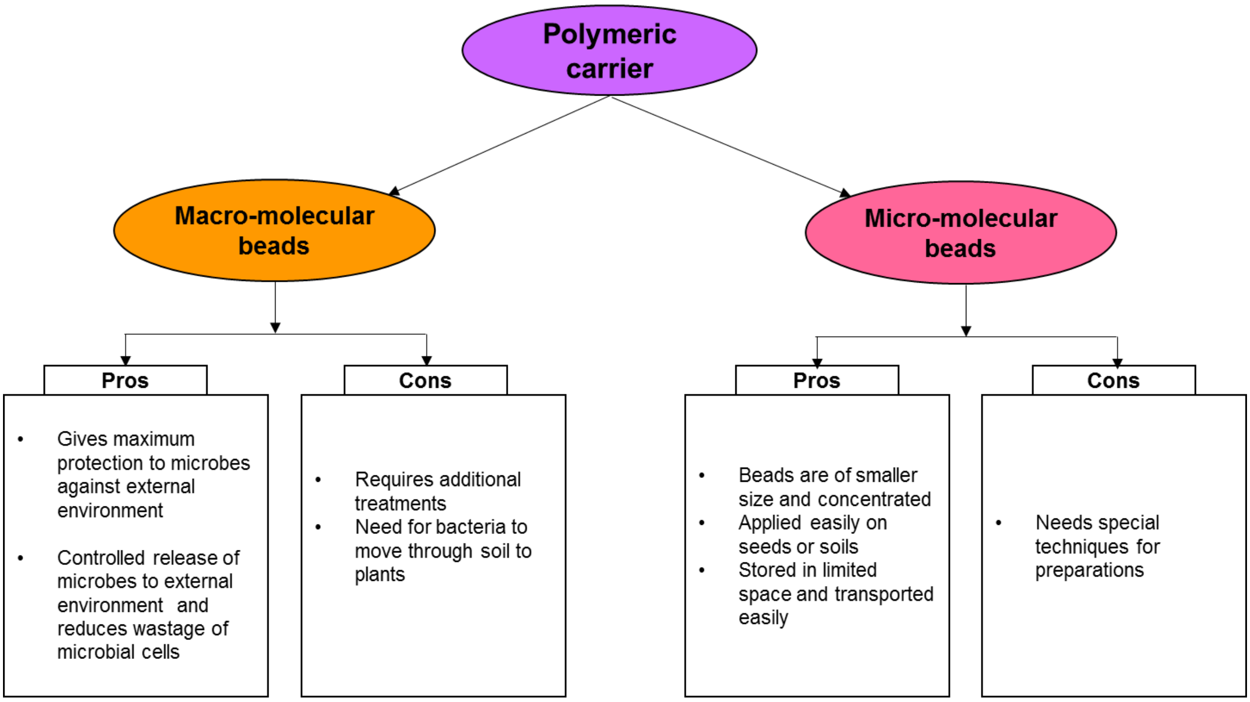

Figure 3.2. Types of polymeric carrier and their pros and cons.

3.2.5.1 Macro-encapsulation

In macroencapsulation, the microbes are entrapped in larger sized molecules extending from a few millimeters to centimeters. Usually, the macro-alginate beads are used for encapsulation of several PGPB and mycorrhizae (Table 3.2).

Table 3.2. List of different carrier material used in the microencapsulation of microbial cells.

Macromolecular beads	**Encapsulated bacteria**	**Reference**
Alginate- humic acids	PGPB – *P.putida*	(Rekha et al., 2007)
Alginate – kaolin, starch, talc	*Streptomyces* sp.	(Sabaratnam and Traquair, 2002)
Alginate – peanut oil	*Beauveria bassiana*	(Bextine and Thorvilson, 2002)
Alginate- Skim milk	*Azospirillum brasilense*, *Pseudomonas fluorescens*	(Bashan and González, 1999)
Alginate - Glycerol	*Pantoae aalomerance*	(Zohar-Perez et al., 2002)

The macro-alginate bead formulations have solved many problems associated with the commonly used organic carrier peat (Bashan, 1998). The macroalginate beads can be wet or dry. It is demonstrated in the earlier research that the dry alginate beads increased the survival time of PGPB *Azospirillum brasilense* and *Pseudomonas fluorescence* (Bashan and González, 1999). The successful plant growth promotion by macro-encapsulated PGPB *Bacillus subtilis* was demonstrated in the lettuce (Young et al., 2006) in which PGPB was encapsulated in the alginate beads with humic acid as an additive. The humic acid served as the carbon source for the encapsulated *B.subtilis* and helped the survival of the bacteria during the storage conditions (Rekha et al., 2007). Also, the alginate formulations offer protection against phosphate solubilizing bacteria *Pseudomonas striata* and *Bacillus polymyxa* even when the storage temperature reached 40°C (Viveganandan and Jauhri, 2000).

The hydrogels formed by the microencapsulation method usually have the chemical stabilization of hydrophilic polymers in the three-dimensional network. The main dispersion phase in the hydrogels is water and present in the substantial quantity (Narjary et al., 2012). The use of hydrogels as carrier material has improved with the demonstrated advantage of increasing the activity of the microbes that are entrapped in the hydrogels. Also, the hydrogels are environmentally safe, increases the shelf-life of bio-inoculants. Moreover, in sandy soils, the application of hydrogels improves the water availability to plants by increasing the water retention in pores and reducing hydraulic water conductivity by reducing water drainage through pores (Schoebitz et al., 2014).

Even though the macro encapsulation with alginate as a potential carrier has several advantages over peat, they have two major disadvantages which cannot be ignored, this includes 1) the growers require an additional treatment to disperse the inoculants during the sowing even if the inoculants were planted using seeding machines, (2) in the field conditions the macro molecular gels may land few centimetres away from the plants, therefore the inoculants are needed to migrate from soil to the plants and have to face competition with the native microflora and 3) alginates are more expensive than peat (Bashan, 2016).

3.2.5.2 Micro-encapsulation

Smaller beads of 10-100 µm are able to encapsulate an adequate number of the bacteria. The encapsulated materials can be rounded beads, cubes or even sheaths. The micro-encapsulation was developed to overcome the difficulties in micro-encapsulation techniques. Also, the loss of the microbial cells during the preparation of the microencapsulation technique is minimum compared to the micro-encapsulation methods (John et al., 2010). The microcapsules were prepared by the techniques such as extrusion, emulsion, coacervation, spray drying, solvent extraction /evaporation, thermal gelation, droplet freezing, microfluidic and Shirasu Porous Glass (SPG) membrane emulsification technique (Table 3.3) (John et al., 2011; Naqvi et al., 2016). The macromolecular beads can be produced as powder like formulations, which are known as the “bead–dust.” This powder formulation can be coated with seeds. This pre-coated seeds with the micro-bead inoculants are convenient to farmers by eliminating the need for the additional field treatments (Bashan, 2016).

Table 3.3. List of different carrier material used in the microencapsulation of microbial cells.

Micro-molecular beads	**Encapsulated bacteria**	**Technique involved**	**Size**	**Reference**
Sodium alginate-bentonite	*Pseudomonas putida* Rs-198	Spray-drying	25 -100 µm	(Li et al., 2017)
Sodium alginate – calcium chloride	*Klebsiella oxytoca* Rs-5	Pore coagulation bath	0.85 - 1.10 mm	(Wu et al., 2011)
Sodium alginate - chitosan, peat and skim milk	*Burkholderia cepa, Bacillus* spp. *Trichoderma virens*	Emulsification in oil	10 - 110 µm	(Szczech and Maciorowski, 2016)
Sodium alginate – humic acid	*Bacillus subtilis*	Cell suspension	0.04 and 0.5 µm	(Young et al., 2006)
Ethylcellulose- silica	*Pseudomonas fluorescens*	Spray drying	-	(Amiet-Charpentier et al., 1998)

Usually, the entrapped micro-organisms will be released slowly through the capsule walls by diffusion (Bashan, 1998). Microencapsulation of the bacterial cells in the polymeric matrices provides a controlled release of the encapsulated bacteria and provides protection to the bacteria under adverse environmental conditions (Table 3.4). The microencapsulated formulations are more efficient than the macroencapsulation technique and are highly significant in the foliar spraying and seed coating of smaller sized seeds. Also, the microencapsulation formulation can be easily distributed uniformly over seeds thereby making easy access of microbes to plants during the emergence of the radicle or plumule. Also, microencapsulated formulations are considered to be cost-effective, highly concentrated and occupy limited storage space and easily transportable (John et al., 2011).

Table 3.4. **Advantages and disadvantages of existing microbial carriers.**

Carrier	Advantages	Disadvantages	References
Liquid carrier (culture, media or water)	Has improved soil stickiness, stabilization, surfactant, easy to handle and dispersal ability.	Impractical for large-scale applications as larger quantities of liquid involved, incubation, refrigeration facilities needed to accompany larger quantities with the involvement of high storage cost.	(Stephens and Rask, 2000; Singleton et al., 2002)
Organic carrier			
Peat	Suitable for the wide range of microorganisms, strong buffering capacity	Not readily available, Not Eco-friendly	(Herrmann and Lesueur, 2013)
Coir dust and coco peat	Has high moisture holding capacity, low cost, mass multiplication	Bulky involves high storage and transportation cost, often used as non-sterile carriers	(Van Nieuwenhove et al., 2000)
Vermicompost	Supports the survival of the microbes	High input cost	(Sekar and Karmegam, 2010)
Sawdust	Best carrier for maintaining bacterial populations individually and together	High hydrophilicity	(Podorozhko et al., 2008)
Wheat or oat bran	Successfully limits the growth of fungus *Sclerotinia minor* and other contaminants	Often used as non-sterile carriers	(Amer and Utkhede, 2000)
Bagasse	Good mechanical strength	Due to the limited availability, they cannot form the base for the larger industries	(Albareda et al., 2008)
Biochar	Positive effects on moisture retention	Increases soil pH and EC, releases toxic substances	(Hale et al., 2015)
Poultry manure	Improves soil physical and microbiological properties.	May contain pathogens and antibiotic compounds.	(del Carmen Rivera-Cruz et al., 2008)
Wastewater sludge	Limitless availability	Needs pre-treatments to enhance the growth of bacterial cells.	(Rebah et al., 2002)
Inorganic carriers			
Clay pellets	Bacterial cultures can be mixed easily and immediately with clay pellets before application.	Used only on a small scale for crop production	(Schoebitz et al., 2014)
Turf	Supports viability of microorganisms	The possibility of high contamination	(Garcia and Sarmiento, 2000)

Talc	Effective formulation of plants against pest, diseases, and nematodes.	Short shelf life, high contamination, and low field performance	(Bharathi et al., 2004; Saravanakumar et al., 2007)
Perlite	Maintains the survival of Rhizobia and PGPB	Causes root blockage in plants with excessive root systems and affect percolation when used in an excessive amount	(Albareda et al., 2008)
Polymeric carriers			
Alginate	Non-toxic, biodegradable, slow release of entrapped microorganisms into the soil.	Low physical strength and not suitable for continuous conditions	(Bashan et al., 2002)
Chitosan	Non-toxic, inexpensive, biodegradable and acts as a chelating agent for nutrients and minerals and make them available to plants.	Requires expensive handling	(Chanratana et al., 2018)
Ethyl cellulose and modified starch	High microbial survival	Survival of microbes was affected by the addition of additives	(Amiet-Charpentier et al., 1998)
Carrageenan, Xanthan gum, locust bean gum	Polymers of biological origin help in the survival of microbes up to 8 months	The formulation has a moisture content of 50 – 70, therefore, desiccation is the main problem when the formulation was coated over seeds	(Shi et al., 2013)

3.3 Sterilization of carrier materials

The main purpose of sterilization of carrier materials is to ensure purity, quality and effectiveness of microbial inoculants contained within the carrier formulations (Abd El-Fattah et al., 2013). Different sterilization procedures were employed to obtain contaminant free carriers without affecting their quality. The two major sterilization methods were steam sterilization and gamma irradiation. In the steam sterilization or autoclaving follows wet killing mechanism in which in which the carrier material was subjected to high temperature (121 °C) and high pressure (15 pounds/ inch^2) of a speculated period mainly based on the size and component of the material. The main drawback in the steam sterilization process is that the spore-forming microorganism persists in the material even after the sterilization process (Temprano et al., 2002). On the other hand, gamma rays are widely used now as the potential sterilization agent. The mechanism of sterilization by gamma rays is by the direct breakdown of double-strand DNA or the formation of free radicals from the ionized water molecules that disrupt the biological system in the cell (Hansen and Shaffer, 2001). The dose rate of gamma irradiation required for the sterilization of the carrier varies depending on the property of the material, moisture content, contaminating population load and density of the material. Even though, higher gamma irradiation dose rates were used to prepare carrier material, the bacterial spores that are highly resistant to gamma irradiation were still found as contaminants when the carrier was stored for the longer period (Yardin et al., 2000).

3.4 Inoculation techniques

The microbial inoculants can be applied as seed treatments, mainly on the surface of the seeds as seed coatings or directly into soil primarily in the rhizosphere region where plant roots interact directly with the micro-organisms (Philippot et al., 2013). In general, the application of the microbial inoculants through seed treatments was greater than the soil application. In Australia, the most common method used for rhizobia inoculants is to inoculate legume seed with peat slurry just prior to sowing. However, the survival rate and performance of pre-inoculated coated seeds were poor (Hartley et al., 2012). Therefore, the carriers with good adhesion capacity to seeds combined with high efficiency microbial inoculants should be developed for seed coating. Most of the micro-organisms of agricultural importance have the ability to increase plant growth promotion largely belongs to the rhizosphere colonizing group (Babalola, 2010).

3.5 Available commercial inoculant formulations in Australia

Four different commercial inoculant formulations are available in Australia. These includes peat inoculants, granular pellets, and freeze-dried powder and liquid inoculants. Except the granular pellets (applied in furrows) all the other microbial inoculant formulations can be applied either directly to the soil in the seeding furrow or to the seed.

- **Peat inoculants**
  The microbial inoculants using peat is the oldest and most common form of inoculant used in Australia. The inoculants are prepared by mixing a broth culture of rhizobia into sterilised (gamma-irradiated) finely milled peat.
- **Granular pellets**
  The granular pellets are made either from the peat or clay materials that are impregnated with the microbial strains. The granular clay pellet products are produced and sold in the Australian market by Alosca Pty. Ltd.
- **Freeze dried powder**
  The freeze dried powder is prepared by concentrating broth culture into powder form by removing all water content by freeze-drying and storing them in glass vials.
- **Liquid inoculants**
  Liquid inoculants are prepared by suspending microbial strains in liquid formulations.

3.6 Maintenance of microbial inoculants during storage

The main prerequisite for the successful commercialization of the microbial inoculants is their longer shelf–life and their storage requirements which usually vary ranging from 2 months to 2 years at room temperature (Bashan et al., 2014). Numerous parameters affect the storage stability of the microbial inoculants which includes variation in temperature, higher microbial contaminants, varied moisture contents and exposure to various oxygen levels (Morgan et al., 2006). Among them, one of the critical parameters that affect the shelf-life of microbial inoculants is the water activity. It has been previously reported that the high survival rate of *Rhizobia* coated on seeds was achieved only when the water activity is between 0.47 and 0.38. To overcome the limitations of storage process, a fine-tuning of storage conditions has to be performed to maintain appropriate shelf-life of the microbial inoculants (Deaker et al., 2012).

3.7 Quality assurance and quality control

In recent years, many new types of microbial carriers with highlighted benefits have been emerging for commercialization in the global markets. However, there are alarming results on the inferior quality of some carriers that are exceptionally unreliable and inconsistent under field conditions (Herridge et al., 2008; Herrmann et al., 2015). Moreover, it has been reported in earlier studies that, more than 40% of the microbial inoculants produced globally contains only contaminants and not their claimed strains (Herrmann et al., 2015).

In general, the requirements of expensive investments to improve the quality of microbial inoculants limit the manufacturers to provide quality inoculants. Use of non-sterile carries for the inoculant preparation is prevalent to date mainly because of the absence of the formal standards for the production of the inoculants. Therefore, stringent quality assurance procedures must be performed internally throughout the production process of microbial carriers to avoid poor quality carriers and to obtain consistent and reliable performance of microbial inoculants under field conditions. Precise information on the product quality and efficiency of the microbial inoculants must be provided in the manufacturer's label which increases the product fidelity and reliability among consumers. The regulations for the bio-fertilisers and bio-control agents vary between countries. Therefore, universal regulations shall be implemented for the preparation of microbial formulations with the acceptance from all the countries for the commercialization of microbial formulations.

Usually, the microbial strains are selected based on their effectiveness in promoting plant growth, higher survival rate when coated on seed and soil conditions. Also, the strains have to be genetically stable following their introduction into soil and suitable for manufacturing process. In addition, countries like US and EU, Canada possess rigorous regulatory controls for the production and commercial marketing of the microbial inoculants. In Australia, to ensure the microbial strains and their suitability for commercial marketing, stringent quality control under laboratory, glasshouse and field conditions are practiced. As part of this, the microbial strains. prior to commercialization stage will be reviewed and tested for quality standards set by National Code of Practice for legume microbial inoculant products used in Australian crops and pastures and Grain Research and Development Corporation (GRDC) through AIRG (Australian Inoculants Research Group (AIRG) and a panel of independent scientists. Microbial inoculants that qualify the standard will be commercialized and marketed with the “Green Tick” logo (GRDC, 2016). The companies that are signatories to the CoP, producing and selling inoculants carrying “Green Tick” logo are

- BASF Agricultural specialties Pty. Ltd;
- New Edge Microbials Pty. Ltd;
- Novozyme Biologicals Australia Pty.Ltd; and
- Green Microbes Australia Pty.Ltd;

4. Future prospects and recommendations

4.1 Economical and eco-friendly carriers

The material cost for the inorganic and polymeric carrier is higher compared to the other types of carrier materials. Therefore, cheap, easily available and environmentally feasible materials should be explored (Table 3.5). The use of the low-cost materials, like whey (concentrate/powder) instead of skimmed milk (a general additive used in alginate encapsulation technique), supports the growth of the microbial inoculants as a source of carbon during storage and also after applications. Due to their cost-effectiveness, improved shelf-life and eco-friendly attributes, the biodegradable synthetic polymer is another promising option. Also, use of natural gums (locust bean/xanthan), can also be used as stickers, anti-desiccant or gelling agent during inoculant preparations. Biochar remains as a better environment-friendly carrier alternative. There is a paucity of research on exploration of biochar as carrier material. However, limitations such as alkalinity and the release of toxic materials limit the possibility of their use as the carrier materials. Therefore, for example, certain aspects for biochar as carrier materials should focus on the physical such as optimizing pyrolysis temperature and pore size dimensions, chemical characterization and biological effectiveness such as microbial survival and spatial occupation in pores will facilitate their use as a potential bacterial carrier.

4.2 Production technologies

The selection of suitable carrier production technology and optimized production parameters such as duration, temperature and curing time must be considered during carrier development. In addition, compatibility of carriers and microbes with the addition of additives is critically important, since the larger sized additives have a negative impact on the survival of the micro-organisms. Therefore, additives selection is important in such a way that they should not interfere with the microbial load and hinder cell viability after processing and storage.

Table 3.5. Future aspects of microbial carrier research.

Research area	**Carriers**							
	Liquid		**Solid**					
			Organic		**Inorganic**		**Polymers**	
	Existing knowledge	**Future needs**	**Existing knowledge**	**Future needs**	**Existing knowledge**	**Future needs**	**Existing knowledge**	**Future needs**
Developing Eco-friendly carriers	Average	Average	Reasonable	Low	Low	Reasonable	Average	Average
Improving inoculants by supplementation with additives with carriers	Average	Average	Low	Reasonable	Low	Reasonable	Nil	Absolute
Exploring effects of carriers on native micro-organisms	Low	Reasonable	Low	Reasonable	Nil	Absolute	Nil	Absolute
Studying eco-toxicological risk of the carrier in long-term	Nil	Absolute	Nil	Absolute	Nil	Absolute	Nil	Absolute
Quality assessments of commercially available carriers	Nil	Absolute	Nil	Absolute	Nil	Absolute	Nil	Absolute
Standard guidelines to check the fitness of carrier and microbial inoculants during storage	Nil	Absolute	Nil	Absolute	Nil	Absolute	Nil	Absolute
Evaluation of carriers under field conditions	Average	Average	Average	Average	Average	Average	Low	Absolute

Nil – 0%, low ≥ 25%, Average ≥ 50%, Reasonable ≥ 75%, Absolute =100%

4.3 Integrating advanced technology in carrier preparation

Use of advanced technology like nanotechnology overcomes the limitations in the production of conventional carrier materials. Recently, the silver and gold nanoparticles are used as carriers of growth promoting micro-organisms such as *Pseudomonas fluorescens*, *Bacillus subtilis,* and *Peani bacillus elgii* exhibited good growth promotion under in-vitro conditions (Shukla et al., 2015). Formulations with the polymeric nanoparticles have been utilized to coat bio-fertilisers, which provides resistant to desiccation. The future research should focus on the development of “**biobeads”** technology to overcome the desiccation – an important drawback in the carrier technology. Moreover, the issues regarding the cell sedimentation during storage would be rectified by coating the microorganisms with hydrophobic silica nanoparticles (Vandergheynst et al., 2007). On the other hand, hydrogels are the promising means of reducing desiccation of PGPB which remains as the major problem faced by PGPB during storage. Since research demonstrated that the application of hydrogels to the sandy soils improved water availability to soils by improving retention of moisture in the pores. The carrier preparation can further be advanced by integrating technologies such as nanotechnology and encapsulation techniques.

4.4 Enhancing carrier shelf-life

The major constraints in the microbial carrier are short shelf-life, poor survival of inoculated microbes under adverse environmental conditions, sensitivity to temperature and desiccation during storage, a high degree of contamination and inconsistent field performances. Maintaining the inoculants viability remains a major concern during storage and post application. Researchers need to step up to tackle these constraints and challenges on the microbial inoculants for sustainable agriculture. New microbial carriers are needed to overcome the limitations of peat and to enhance the viability and shelf life during storage and also after soil inoculation.

5. Conclusions

Many types of solid and liquid inoculants such as microbial biofertilisers or biocontrol agents were developed with the varying degree of successes for the application and to promote agriculture in Australia. However, to enhance Australian soil health, existing research on microbial inoculants with P, K solubilizing, surfactant-producing capability needs to be revisited to overcome the constraints of SWR and soil nutrient deficiency. In addition, the exploitation of advanced technology such as microencapsulation and nanotechnology for the development of effective microbial inoculant formulations provides a promising step for the enhancement of shelf-life and protecting the viability of microorganisms under adverse environmental conditions. Also, these technologies produce formulations with the ability for the controlled, effective and slow release of soil health promoting and beneficial microorganisms. In addition, selection of carrier materials for the development of promising inoculant formulation is vital. Advanced technologies and tools that are currently utilized in food processing and pharmaceutical industries can be efficiently deployed for the inoculants production specifically, for the development of microbial formulations for agricultural applications. Further, cost-effective agricultural by-products such as organic wastes and biochar can be explored as low cost, easily available and eco-friendly carrier material alternatives. The physio-chemical properties of such materials can be improved by various pyrolysis technologies and validating their efficiency under field conditions. Furthermore, understanding the interaction between microorganisms, carrier materials, and additives is essential to produce cost-effective, environmentally friendly, and successful microbial inoculant formulations.

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