



# BIODEGRADABLE POLYMERS IN MICRONUTRIENT FERTILISER FORMULATIONS

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Polymers in liquid formulations (PLFs) are a critical raw material whose widespread use in the industry leads to terrestrial pollution and ultimately contributes to marine litter. Green chemistry principles can be applied to help mitigate microplastic pollution by addressing three sustainability challenges: (1) prevention of non-biodegradable polymer use with the same efficiency, (2) use of renewable feedstocks, and (3) design for degradation. PLFs are essential in many industries, however, are not always captured in waste management systems due to their size and mobility, and often exist in the environment far longer than their intended useful service life. The potential impacts of microplastics on the environment, associated with their intentional or incidental use in products, have generated a lot of concerns worldwide. The European Chemicals Agency (ECHA) estimates that 145,000 tonnes of microplastics are released each year into the environment where they accumulate and are likely to persist for hundreds of years<sup>1,2,3</sup>. Whilst microplastics do not fall directly in the scope of published European Union (EU) Directive 2019/904, the EU encourages a proactive approach for producers to strictly limit microplastics in their formulations until a comprehensive approach is adopted<sup>4</sup>. PLFs are essential for use by many industries, including the agricultural sector, however, emerging bio-based and green chemical technologies offer alternative, renewably sourced materials to produce PLFs. In this study polymer alternatives to PLFs in agriculture for foliar nutrients, and sprays are explored from feedstock sources, physical formulation properties, and cost-effectiveness for practical implementation of biodegradable polymers in micronutrient fertiliser formulations.

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## **(ii) Thesis Statement**

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Can biodegradable alternatives to synthetic polymers, currently derived from non-biodegradable, petrochemical feedstocks be replaced with biodegradable, renewable feedstock material, with the same effectiveness and efficacy for foliar nutrition fertiliser suspension concentrate formulations?

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## **(iii) Aims and Objectives**

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The aim is to eliminate the use of persistent or non-biodegradable polymers in foliar fertiliser formulations where suitable biodegradable alternatives exist.

The research will be conducted with the following objectives:

- a) Literature review on the status, scale, production, and use of petrochemical-derived raw materials across industries, polymer liquid formulations (PLFs), and their role in agriculture, with a predominant focus on Green Chemistry Principles 1, 7, and 10:
  - 1. Prevention
  - 7. Renewable feedstocks
  - 10. Biodegradation
- b) Define polymers, and their environmental impact and discuss biodegradability and how this is also defined.
- c) Candidate material sourcing of biodegradable polymers and categorising of biodegradable alternatives based on a literature search review, organic regulation descriptions, Safety Data Sheet (SDS) and Technical Data Sheet (TDS) information on the biodegradability of polymers designed for use in agriculture.
- d) Identifying the most favourable biodegradable raw materials by dispersant demand screening of biodegradable polymers compared to current non-biodegradable polymers using a YaraVita model formulation based on 700 g/l zinc oxide as the nutrient source to be dispersed.
- e) Model the existing YaraVita Zintrac, 700g/l zinc oxide formulation for nutrient content, viscosity, storage stability, and crop safety application as a benchmark for a formulation using biodegradable polymers.
- f) Suggest future work.

### 1.1 Sustainable YaraVita's foliar nutrition water-based suspension concentrate formulations.

The proposed research aims to source biodegradable raw materials commercially available as alternatives to the current widely used acrylic polymers for YaraVita's foliar nutrition water-based suspension concentrate formulations. Yara UK foliar formulations suspending solid, inorganic nutrients in a liquid form are called suspension concentrates and require a dispersing and thickening system, as well as consideration of other adjuvants and particle sizes <50 µm to achieve suspended particles. Suspension concentrates are made up of a continuous water phase, and a discontinuous phase of the solid, active particles as a nutrient source, which could be a primary, secondary or micronutrient, or a combination of.

Whilst foliar nutrition is a primary concern, so too is the stability of the formulation for global transportation, storage at high and low temperatures, and functional product use for the end consumer. Alternatives for the thickening of formulations without synthetic polymers already naturally exist in the form of gums, clays, and silica, and provide the function of increasing viscosity by polymer chain entanglement and hydrogen bonding with water molecules. The greener chemistry application is more challenging for substituting synthetic dispersants, as the properties need to exhibit adsorption onto the inorganic, insoluble particle surface and ionisation of the dispersant, enabling a lowered surface tension of the foliar applied product whilst also providing a stable suspension system. This review details the progress made by industry in their endeavours to utilise, biodegradable compound alternatives aligned with the Green Chemistry Principles of Anastas and Warner (1998)<sup>5</sup>.



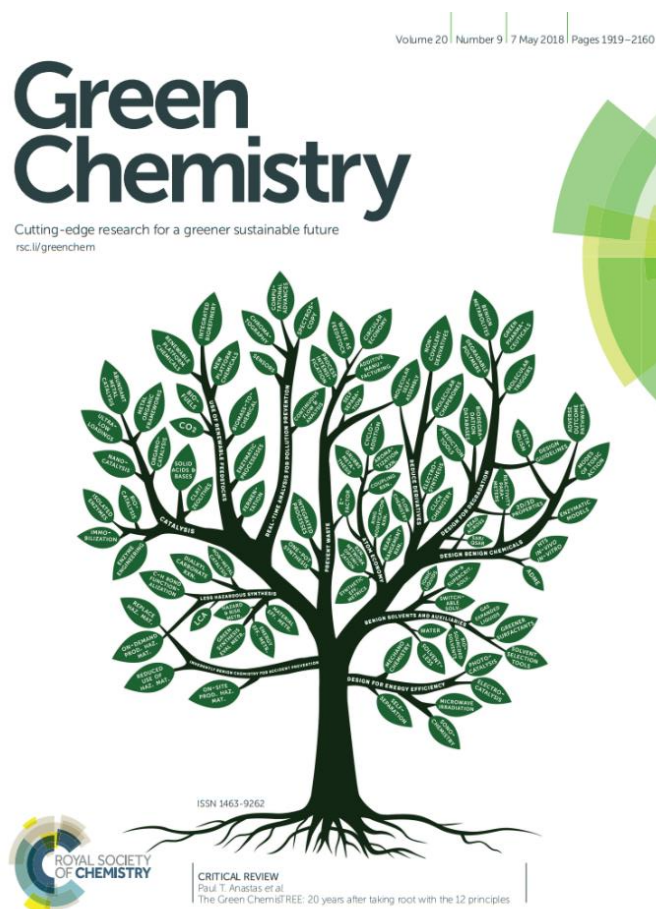


Fig. 1 Front cover page from the Green Chemistry Journal<sup>6</sup>.

In the field of agriculture, formulation ingredients are not limited to directly active, nutrient sources. Other formulation components are commonly referred to as adjuvants, inert materials, surfactants, dispersants, wetters, or stickers<sup>7</sup>. Referred to by the Royal Society of Chemistry, polymers in liquid formulations (PLFs) is the appropriate term for the commodity, petrochemical-derived polymers typically used in formulation chemistry across a broad spectrum of markets and industries. Of the polymer use industries, agriculture is listed third with a global market value of \$213 billion, amongst personal care and cosmetics (\$455 billion) and household cleaning (\$164 billion) for global market value<sup>8</sup>.

In the field of PLFs, there is substantial effort and global concern to evaluate the use of primary-use plastics. In the EU polymer mandate Directive 2019/904, microplastics have no singular policy with a comprehensive approach to the reduction of the impact of certain plastic products in the

environment, however, are recognised as contributing to marine litter:

*‘Terrestrial pollution and contamination of soil by larger items of plastic and resulting fragments or microplastics can be significant and such plastic can leak into the marine environment’<sup>4</sup>.*

As a proactive approach to PLFs use, and with the growing global concern about microplastics in the environment, producers are encouraged by the European Union through the release of directive 2019/904 on 5<sup>th</sup> June 2019 to strictly limit microplastics in their formulations<sup>4</sup>. Policy on some PLFs has had a positive drive towards biodegradable surfactant use. The European Detergents Regulation came into law on October 8, 2005, and states:

*“All surfactants used for domestic detergents have to be ultimately biodegradable”<sup>9</sup>.*

The Fertilising Products Regulation adopts the Circular Economy Action Plan which implements biodegradability criteria for control release fertilisers, although there is no EU law in place applying bio-based, biodegradable, and compostable plastics<sup>18</sup>. Currently, the European Committee for Standardisation (CEN) provides standard methods for all relevant elements in EN 17351:2020, to determine the oxygen content in

bio-based products and certify bio-based products<sup>10</sup>. In the EU, sustainability is a criterion that applies to bio-based plastics and exists for packaging under harmonised EN 13432 standards for industrially compostable packaging, however, there is no general standard for marine biodegradation<sup>11</sup>.

Polymers are macromolecules made up of individual components, and monomers bonded together, which can be synthetic or natural. Natural polymers from renewable sources include proteins, polysaccharides, and nucleic acids which in nature are degraded by the action of enzymes and chemical deterioration and breakdown associated with living organisms in the environment<sup>12</sup>. Synthetic polymers are produced from non-renewable resources and conventionally are often resistant to degradation. So far polymers have been exempted from REACH, however, the concern is shared amongst the industry that micro- and nano-synthetic plastics should be considered as substances of concern, registered and monitored under REACH due to their persistence, ensuring the protection of human health and the environment<sup>13,14</sup>. Their size (<5 µm) makes them readily available for ingestion and potentially liable to transfer within food chains<sup>15,16</sup>. Plastics are conventionally resistant to degradation and are typically found in terrestrial and marine environments, however, in June 2022, CEN published a methodology to quantify the global agricultural crop footprint including soil impacts, which does not include the influence of plastics on the soil environment<sup>10</sup>. Despite soil, sediment and water biodegradation parameters and TG 304A <sup>14</sup>C testing available by The Organisation for Economic Co-operation and Development (OECD) test methods, there is evidence to suggest microplastics released into the environment may affect agricultural soil regeneration and productivity by roundworms<sup>17,18</sup>. This indicates the requirement for more research and development into microplastic effective removal and or mitigation for the future<sup>8</sup>.

Polymers in Liquid Formulations (PLFs) is a sector comprising critical speciality chemicals utilised in everyday life. Relatively few outside the chemical industries will have heard of PLFs, yet across the globe, people interact with PLFs daily. Constituting \$125.2 billion to the global economy, PLFs are polymers based on solvents, such as water or oil<sup>8</sup>. They can be liquid or curable and play a vital role in society from improving food productivity and treating wastewater to enabling construction advancements and providing consumer products in the sectors of homecare, health, and wellbeing – from paints to cosmetics, to fertiliser, the functionality and presence of PLFs in the industry is substantial. More than 36.3 million metric tonnes (equivalent to 14,500 Olympic-sized swimming pools) of PLFs are produced per annum, from categories including acrylic, epoxy resins, polyester, and water-soluble polymers<sup>8,17</sup>. Primarily, synthetic polymers are the most commercially significant for their volumes of production, diversity of use, cost-effectiveness, and wide availability. As the population increases, there will be greater demand for PLFs. The Organisation for Economic Co-operation and Development (OECD) stated that by 2050, annual waste generation will increase by 70%<sup>19,20</sup>. Challenges faced with the existing and increased use of PLFs are the release of carbon dioxide into the atmosphere as the polymers break down into their monomers. This is a poor circular economy as polymers and monomers elude wastewater and treatment systems, accumulating physical waste at the microscopic level, and utilising earth's finite resources for a single useful lifetime.

There has been little coordinated effort to target the sustainability of PLFs across industries compared to the use of plastics. This is also the case for ionic liquids (ILs), where the adoption of solvents in industry and academia has historically not accounted for biodegradability challenges, or accidental release into terrestrial or marine environments, where desirable properties of ILs and PLFs often are designed for desirable wide range parameters for thermal and chemical stability<sup>19</sup>. In this study, the focus is on polymers used in agriculture in the form of liquid formulation systems. Generally, PLFs in this category are used in short to medium timeframes, utilised from primarily sourced raw materials for single use, and are likely to elude waste management systems, entering the environment as marine litter at the end of their current life cycle. In the direct introduction of microplastics into the environment, where agriculture is a primary runoff into waterways and ultimately oceans, the biodegradability of products should be clear and prioritised in the industry. The propensity of microplastics to absorb and concentrate as persistent organic pollutants is a serious concern, where the longer-term effects on agriculture, fisheries and human health are still largely unknown<sup>16,18,20</sup>. The potential ingestion of polymer fragments by marine species such as micro and nanoplankton has a strong likelihood to deliver toxins across trophic levels<sup>15</sup>. This is highly dependent on the residence time within the organisms and the potential for adverse toxic endpoints by endocytosis of the plastic particles. Marine food webs are based on the foundation of microorganisms as the primary food source. Photoautotrophs including plankton species are at the beginning of the marine food web and as a basis of marine life can have a significant ripple effect on the sequential constituents of the marine ecosystem in the world's oceans<sup>16</sup>.

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## 1.2 Polymers

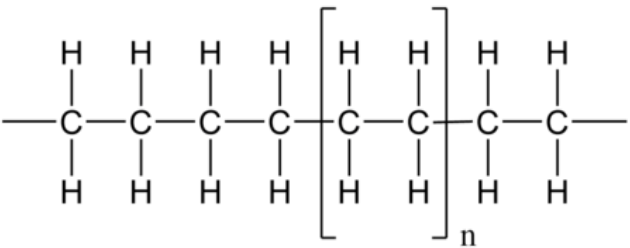
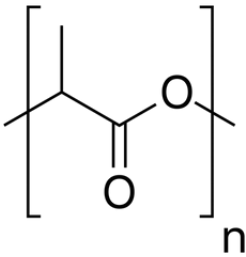
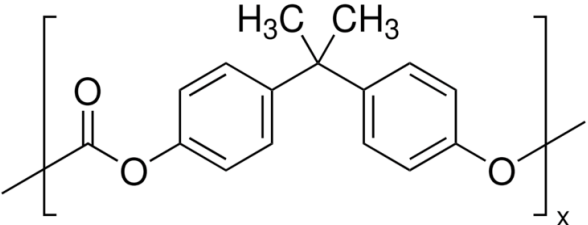
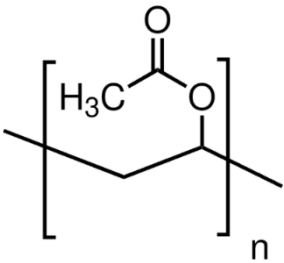
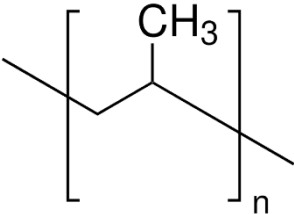
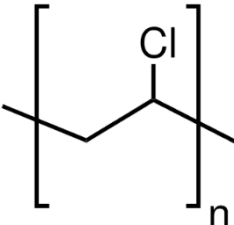
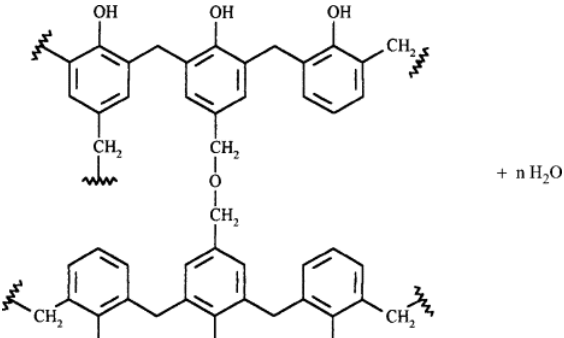
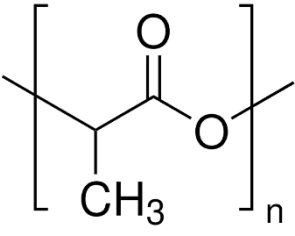
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### 1.2.1 Polymer structure

Polymers are repeating units of monomers, typically high in molecular weight. Monomers are the individual building blocks and when repeated and linked, monomer units form polymers through a process of polymerisation. In the manufacture of polymers, the molecular weight of the repeating units combined shows a range of different molecular weights per polymer sample. Polymers can be natural or synthetic and are often made up of two or more different types of monomers. As molecules, polymers are a global commodity, with versatile properties, cost-effective production, and wide availability in many industries <sup>21</sup>. Perhaps more detrimentally for a circular economy, a characteristic most concerning is their persistence in the environment.

Polymers are not uniform as one might imagine a series of repeated monomer units to be, and so polymers are reported by number-average molecular weight ( $M_N$ ) or weight average molecular weight ( $M_W$ ). An example of polymers and monomer molecular weights are listed in Table 1.

Monomer	Monomer(s) $M_W$ (g/mol)	Polymer
ethene	28.05	Polyethylene (PE)
acrylic acid	72.06	Polyacrylic acid (PAA)
carbonate	61.01	Polycarbonate (PC)
vinyl acetate	86.09	polyvinyl acetate (PVA)
propylene	42.08	Polypropylene (PP)
vinyl chloride	62.50	Polyvinylchloride (PVC)
Formaldehyde, phenol	30.03, 94.11	Phenol formaldehyde (Bakelite)
Lactic acid	90.08	Polylactic acid (PLA)

 <p style="text-align: center;"><b>PE</b></p>	 <p style="text-align: center;"><b>PAA</b></p>
 <p style="text-align: center;"><b>PC</b></p>	 <p style="text-align: center;"><b>PVA</b></p>
 <p style="text-align: center;"><b>PP</b></p>	 <p style="text-align: center;"><b>PVC</b></p>
 <p style="text-align: center;">A representative segment of phenol-formaldehyde polymer</p> <p style="text-align: center;"><b>Bakelite</b></p>	 <p style="text-align: center;"><b>PLA</b></p>

**Table 1. Common monomers and polymers showing their repeating units.**

Polymers can be linear or have repeating units that are branched. Typically, linear polymers have a low resistance to heat and will melt, whereas crosslinked, branched polymer chains have strong primary covalent bonds which are heat resistant and thermosetting in their 3D structure<sup>22</sup>. Copolymerisation is a method used to produce repeating units of two or more different monomers, forming bespoke copolymers of different properties and the availability of a wide variety of different materials that can be manufactured from two or more different monomers. Homopolymers are consistent chains formed from one monomer repeated.

Polymerisation uses monomers from petrochemical feedstocks to produce plastics, fibres, and synthetic rubber. Polypropylene as an example, is made from carbon and hydrogen monomers of ethene. The alkene double carbon bonds break at high temperatures (200°C) and pressure (2000 atm) addition polymerisation repeats the ethene monomer to form chain lengths of  $10^4$ - $10^7$  long chain lengths of low-density (LDPE) and high-density polyethene (HDPE)<sup>23, 24</sup>. LDPE is a low-strength polymer and is commonly used to make plastic bags, in contrast, HDPE is strong with a high boiling point and can be purposed into food containers, plastic bottles, and pipes for plumbing. Polypropene is also made from carbon and hydrogen atoms, and propene monomers through addition polymerisation making a strong, temperature-resistant polymer suitable for dishwashing/autoclaving.

Chlorine, nitrogen, or oxygen can be incorporated into petrochemical derivatives to create gels, lubricants, elastomers, plastics, and fibres<sup>25</sup>. For example, replacing one of the hydrogen atoms of ethene with a chlorine atom produces chloroethene. Chloroethene monomers are used to produce polychloroethene, previously known as polyvinylchloride (PVC) and used in plastic PVC windows and doors, to make signs and used in the manufacture of clothing. In some cases of polymerisation, they are finished products; in others, more steps are needed to arrive at the desired composition.

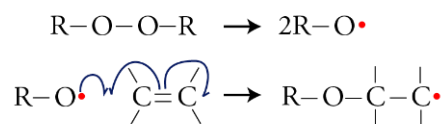
### 1.2.2 Polymer Synthesis

Typical organic syntheses of polymers begin with crude oil-derived petrochemical feedstocks and use two main methods. Addition reactions also referred to as chain growth or chain reaction polymerisation, are a three-step process of monomers containing carbon-carbon double bonds that can form long chain molecules.

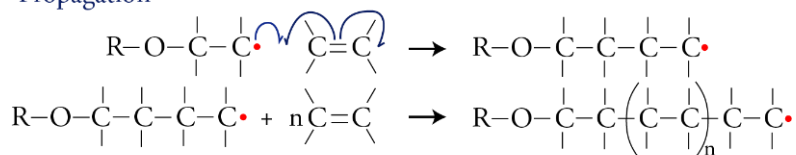
The mechanism of radical polymerisation reactions follows three stages (Fig. 2):

1. Initiation - active species where a free radical or a coordination complex are the initiators of the chain reaction and incorporation of the first monomer molecule into the chain occurs.
2. Propagation – repeated addition of monomer molecule to the chain, which remains a radical.
3. Termination – a reaction to end the radical chain reaction resulting in a non-radical polymer molecule..

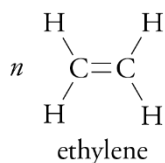
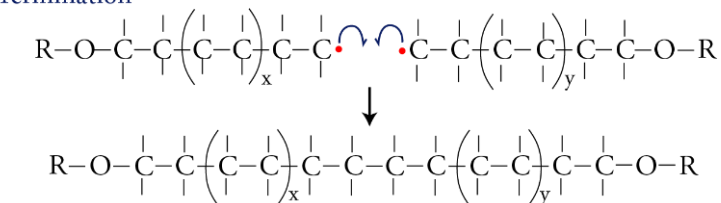
### Initiation



### Propagation



### Termination



polymerization

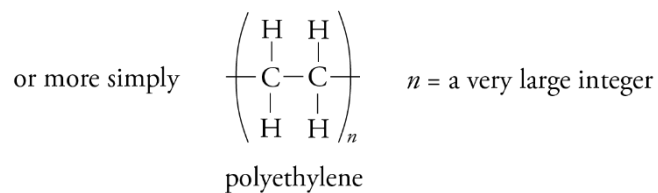
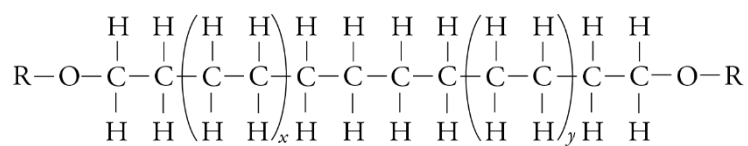


Fig. 2 Ethylene polymer synthesis and the three mechanism stages of initiation, propagation and termination<sup>26</sup>.

An example of a condensation reaction polymerisation is by forming an ester bond from carboxylic acid and alcohol functional groups, typically losing a water molecule when reacting under acidic conditions<sup>23</sup>.

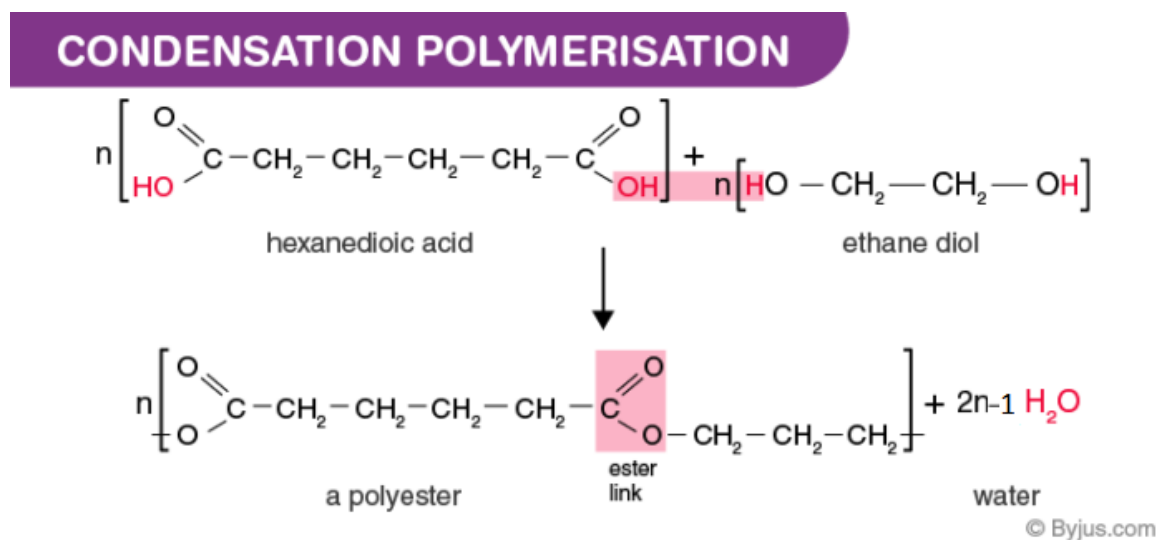


Fig. 3 Condensation polymerisation of two monomers, hexanedioic acid and ethane diol to produce the polymer polyester and water by-product<sup>27</sup>.



### 1.2.3 Polylactic acid- bioresource-derived polymer

Polylactic acid (PLA) can be made from condensation polymerisation of lactic acid monomers copolymerised with glycolic acid monomers. To increase the rate of degradation for disposable packaging and takeaway food and drink thermoplastic containers and cutlery, PLA is produced from natural and renewable feedstocks such as corn, and sugar cane plant starch, where the ester group can be hydrolytically cleaved for biodegradation and assimilation in the environment<sup>24,28</sup>.

### 1.2.4 Alternative polymers and synthesis

After cellulose, the second most abundant polymer in the world is lignin. Lignin, cellulose and hemicellulose have an important structural role in plants, from cell walls to water transport and protection from plant environmental stresses and insects and pathogens<sup>29,30</sup>. Lignosulfonates are a product of lignin extracted from wood pulp and in the process of sulfonation or condensation produce water-soluble biopolymer<sup>31</sup>. Emulsification helps the polymerisation process by stabilising monomers through coupling water and oil phases. Emulsifiers have a hydrophobic head and a hydrophilic tail. Alky sulfates or sulfonates are examples used in synthetic latexes used as binders for example in coatings and paint<sup>22</sup>.

### 1.2.5 Polymer uses in agriculture

In agriculture, the predominant plastic initially considered is of low-density polyethylene (PE), introduced from in 1930s as mulch films<sup>12</sup>. Mulch films are a widely available, affordable, common practice for one-season use, and benefits field weed control, humidity retention, improved soil heat capacity, minimised insect damage, and increase in crop quality and yield<sup>32,33</sup>. The consumption of plastic films suggests that in Europe (2003-2005 data) the tonnage of mulching films consumed was around 1 500 000, and 26 000 000 worldwide<sup>34,35</sup>. Considered to occupy onward of 40 % of plastic films, the visible 'white pollution' associated with mulch films is considered a primary source of microplastics found<sup>20,36</sup>. Although mulches are considered a secondary source of microplastics, the focus of this research is on the requirement for biodegradable polymers at the micro level of formulation chemistry, where primary-use plastics are added into formulations as adjuvants, commonly referred to as co-formulants, for properties not limited to water retention, coatings, and film-forming agents.

Agricultural polymers are not limited to PE, and natural and synthetic polymers use in the field include proteins, polyacrylates, polyacrylamides, and polysaccharides for use in pesticides, herbicides, molluscicides, biocides, super absorbent polymers, soil remediation and drag resistance, encapsulation or heterogenous dispersion<sup>32</sup>.

Primary source microplastics are defined as less than 5  $\mu\text{m}$  in size<sup>37</sup>, purposely designed for their direct raw material use as formulants in industries of cosmetics, cleaning products, agriculture, and paints. Secondary source microplastics are a result of larger pieces of plastic that have fragmented or broken down<sup>38</sup>. Acrylic polymers and their copolymers are widely varied in chain length, chemical properties, functionality and uses, from the coating industry to textiles, paints, road construction, and agriculture<sup>39,40</sup>. Often, acid monomer

esters, for example, propenoic acid (acrylic acid) are used to prepare acrylic polymers (Fig. 4) using basic acrylic free radical polymerisation and are the primary plastic to benchmark biodegradable, renewable alternatives in this study<sup>41,42</sup>.

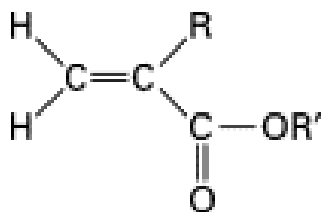


Fig. 4 Acrylic ester. R = H for acrylates, R = CH<sub>3</sub> for methacrylatesm R' = alkyl groups

The degradation of agricultural plastics after they no longer become functional for their designed purpose should be considered as a responsible consumer, environmental, government and legislative issue. Environmental degradation and biofragmentation naturally occur to reduce the typical use of agricultural polymers into smaller particle sizes. The main cause of the degradation of agricultural plastics during their useful lifetime are photodegradation and oxidation<sup>43</sup>. With no economic or practically available direct disposal options for non-biodegradable polymers at the level of PLFs, still the degradation of agricultural plastic waste, at the macro or micro level, should not result in contamination of soil, water or environmental pollution. Aligned with the Green Chemistry Principles, identifying plastics degradation, measuring it and controlling it can be considered by three major factors of polymer degradation, environmental conditions and polymer composition.

#### 1.2.5.1 Polymer degradation

Plastics degrade through many routes, fragmentation from physical and environmental mechanisms and chemical changes within the plastic that arise from abiotic degradation. Chemical reactions can cause chemical degradation with surrounding chemicals in the environment, such as agrochemicals. Chemical reactions typically involve polymer chain scission via surface erosion or chemical hydrolysis which fragments the polymer. Microorganisms that can biochemically interact with the plastic are the onset of biodegradation, which begins with enzyme and non-enzyme-catalysed reaction mechanisms fragmenting the polymers further, reducing the molecular weight and cleaving as monomer units<sup>2,44,45</sup>.

#### 1.2.5.2 Environmental conditions

Environment conditions for degradation during and after the useful lifetime are dependent on the environment that the polymer has been in. This can vary from aerobic, humid, dry, soil, landfill, composting environment, sewage, fresh water and marine. Light, darkness, oxygen, water, microbial community and presence of chemicals, and in what concentration, are characteristic environmental profiles that also determine the efficiency of biodegradation<sup>46</sup>. Microorganisms responsible for the end stage of biodegradation are sensitive to temperature, humidity, atmospheric pressure, gases, pH, and light exposure<sup>47</sup>. Substrate and or microorganism concentration, and nutrient availability also can increase or decrease the rate of biodegradation, even inhibiting where conditions are not met.

### 1.2.5.3 Polymer composition

The chemical composition is the key to the potential rate and degree of biodegradation. The polymer is a substrate for the environment and enzymes to degrade into readily bioassimilate materials. Assimilation can only occur where the nature of the chemical bonds present in the feedstock input and industrial product output are cleavable for chemical and biodegradation. In the case of petrochemical feedstocks, carbon-carbon single-bond backbones are chemically stable, hydrophobic and particularly resistant to biodegradation. Hydrolytic cleaving is not possible, where oxidative mechanisms are limited. Oxidation mainly occurs in amorphous regions; however, polyolefins typically are very crystalline in structure making oxygen permeation difficult<sup>2</sup>. Molecular weight, surface and crystallinity are also factors to consider<sup>47</sup>. Originally designed for ultimate strength and durability, it is important to process feedstocks with not only the functional use of the life of the product but also the environmental aftermath of the raw materials selected for use. Hence replicating chemistry used in naturally derived materials also ensures the same motifs of chain branching and stereochemistry that environmentally existing enzymes typically handle<sup>2</sup>.

### 1.2.5.4 Applied use in industry

The approach in this study is to consider the Green Chemistry Principles originally addressed by Paul Anastas and John Warner in 1998<sup>5</sup>. Applying knowledge of the industry combined with the Green Chemistry Principles can implement a significant change in the formulation chemistry to design alternatives to synthetic, primary microplastic polymer use. In PLFs designed for agricultural use, internal production at Yara Pocklington has increased by 30%, inclusive of raw material demand and processing. Up to 60 tonnes of polyacrylate raw material have been used in the last year following increasing demand for fertiliser. An improvement in formulation sustainability would be to use PLFs that are from renewable, biodegradable sources that are equivalent in quality and performance and assess the life cycle of the raw materials as individual components.

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## 1.3 Implementation of the Green Chemistry Principles in Industry

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With significant global market share across industries, petrochemical plastics have shown in recent years, the largest volume growth of any chemical material, with significant rising costs of oil as the input raw material feedstock<sup>8,48</sup>. Not limited to this are the finite raw material sources and persistence in the environment that give rise to an opportunity to switch from non-renewable petrochemical-based chemistry to renewable carbohydrate-based chemistry. Challenges with market transformation exist where policy is not defined, and the availability, economy, persistence, and diverse functionality of widely available commodity petrochemical plastics make their continued use attractive. For the practising chemist, the application of Green Chemistry Principles (Fig. 5) outlines a proactive approach to drive a sustainable chemical economy for the future. Societal demands and targets for sustainable, nature-positive food security, especially in agriculture are changing; Fertilising Product Registration (FPR) and representative bodies for organic farming, including The Soil Association, Ecocert, FiBL, ABCERT and OMRI, illustrate the evolution of societal concerns regarding toxicity and environmental effects<sup>49</sup>. The prospect of a large-scale

shift from the dependence of the chemical industry on petrochemicals to renewables is a key principle in Green Chemistry, found in the framework by Anastas and Warner's principles in Fig. 5<sup>5,49</sup>.

### Green Chemistry Pocket Guide

#### The 12 Principles of Green Chemistry

Provides a framework for learning about green chemistry and designing or improving materials, products, processes and systems.

1. Prevent waste
2. Atom Economy
3. Less Hazardous Synthesis
4. Design Benign Chemicals
5. Benign Solvents & Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis (vs. Stoichiometric)
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Inherently Benign Chemistry for Accident Prevention

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ACS Chemistry for Life™ ACS Green Chemistry Institute

### The Chemistry of Nature

**Green Chemistry Definition:** *The design, development and implementation of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.*

Green Chemistry is doing chemistry the way nature does chemistry – using renewable, biodegradable materials which do not persist in the environment.

Green Chemistry is using catalysis and biocatalysis to improve efficiency and conduct reactions at low or ambient temperatures.

Green Chemistry is a proven systems approach.

Green Chemistry reduces negative human health and environmental impacts.

Green Chemistry offers a strategic path way to build a sustainable future.

*To catalyze and enable the implementation of green chemistry and engineering throughout the global chemical enterprise*

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Fig. 5 Developed by Paul Anastas and John Warner in 1998, the list of principles outlines a framework for making a greener chemical, process, or product<sup>5,48,50</sup>.

Microplastics most often detected in the environment are polyolefins (polyethylene (PE) and polypropylene (PP)), and polyethylene terephthalate (PET)<sup>51</sup>. These polymers have a high molar mass, and the molecular weight is primarily contributed to by either stable carbon-carbon backbone or C-heteroatom bonds, enabling a strong and permanent structure for resilience against harsh chemical and environmental conditions, enabling persistence in the environment for up to several tens and to hundreds of years<sup>2,3</sup>. In an approach to one of the Green Chemistry principles, biodegradability, polymers made from biodegradable materials are often discussed as one of the solutions to substituting microplastics from non-biodegradable materials. As microplastics are inherently non-biodegradable, polymers that could substitute the manufacture of polyolefins could contribute to better biodegradation and reduce the presence of persistent materials known to enter waterways and elude waste management systems (Fig. 6). As depicted in Fig. 6, in this century, the expanse of the problem of microplastic waste is a common topic of attention from industry policymakers, conservationists, the public and scientists<sup>3,52</sup>.

### 1.3.1 Sources of microplastics, release routes, waste, and sinks

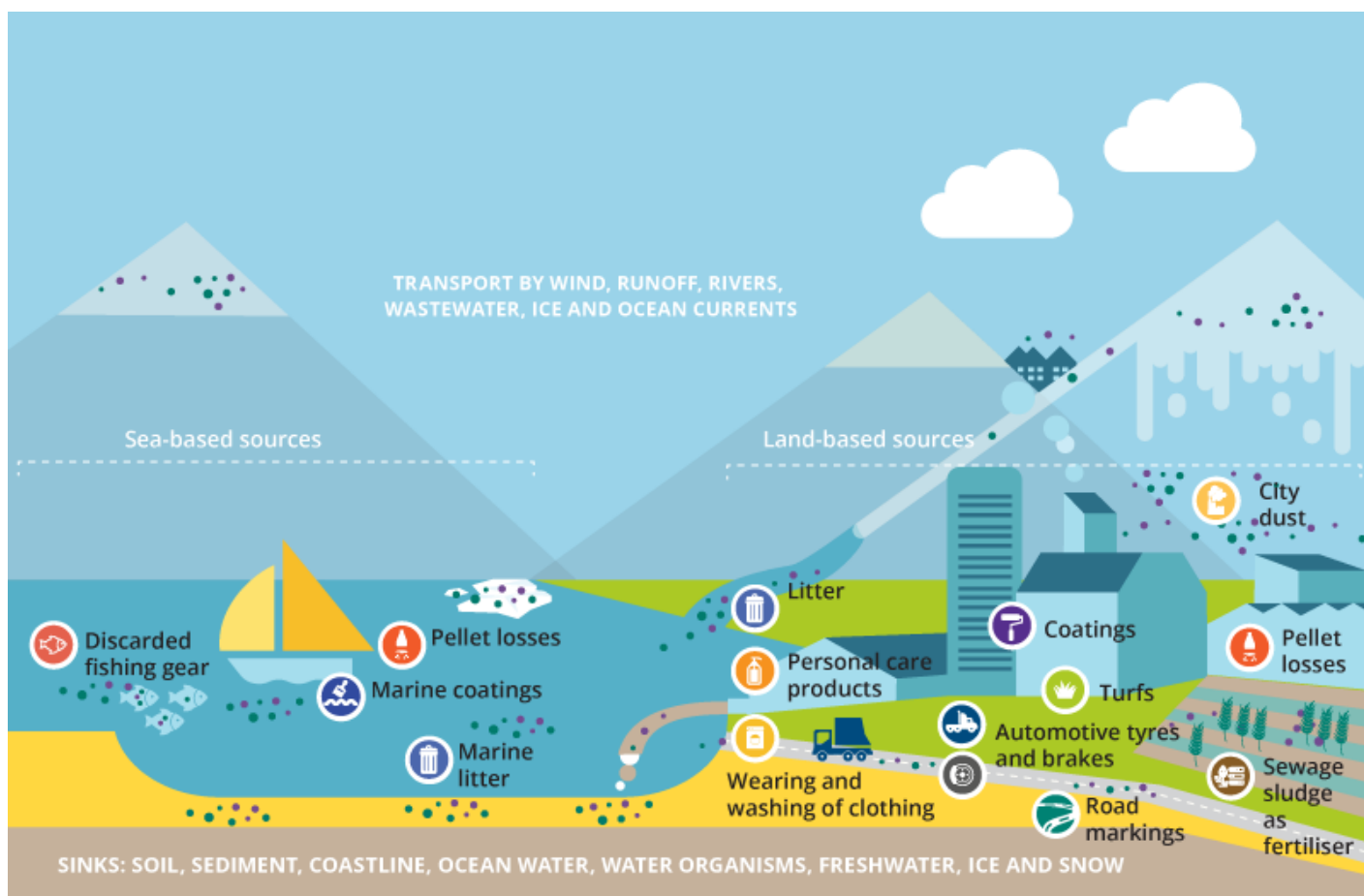


Fig. 6 Illustration by the Collaborating Centre on Sustainable Consumption and Production (CSCP) for the European Topic Centre on Circular Economy and Resource Use (ETC/CE) and the European Environment Agency (EEA) showing the current use economy of textiles in Europe<sup>52</sup>.

To begin the journey of addressing microplastics as a direct environmental pollutant from agriculture as an industry, the most obvious route is to eliminate the use of persistent chemicals or non-biodegradable chemicals in practice. It is also necessary to assess requirements for biodegradable alternatives where currently non-biodegradable materials are used. Exploring this potential in the agricultural industry is primarily considered in plastic mulch films, however, ILs and dispersants also play a role in foliar nutrient sprays as a form of industrial-scale agricultural fertilisation and are predominantly directly applied into the environment for the entirety of their life in and out of service. Further work is to be assessed on the biodegradability of solutions and compounds. Assumed in their liquid form, PLFs are not an obvious challenge for biodegradability, however, it is of future and current relevance and concern for policy and practice.

The focus of this study is to eliminate the use of petrochemically sourced formulants of YaraVita foliar nutrient spray formulations that are of the greatest volume of bulk production and raw material use. Market

volumes of products produced locally on-site at Pocklington, UK, and exported globally, highlighted suspension concentrate technology as the main contributor to manufacture which uses a dispersion and thickening system. As opposed to the alternate powder and liquid solution foliar nutrient fertiliser applications, the thickening dispersion system of suspension concentrates is a major contributor to the petrochemical-derived polymers used and of interest in this research. The aim is to eliminate the use of persistent or non-biodegradable dispersants where suitable biodegradable alternatives exist relative to this sector of industry and production scale.

### 1.3.2 Principle 1: Prevention

*“It is better to prevent waste than to treat or clean up waste after it is formed”<sup>53</sup>.*

Synthetic polymers are currently used in a third of the YaraVita foliar formulations, with typical inclusion rates ranging from 0.1 – 5.0 % w/w. The primary uses of polymers in fertiliser are as surface-acting agents, or surfactants, and thickening agents in suspension concentrate formulations. Surfactants in chemistry have a multitude of uses, not limited to agriculture, which makes them widely available, cost-effective, and a commodity for many industrial applications.

The polymers used for co-formulant properties critical to the function of the foliar nutrient spray are currently not biodegradable due to the polymer chemical composition as described. The inherent persistence in the environment is from the raw material feedstock processing (Fig. 7). Crude oil is the primary material from which petrochemicals and petroleum products are derived. Petrochemical products are referred to as organic, hydrocarbon compounds, the secondary products from the refining of crude oil that are not burned as a fuel. Petrochemicals are chemically characterised into three categories: olefins, aromatics, and synthetic gas<sup>54</sup>.

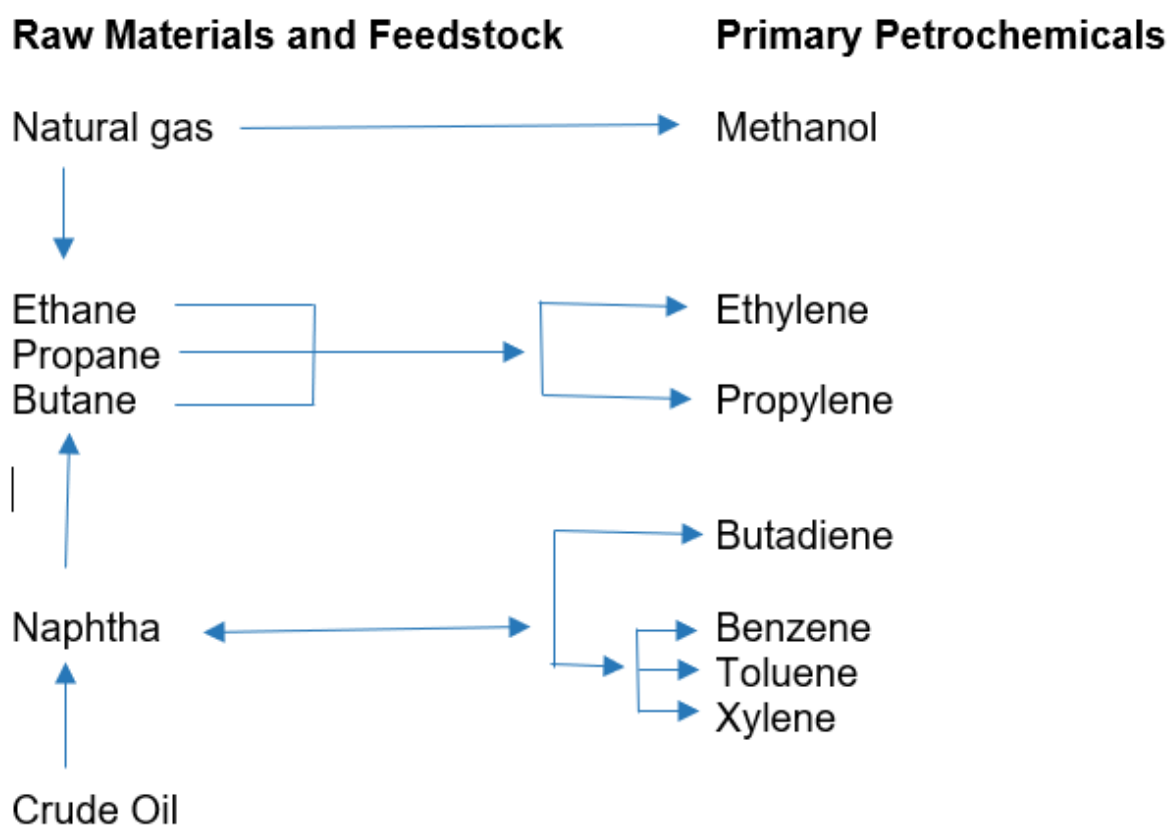


Fig. 7 Raw materials and primary petrochemicals derivatives.

As shown in Fig. 7, primary petrochemicals are the basis for further refinement. In the category of aromatics, benzene, toluene, and xylenes are major components and are important inputs for the processes of manufacturing synthetic detergents, polyurethanes, plastic, and synthetic fibres. Butadiene is an olefin used to make synthetic rubber, whereas ethylene and propylene are important resources for the manufacture of plastics<sup>54</sup>. Ammonia and methanol production from the inputs of carbon monoxide and hydrogen in synthesis gas are also contributors to the production of synthetic materials and chemicals, such as gasoline, diesel, methanol, and dimethyl ether<sup>25</sup>.

Existing formulations of foliar nutrient sprays generate microplastic waste from PLFs predominantly from polyacrylate thickeners and dispersants. Other co-formulants that can be considered as polyolefin-derived synthetic polymers of anti-foams, wetting agents and biocides, though these PLFs are required in significantly less concentrations than the thickening and dispersion systems (<2%).

In foliar micronutrient formulations, hydroxide ions are available in the suspension concentrate formulations from one active nutrient source of potassium (K) from the strong alkali potassium hydroxide (KOH), and it is often used as a precursor for thickening systems if not an intentional active nutrient source. Carboxylated acrylic polymers and their copolymers swell with electrostatic forces and interactions between monovalent alkali metal ion hydroxides, such as salt ions of potassium. Swelling can be highly effective, as an example from Wiese & Rupaner (1999) describes, a poly(n-butyl acrylate) latex copolymerized with 15 wt % methacrylic acid (MAA) and 7 wt % acrylonitrile, the particle volume increases by a factor of 30<sup>55</sup>. With many commercial acrylic polymer dispersions contain small amounts of copolymerized acrylic or methacrylic acid



for stabilisation of the latex particles, a high degree of swelling can be achieved with low glass-transition temperatures polymers and by distributing the carboxyl groups evenly within the latexes<sup>55</sup>. Such thickening gives a cost-effective, commodity approach that is chemically accepted and standardised across industry use, not limited to agriculture. Free radical polymerisations of acrylic polymers and copolymers in aqueous dispersions are synthesised from acrylic and methacrylic esters (Fig. 4)<sup>40,42</sup>. The acrylate emulsion and solution bulk grades are commercially available and extensively used for thickening and coating<sup>56</sup>. Whilst also known for their multifunctional and adaptable use, in selecting the desired property relative to the R and R' groups, acrylates and their copolymers have outstanding stability under severe service conditions, not limited to their industrial life cycle (Fig. 8).

Once the applied formulations have performed their spray function, optimising the delivery of foliar plant nutrition, the PLFs after a useful lifetime are destined to be microplastics in the environment. Fig. 8 shows the land application of agricultural products and indicators of resulting environmental release, which suggests that PLF materials result in air, water, and land emissions<sup>8</sup>.

At the agricultural scale, the entry of microplastics into the environment covers a large area, and is direct, from the application of seed coatings, foliar fertilisation and granular fertiliser coatings or encapsulations. Currently, no clean-up operation exists for waste at the microscopic level for persistent molecules or microplastics. The physical properties of microplastics make them ubiquitous in terrestrial and aquatic environments. One of the most prevalent areas where microplastics are detected is in the water cycle. Microplastics of an approximate length of 200  $\mu\text{m}$  and width of 50  $\mu\text{m}$ , were commonly found fragments when quantifying microplastic presence in UK mainland water. Using a cost-efficient method for the collection and identification of microplastics in UK inland waters, microplastics have been detected in marine, fresh, waste and tap and bottled water<sup>38,57,58</sup>.



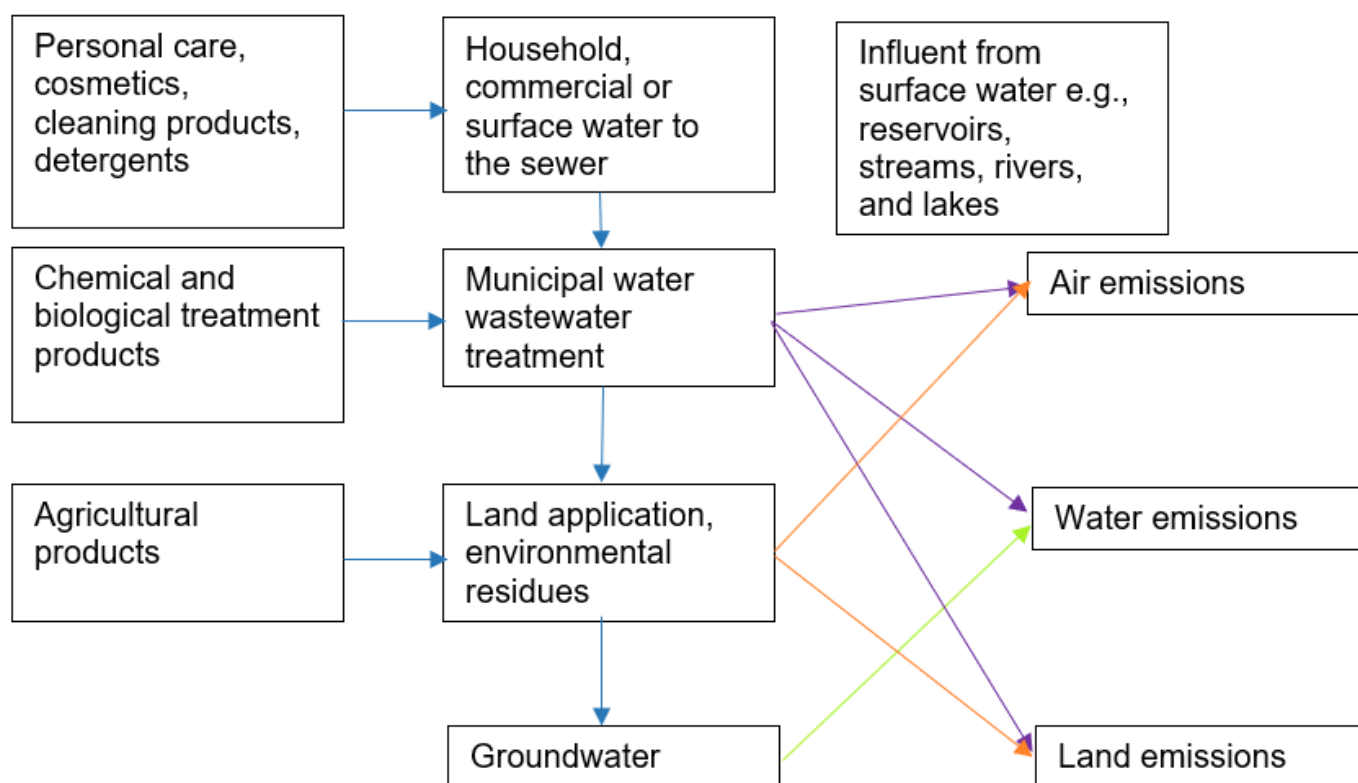


Fig. 8 Environmental fate of liquid formulation systems.

Where agricultural PLF products are applied directly to the land by farmers, these do not enter water treatment facilities. The persistence in the environment is likely to be of solid microplastic fragments and their biofragmentation in the environment, which can further release air emissions such as NO<sub>x</sub><sup>8</sup>. PLFs may persist in the soil and groundwater after a useful lifetime, whilst their microscopic size enables transportation through watercourses into lakes, rivers and seas. Dunn et al. found pieces of microplastic from all sample sites ranging from over 1000 L<sup>-1</sup> in the River Tame, Greater Manchester, to 2.4 L<sup>-1</sup> in Loch Lomond National Park, Scotland<sup>38</sup>. Whilst fragments of this study were found to be greater than 5 µm, smaller microplastic fragments are likely to have greater mobility and surface area cover in terrestrial environments<sup>38</sup>. A recent investigation tracing water-soluble polymers from cosmetics indicated that PLFs of acrylic acids, polyethylene glycols and polyquarterniums are effectively removed from wastewater treatment plants. Where PLFs remained by sorption in sewage sludge, researchers concluded the PLFs are likely to remain at the site of entry to soil where slow biodegradation is expected<sup>8</sup>. So far, the environmental scale of the problem is not apparent.

One impactful solution is redesigning consumer products to make them resource-efficient. Preventing and reducing consumption of products are implemented, and existing examples include the design of durable, refillable packaging alongside direct-to-consumer refill-and-reuse models as seen in no-food-waste shops,

and personal care brands as a way of reducing the amount of plastic used in products and packaging<sup>59</sup>. Recycling is widely implemented for certain plastics, glass and paper, however, is not as sustainable as preventing waste by reducing or reusing. The government outlined guidance for businesses on how to apply the hierarchy of waste management, however, there is no specific guidance for materials such as PLFs<sup>8,60</sup>. Typical polymer content in formulations is 1% or less by weight, resulting in the usage of 10 million tonnes per annum globally of PLFs<sup>8,61</sup>.

The current best example of reduced polymeric waste in agriculture is the introduction of organic farming. The aim of organic farming is to produce nutritious food at a high quality using natural and sustainable practices. Such practices manage food production without the use of synthetic chemicals, or genetically modified organisms (GMOs). Organic farms are regulated by organic farming bodies and play a key role in soil health and biodiversity through crop rotation, composting and targeted use of specific nutrient fertiliser suitable for organic farming only where there is a proven deficiency<sup>62</sup>.

By producing high-quality, nutritious food, organic farming practices will play an essential role in developing a sustainable food system. The EU has adopted a target for organic farming practices to be established in at least 25% of the EU's agricultural land, operating specifically for growing organic produce by 2030<sup>63</sup>. Currently, an organic area made up 9.1% of total EU agricultural land in 2020<sup>63</sup>. Whilst foliar nutrient sprays are not organic themselves, bodies for organic certification rigorously test formulation and product composition to ensure sustainable practices and naturally derived ingredients are compliant and meet the stipulated stringent guidelines on chemicals that are naturally sourced. Currently aligned to the European Green Deal, the Farm to Fork Strategy initiative has set a significant challenge for sustainability for agriculture, fishery and aquaculture<sup>63,64</sup>. Such actions stimulate sustainable practices and drive market demand and industry compliance for the supply of sustainable products, integrating sustainability into corporate strategies, where renewable feedstocks and their implementation are essential.

Implementing Green chemistry is a type of pollution prevention, which in this study concerns a fundamental change in the intrinsic nature of the feedstock for the product's environmental outcome. By designing and redesigning chemical alternatives, the prevention and elimination of marine microplastic pollution implement an active industrial approach to pollution prevention as opposed to end-of-pipe control. Launched in 2016, UN sustainable development goals are aligned with addressing global challenges for countries to make an impact socially, economically, and environmentally by 2030<sup>65</sup>. Of the 17 sustainable development goals, affordable and clean energy is number 7 and a target to reduce the use of oil and petroleum-derived fuels for a sustainable future not limited to farming or agriculture<sup>46,48</sup>.

### 1.3.3 Principle 7: Renewable Feedstocks

The 7<sup>th</sup> principle states:

*“a raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable”<sup>5</sup>.*

One of the greatest challenges in replacing petroleum oil derivatives with materials from a renewable source is their degree of oxidation. Current processes are widely adopted to accommodate hydrocarbon compounds for ratios of C:H:O 85-89% carbon, 10-14% hydrogen, <1% oxygen<sup>6,66</sup>. Renewable biomass, on the contrary, is ca. 75% carbohydrate, 20% lignin and 5% fats, proteins, and vegetable waxes/secretions, with C:H:O ratios of 50-75% carbon, 6-13% hydrogen and 11-45% oxygen<sup>6</sup>. This indicates new process development must be established to accommodate the chemical processing of renewable resources, preferably with atom economy in mind. A closed-loop system for the similarities and differences is highlighted in Fig. 9.

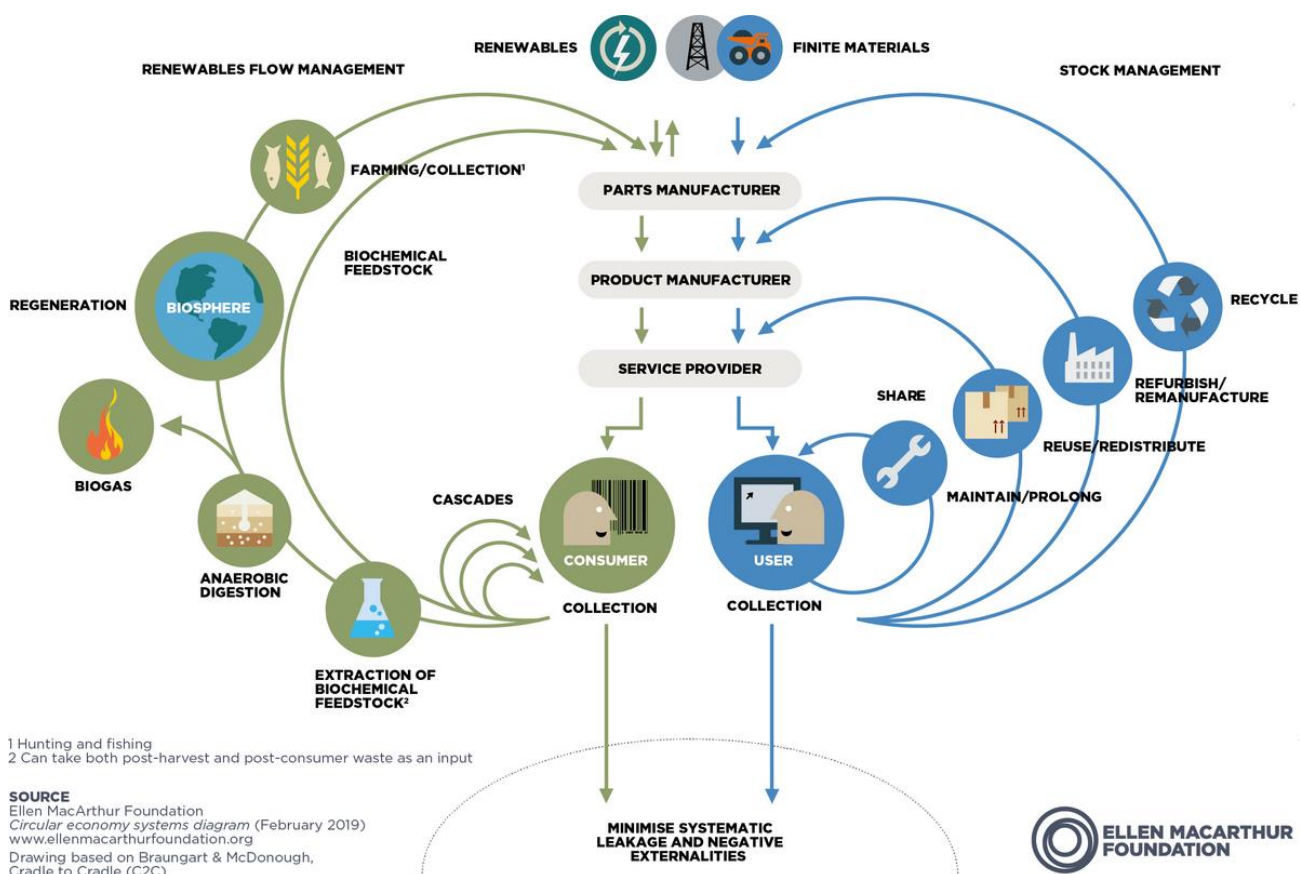


Fig. 9 Closed loop biorefinery approach for bioplastic production, the butterfly diagram shows how a circular economy could work, comparing renewable and non-renewable feedstock systems<sup>67</sup>.

Lignocellulosic biomass is considered a renewable feedstock. Biomass including agricultural waste, forest residues, and woody biomass, is an abundant (130 billion t y<sup>-1</sup>) source already used to produce

polyhydroxyalkanoates (PHA) and is not limited to products of PHA. Alternative renewable feedstocks and the possible additions of fossil-based fuels available for processing as shown in Fig. 10 and Fig. 11.

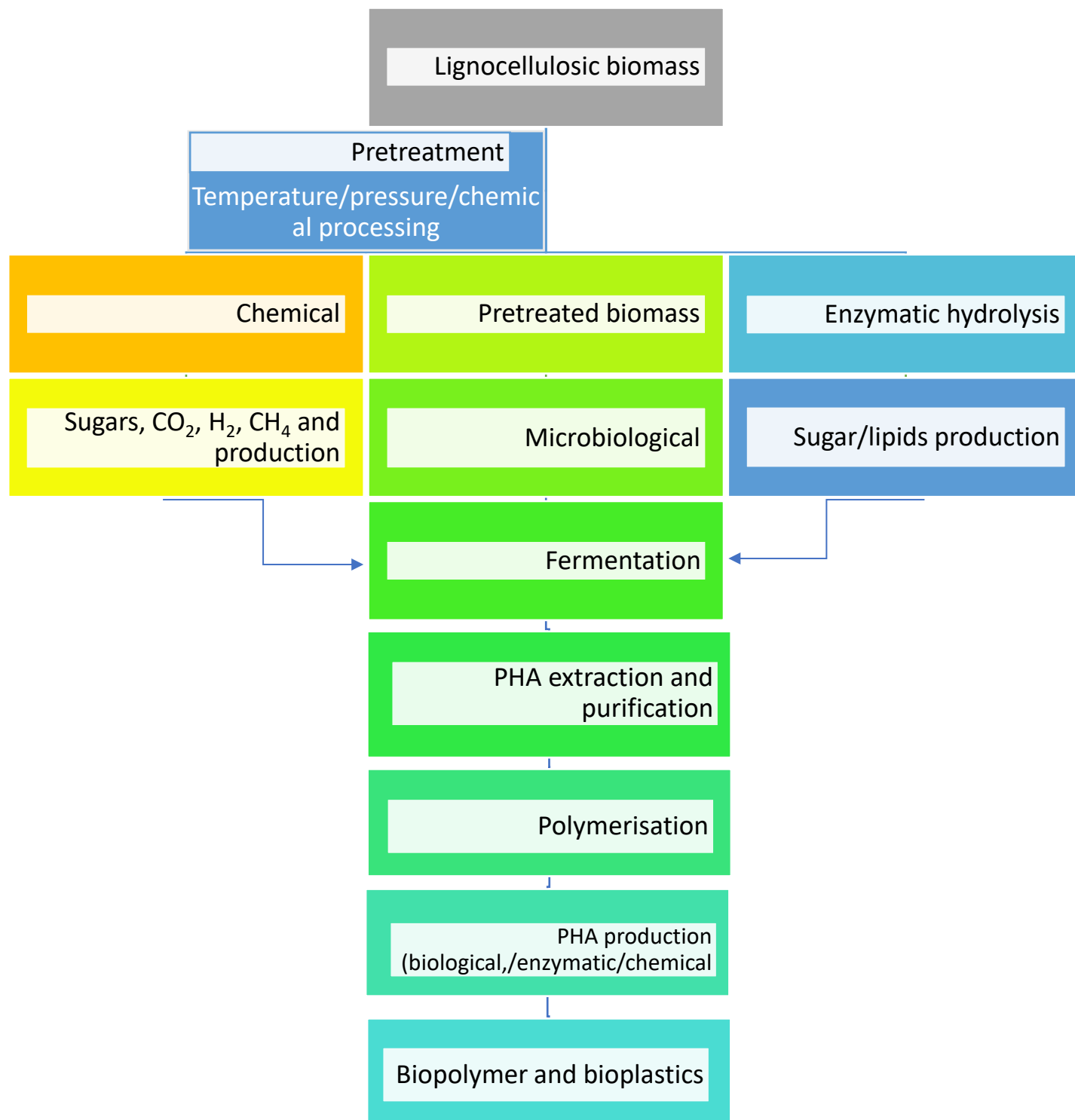


Fig. 10 Polyhydroxyalkanoates (PHA) monomer and polymer syntheses, of different feedstocks, can be combined to produce many structures of biodegradable polymers available commercially today, adapted

from Raj et al., (2022). Lignocellulosic biomass as renewable feedstock for biodegradable and recyclable plastics production: A sustainable approach<sup>68</sup>.

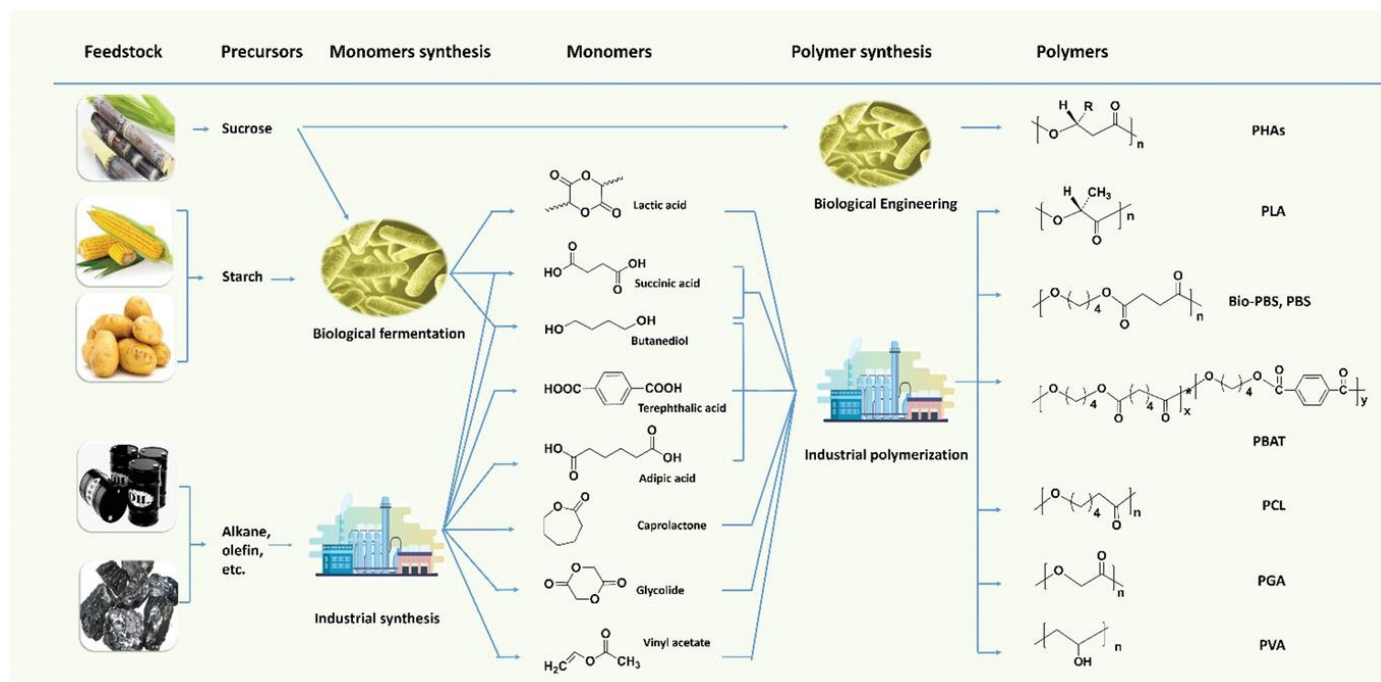


Fig. 11 Structures and sources of commercial biodegradable polymers (bio-based and fossil-based). Seawater-degradable polymers: Seawater-degradable polymers—fighting the marine plastic pollution<sup>46</sup>.

Natural gas and oil are costly, finite resources. Challenges to current methods of production are increasingly pursued by consumers and legislation-driven action to supply more sustainable alternatives in industries. Aligning industries with renewable feedstocks is a Green Chemistry Principle that can drive the industry to switch from non-renewable petrochemical-based chemistry to renewable carbohydrate-based chemistry for such areas of polymer use and manufacture<sup>28</sup>.

### 1.3.4 Principle 10: Biodegradation

The 10<sup>th</sup> principle states,

*“Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products”<sup>5</sup>.*

Biodegradation of polymeric material can be considered in two steps, typically classified according to the agency causing it. First, the macromolecules can be fragmented into lower molecular mass molecules or monomers by abiotic reactions; oxidation, photodegradation, thermo-oxidative degradation, thermal degradation, hydrolysis, or by biotic reactions, degrading polymers by microorganisms<sup>12</sup>. Secondly, the monomers are bio-assimilated by soil microorganisms and their mineralisation is depicted in the polymer biodegradation process in Fig. 12<sup>16</sup>.

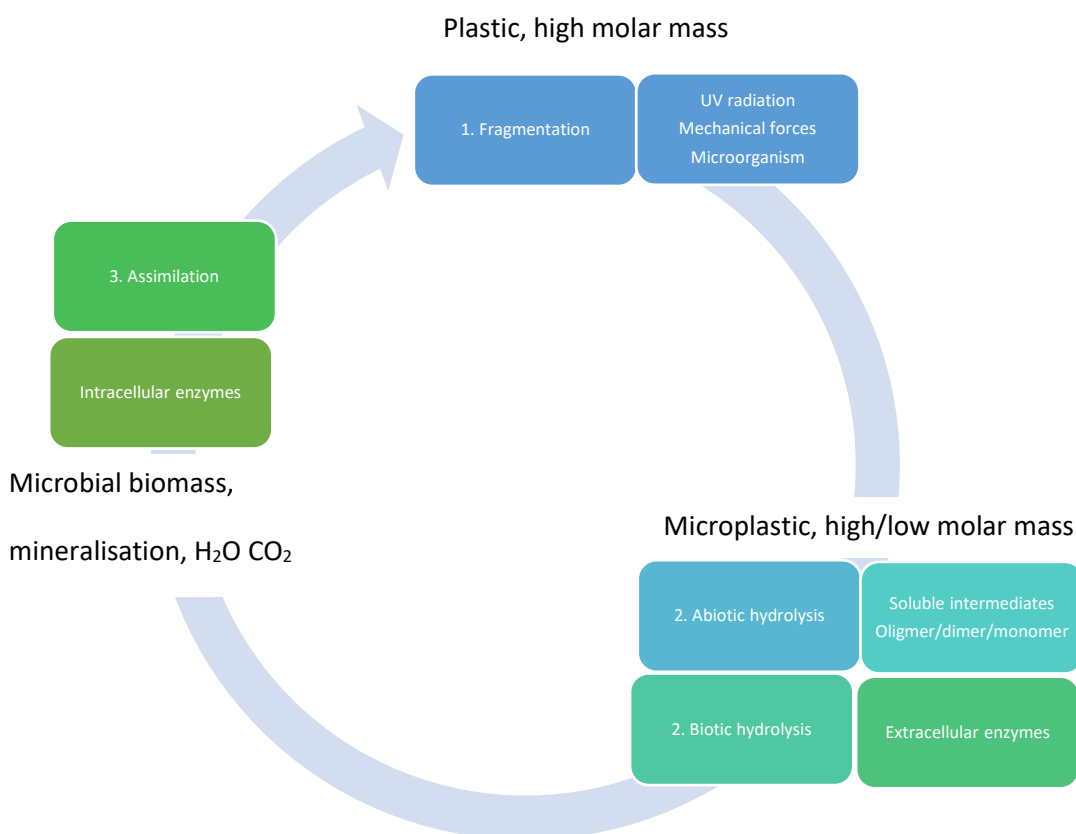


Fig. 12 Schematic representation of the different steps involved in biodegradation<sup>46</sup>.

The origin of the polymer, the chemical composition and environmental conditions for degradation are variables for macromolecule degradation. It is necessary for a standard biodegradability test to estimate the

impact of industrial polymer production on the environment and find alternative solutions to the current extent of exposure to non-biodegradable polymers in the environment. Biodegradation can be challenging to replicate under laboratory conditions, and different test methods have been suggested however, it is necessary to consider each step of biodegradation individually<sup>68,69,70</sup>. By testing independent parameters for each degradation step as an analytical method and indicating standard reference points for each biodegradation process step, inclusive of biofragmentation and biodeterioration, clear parameters for biodegradability can be established.

Vroman and Tighzert (2009) present an overview of biodegradable polymers in current use, however, do not define the array of polymers available and their biodegradability relative to each other, or in relation to a standardised testing method for biodegradability<sup>12</sup>. In agriculture, the biodegradation of polymers used is a significant priority and has application uses across the sector which has a direct impact on the environment, where the end of service life is a concern. In marine agriculture, biopolymers are used to make ropes and fishing nets and natural polymers can be used in controlled release systems. Mulch film development from use in the 1930s to 1970s has now been developed for biodegradability, where after a successful season conserving moisture, soil temperature and reducing weeds films can be left in the soil to biodegrade<sup>47</sup>.

Limited biodegradability has been recognised since before Anastas and Warner's Green Chemistry Principles. From 1965, detergent manufacturers and chemical suppliers removed the use of branched-chain alkyl benzene sulfonates from household detergent manufacture<sup>58</sup>. This voluntary agreement was reinforced with policy in November 1973, covered by two EEC directives; 73/404/EEC<sup>71</sup> and 73/405/EEC<sup>72</sup>, where the average biodegradability of each class of surfactant (anionic, non-ionic, cationic, or ampholytic) is stipulated as 90% or more, and test methods are established for anionic surfactant biodegradability with a test error permitting 80% minimum biodegradability, respectively<sup>58,73,74</sup>. Boethling notably documented 'rules of thumb' for biodegradability, identifying factors such as hydrolysable groups, aromatic rings, and long non-substituted alkyl chains that enable microbial degradation<sup>73,74</sup>.

In 1989 Hollis, in relation to surfactants, states that either linear or straight-chain alcohols give rise to biodegradable products, however, unique proof of whether a polymer is biodegradable or not is determined by international standards and whether a polymer can be assimilated by microorganisms, resulting in the release of CO<sub>2</sub><sup>75,76</sup>. Where carbon coming from one polymer is the only carbon source, it is possible to use the recommended internationally recognised standard methods. If there are multiple carbon sources, for example, the application of a suspension concentrate fertiliser containing PLFs, or a matrix of fertiliser in the soil, where multiple carbon sources are present, the carbon cannot be directly correlated to one single source. Where the carbon can come from the matrix, the polymer, or both it is challenging to analyse the content origins in a cost-effective manner. An isotope analysis can label one carbon source, for example, the polymer, using a stable isotope, also known as a radioelement or fluorochrome and using skilled technicians, specific chemicals, and analytical equipment it is possible to label the carbon identification. An innovative approach by Lucas *et al.* (2008) is to label microbial biomass, produced from the assimilation of carbon source<sup>47</sup>. Labelling by this method is determined by the metabolic processes of plants of how carbon is metabolised into CO<sub>2</sub> from different plant species. There are three different photosynthetic pathways that can produce three identifiable microbial assimilations:

1. C3 plants: CO<sub>2</sub> is incorporated into a 3-carbon compound.

2. C4 plants: CO<sub>2</sub> is incorporated into a 4-carbon compound.
3. Crassulacean acid metabolism (CAM) plants: CO<sub>2</sub> is stored in acid form before incorporation.

If further nutrient assimilation occurs past these stages, the isotope would be modified, indicating there is a further change or assimilation of polymeric material used as the substrate, and can be correlated to polymeric materials and products of a more complex carbon matrix<sup>47</sup>. To replicate the growth and environment of the microbial communities and correlate this to specific plant species representative of the C3, C4 and CAM plants, is however an extensive study.

A repeatable and standardised test method is needed to advise the industry of the biodegradable alternatives and their biodegradation status explicitly. How can it be determined what biodegradable polymer would be most ideal for agricultural use whilst also acting as a functional formulation adjuvant in foliar fertiliser? In the sector of agriculture, application rates of foliar fertiliser, seed coatings or granular coatings, there is a runoff of residual material after end-of-life use which is entered directly into the environment. It is, therefore, necessary to ensure biodegradation occurs at the most critical level, at the end of the polymer's primary designed usage. To be considered and designed as a completely biodegradable material, the final stage is the biodegradation determining step following abiotic involvement, biodeterioration, and biofragmentation is the result of assimilation.

Assimilation integrates atoms and fragmented polymeric substrates from the environment to feed into the microbial system, as monomers pass through the cellular membranes. Microorganisms can utilise mineralised elements and monomers as sources of energy for cellular growth and reproduction through catabolic pathways<sup>47</sup>. Assimilation consists of three essential microbial catabolic pathways: aerobic respiration, anaerobic respiration and fermentation. Through aerobic respiration, microorganisms use oxygen as the final electron acceptor, the opposite of anaerobic respiration where microorganisms are unable to use oxygen and use SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, CO<sub>2</sub>, Fe<sup>3+</sup> and fumarate as final electron acceptors<sup>77,78</sup>. If microorganisms have no electron transport systems, oxygen or alternate exogenous mineral molecules are not able to be used. Fermentation has an incomplete oxidation pathway and uses cells' internal resources of organic molecules as final electron acceptors. Fermentation products include CO<sub>2</sub>, ethanol, lactate, acetate and butanediol<sup>78</sup>. Such molecules are substrates for other organisms as the carbon sources still have a reduction capacity. The molecules released from catabolic pathways at the microbial level present products for further biogeochemical cycles, and generally do not represent any ecotoxic risk.

When designing and formulating fertilisers of any form, products should be considered biodegradable. In the absence of a waste management system, and directly applied to the environment, the material can be self-managed after useful service life.



### 1.3.5 Biodegradation standardised tests

Many polymers that are claimed to be 'biodegradable' are only partially biodegradable, following degradation only by environmental conditions such as UV fragmentation, photodegradation, hydrolysis, and hydro biodegradation, though are ultimately not biodegradable or able to be assimilated by microorganisms to the microbial substrate level. At the consumer level, misleading terminology such as 'environmentally biodegradable polymers' more accurately refers to the fragmentation of polymers in the environment<sup>2</sup>. A chemical change can occur in the environment to chemical structures that are exposed to environmental conditions and fragment these polymers partially (Fig. 12). For the term biodegradation, microbial assimilation must follow the chemical changes and result in the final products of carbon dioxide and water.

Biodegradability represents a complex phenomenon difficult to measure. As stated, biodegradable material can be fully and environmentally safely degraded by microorganisms<sup>75</sup>. Whilst it is challenging to replicate the exact assimilation that occurs in nature, under special conditions a standard lab testing method can provide an estimation of biodegradation by estimating the degree of biodegradability of a product and assimilation products. Complete biodegradation results in the formation of water, CO<sub>2</sub> and/or CH<sub>4</sub>, minerals and new biomass contributing to the biogeochemical substrate.

According to the OECD and the International Organisation for Standardisation (ISO), commonly referred to in Europe and the UK, there are several accepted methods that, if implemented correctly, will provide definitive biodegradation data. Established international standards and test methods for biodegradation exist from the international bodies in Table 2<sup>75</sup>.

American Society for Testing and Materials (ASTM)	 ASTM INTERNATIONAL
European Standardisation Committee (CEN)	
International Standards Organisation	
Organisation for Economic Co-Operation and Development (OECD)	
National Institute for Standards Research (ISR) (USA)	
German Institute for Standardisation (DIN)	
Association Francaise de Normalization (AFNOR, France)	

Table 2 Established international standards and test method standards for biodegradation.

The testing strategy suggested and described by the OECD is represented in the process flow diagram in Fig. 13 and Fig. 14.

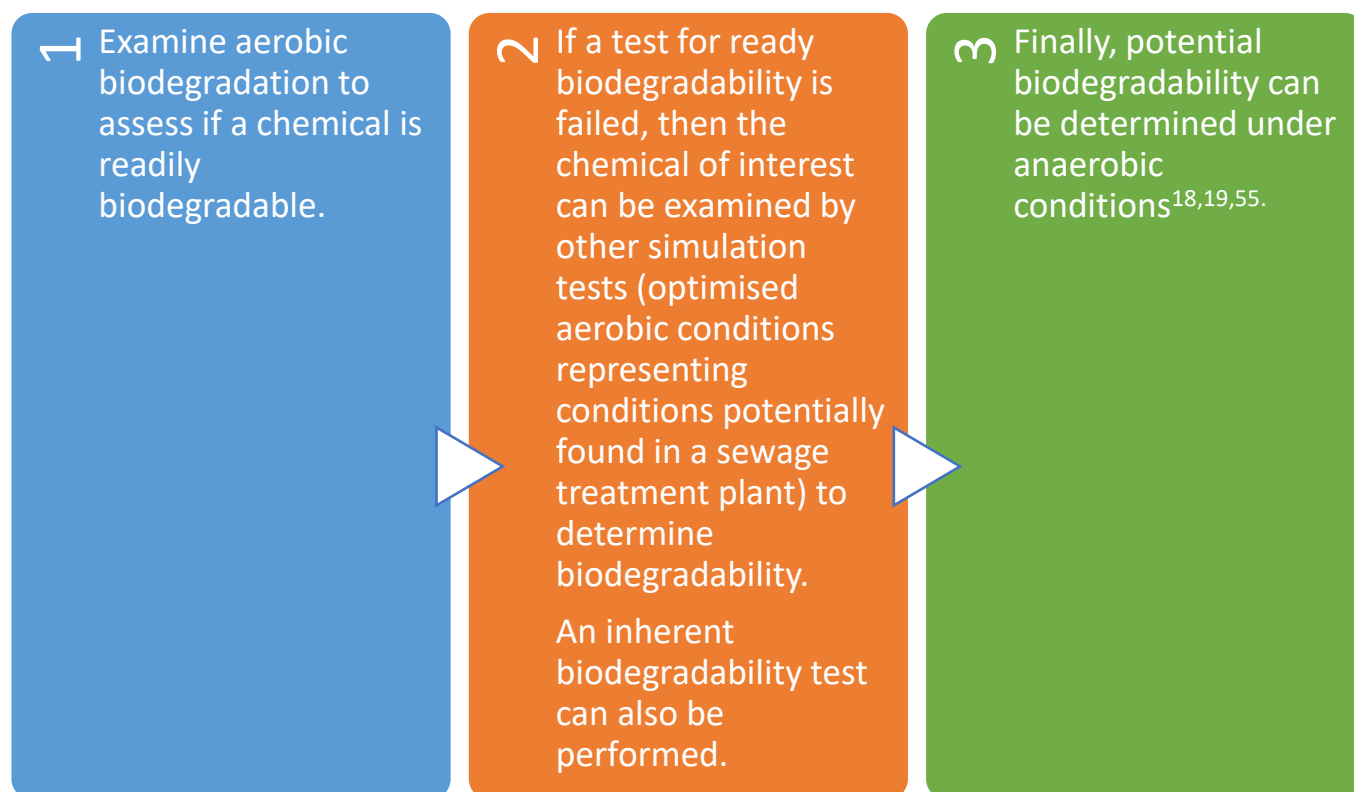


Fig. 13 Testing strategy steps 1-3 for biodegradation analysis by OECD (2006)<sup>17</sup>.

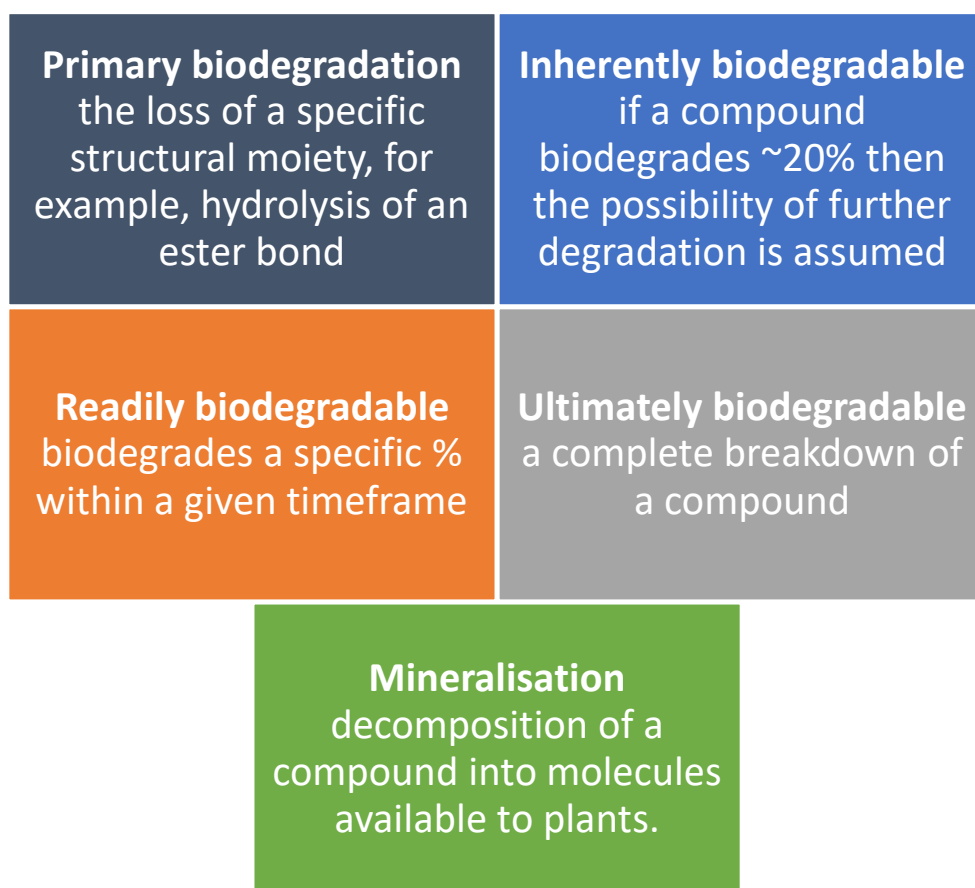


Fig. 14 OECD standard categories of biodegradability, OECD (2006)<sup>17</sup>.

Typical tests used for the assessment of biodegradation are the CO<sub>2</sub> headspace test (OECD test 310) and the Zahn-Wellens test (OECD test 302B)<sup>17</sup>. The “CO<sub>2</sub> Headspace Test” measures the evolved CO<sub>2</sub> and compares this to the theoretical amount of carbon present in the material. The evolved amount of CO<sub>2</sub> after 28 days must be at least 60% of the theoretical to pass the test. The “Zahn-Wellens test” measures dissolved organic carbon (DOC). More than 70% of the DOC must be removed within 28 days to pass the test<sup>17</sup>. In both tests, the degrading substance is dissolved in a solution. The methods used for testing biodegradability, are standard for testing raw materials in a controlled microbial simulated environment, though do not give much information about the fate of materials in the natural environment, or as part of a product in the environment<sup>30</sup>. The tests do not consider the environment that was considered for the product which could be very different if the assumption is made that products tested under these regimes are considered as entering municipal waste systems, which as discussed is often not the case with PLFs. Another factor that is not considered with biodegradability testing is the test material degradation evaluation when combined with other materials to produce a finished product or formulation and how, as a composite, the material behaves when under biodegradation testing<sup>79</sup>. CESIO as a representative of the European surfactants industry argue that surfactants are mixtures of homologues, and the biodegradation parameters evaluated (lag period, growth rate and yield) of individual compounds and the mixture are not the same<sup>80</sup>. This highlights that although the individual components or raw materials are considered biodegradable when formulated as a mixture, this may not result in the same for the product.

### 1.3.6 Suitability for organic farming

As an industry, agriculture aims to optimise nutrient uptake and efficacy of the fertiliser applied to increase yield and profit, whilst adhering to consumer environmental concerns and enforcement of regulatory affairs<sup>7,13, 49</sup>. Organic farming has become a more profitable area of agriculture and is driven by EU initiatives to increase agricultural land use for organic farming from 9.1 % of total EU agricultural land in 2020, to 25% by 2030<sup>64</sup>. Fertiliser for use in organic farming can be optimised for micronutrient use efficacy with suitable co-adjuvants in formulations, provided those formulants are from renewable feedstocks biodegradability certified and accepted by standardised organic international bodies.

In June 2022, CEN published a methodology to quantify the global agricultural crop footprint including soil impacts, this does not include the influence of plastics on soil<sup>9</sup>. OECD testing for biodegradation has the potential to further consider the implications of soil impact and contribution to agricultural crop footprint<sup>17, 20</sup>. It is therefore a proactive approach for consumers to consider not only product use and efficacy but to consider the product's environmental cycle after use explicitly through recognised bodies and certification. The presence of microplastics in all waters tested suggests it should now be classed as an emergent contaminant, with routine monitoring required Dunn 37<sup>39</sup>. Whilst routine monitoring has been suggested, certification for use in organic farming, and certification of biodegradation from registered bodies is a recommended structure to apply to fertilisers as a strategy for consumer knowledge and future corporate governance. The fabrication of industrial products must consume less energy and the raw materials from renewable resources prioritised<sup>47</sup>. We should act this way to preserve fossil resources and reduce the Earth's pollution, considering industrial product function, design, and biodegradation.

A paper claiming that organic farming could provide sufficient food for a growing world population by Badgley *et al.* in 2007 was followed by a critical assessment in a paper by Gouling *et al.* in 2009<sup>81,82</sup>. Also in 2019, organic farming activity reached an all-time high, with a key indicator of 187 out of 195 countries of the world with organic activities<sup>83</sup>. A global increase of 1.1 million hectares or 1.6% of organic farmland in 2019 and a global market reaching 106 billion euros in organic food and drink sales from 3.1 million organic producers is shown in Fig. 15<sup>83</sup>.

3.1 million organic farmers

- + 13% from 2018

472.3 million hectares of organic farmland

- +1.6 % from 2018

Australia 35.7 million of hectares

Argentina 3.6 million of hectares

Spain 2.4 million of hectares

- Top 3 countries in the world of organic agriculture 2019

44.7 USA market in billion euros

12.0 Germany market in billion euros

11.3 France market in billion euros

- Top 3 countries in the world of organic agriculture 2019

Fig. 15 Organic agriculture worldwide – Key Indicators from FiBL's 2019 survey<sup>83</sup>.

Although it is not considered organic farming can feed the growing population with current technologies, the view of improving soil quality, by adding organic material for the rhizosphere and microbial communities in consideration of regenerative agriculture, agrees with the view of Badgley et al. in 2007<sup>81,82</sup>. Developing fertilisers where the organic matter of polymers after a useful lifetime can be broken down and utilised by microbes, rather than those carbon sources applied as in an unavailable source such as plastic, can be exchanged for renewable, organic material that can biodegrade and offer soil enrichment through renewable organic matter.

### 1.3.7 Biodegradable dispersant studies

Biodegradability is not an inherent property of a chemical compound, but a function of the compound and its environment. Biodegradation is a method of study in the context of Green Chemistry to analyse and predict how a compound (e.g., dispersant) interacts with the environment as a result of use and final life cycle. Analysis of biodegradability in laboratory conditions offers a measure of the persistence of materials in the environment. Ultimately, the aim of finding biodegradable components is to avoid the introduction of persistent molecules, preventing release into undesired environments and the detrimental effects on ecosystems<sup>16</sup>. Currently used persistent molecules related to this study (surfactants, dispersants, biocides, defoaming agents and thickeners) and the results of such fossil fuel-derived polymers have been well documented in the cases of marine litter<sup>15,16,84,85</sup>. Anastas and Warner in 1998 highlighted the importance of biodegradation by incorporating the intention of design for degradation as the 10<sup>th</sup> Green Chemistry principle<sup>5</sup>.

Biodegradable polymers can be made of naturally occurring or synthesised material, whereas blends of non-biodegradable polymers and natural biodegradable polymers are not considered biodegradable materials. The former can be categorised into three general groups with examples in Table 3<sup>2,5</sup>.

#### Biodegradable polymers

Natural polymers; cellulose, proteins, poly-beta-hydroxybutyrate, alginate, starch, sucrose (Fig. 9)

Natural polymers that are biologically or chemically modified; cellulose acetate, lignocellulose esters, and polyalkanoate copolymers.

Readily biodegradable synthetic polymers modified (e.g. complexed or blended) with added natural biodegradable components such as starch, reclaimed cellulose, and natural rubber.

Table 3 Three general groups of biodegradable polymers.

When defining a biodegradable polymer, for its persistence in the environment, guidelines of accepted biodegradation techniques and standards must be considered in relation to the timescale and degradation conditions of the data. Commonly referenced technical standards in literature for biodegradation studies include methodology from ASTM, ISO, CEN and OECD<sup>8,9,34,75,86,87</sup>.

Alternative, natural polymers for potential use in agriculture have been referenced to in literature and include natural surfactants such as *Yucca schidigera*, glycolipids (sophorolipids), and lignocellulosic material (lignosulfonates)<sup>2,5,30,68,88,89</sup>. Such materials are expected to empirically break down, though it is important

to determine the sources of natural and or modified materials suggested in literature do biodegrade in a relative time frame after retaining formulation properties. A standardised method to verify natural and modified polymers as biodegradable is required to compare and contrast the efficacy of co-formulants and their properties after useful service life as a co-formulant. It is also to be verified that the polymers biodegrade and do not propagate ecotoxicity or any negative environmental impact, whether from a natural or partly synthetic composition of renewable material by performing further international standardised ecotoxicity testing<sup>2</sup>.

### 1.3.8 Lignosulfonates

Lignocellulosic biomass is an inexpensive, abundant, renewable source that can be used to produce biofuels and bioproducts from plants<sup>90</sup>. Lignocellulosic biomass has a complex structure predominantly made from polysaccharides cellulose (35-45%), and hemicellulose (25-30%), and an aromatic polymer, lignin (15-30%), as shown in Fig. 16<sup>68, 91,92</sup>.

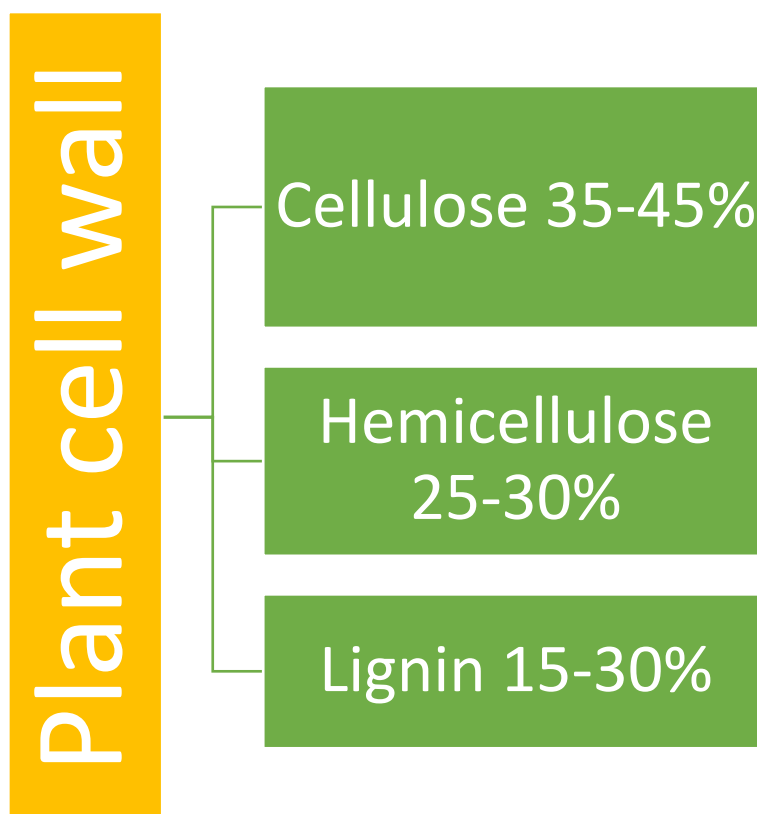


Fig. 16 Lignocellulosic biomass chemical structure and natural recalcitrance adapted from Zoghlami & Paës publication 'Lignocellulosic biomass: Understanding recalcitrance and predicting hydrolysis'<sup>91</sup>.

Lignin as a class is the second most abundant group of biopolymers on earth and, as a natural feedstock, can substitute fossil fuels in energy and non-energy use sectors, contributing to climate change mitigation<sup>69,93</sup>. Lignin is one of wood's most important protective components, forming part of the cell wall and is naturally



recalcitrant to enzyme hydrolysis<sup>30,91</sup>. The phenolic compounds formed from the degradation of lignin aromatic polymer and non-lignin polysaccharides sources of lignocellulosic biomass are important precursors for humic substances, where humic substances form an important part of the natural soil. It is known that humic substances are incorporated directly into growing plants, considered as a biostimulant, to stimulate microbial assimilation and improve soil health where soil organic matter and humic substances will be metabolised by microbes or plants, entering the natural carbon cycle<sup>30,94</sup>.

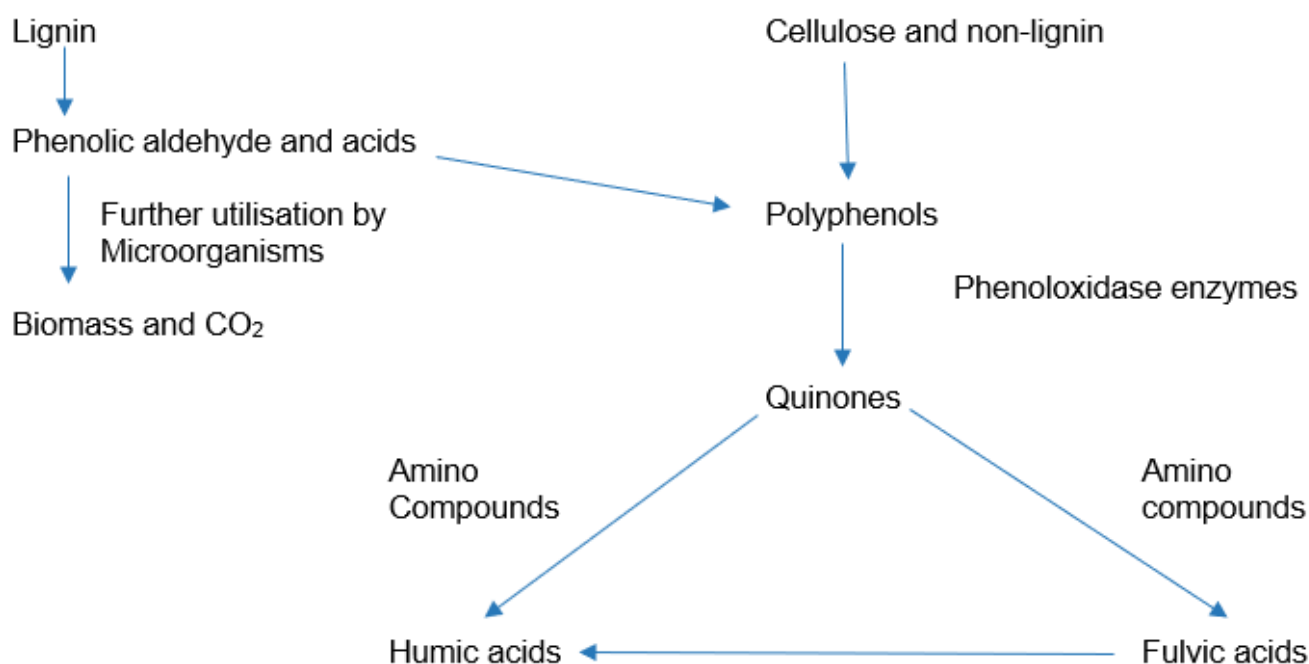


Fig. 17 Degradation of lignin aromatic polymer and non-lignin polysaccharides sources of lignocellulosic biomass.

Lignin-based biopolymers are sustainable alternatives to fossil fuel-derived co-formulants and offer a practical use for substituting current polymers used in agricultural chemical formulations. The benefits of using renewable resources, like wood, are not limited to the abundance, commodity, and affordability of lignin derivatives, as the start of the processing begins with negative carbon emissions. In comparison, fossil fuel-derived materials start at net zero in the cultivation step, where the wood will have actively removed CO<sub>2</sub> from the atmosphere at this phase as shown in Fig. 18<sup>95</sup>.

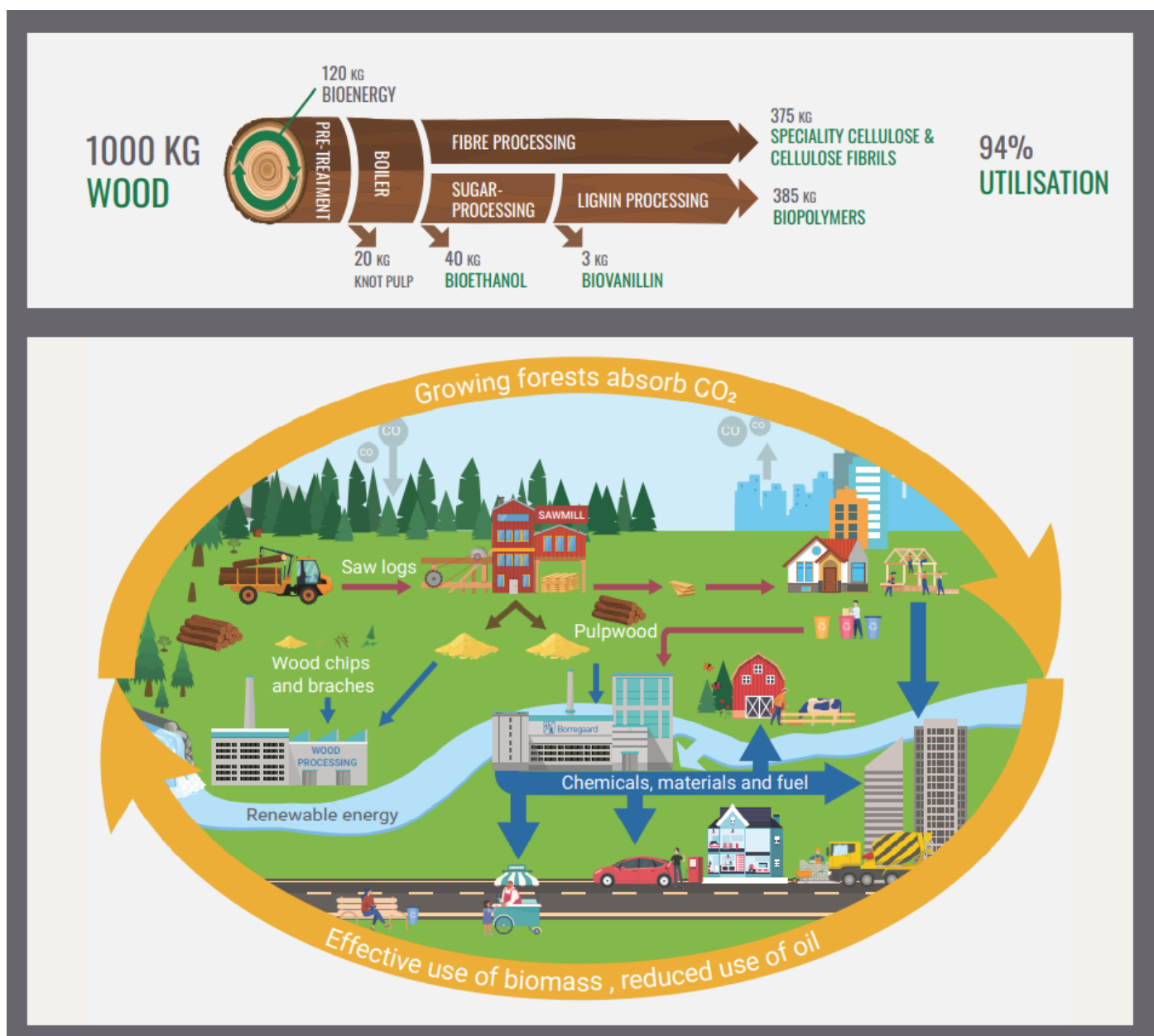


Fig. 18 Life cycle assessment of lignosulfonate production, Borregaard Annual Report, 2021<sup>96</sup>.

The energy required and the CO<sub>2</sub> emissions to produce 1 kg of lignin-based biopolymer are more than 30% lower than those producing 1 kg of synthetic dispersants<sup>96</sup>. In a useful lifetime of the biodegradable polymers, no emissions are considered, however, the lignin-based dispersant would have a negative CO<sub>2</sub> footprint in its service life due to the origin<sup>96</sup>. The last phase illustrated in Fig. 18 is the end of life, considering a calculation of the CO<sub>2</sub> released to the atmosphere if both the lignin-based dispersant and the synthetic dispersant are fully biodegraded. According to international standards, synthetic products would not be considered biodegradable if they are not timely metabolised using the OECD methods for biodegradation<sup>35</sup>. Lignin-based biopolymers have a slow degradation, that can be assimilated to its starting material of wood in nature, however, a significant difference is that biodegradation of the lignin produces natural compounds such as phenolic compounds that are precursors to humic substances. Lignin-based polymers will be useful as a source of organic carbon for microorganisms and plants instead of being an environmentally persistent challenge<sup>96</sup>.

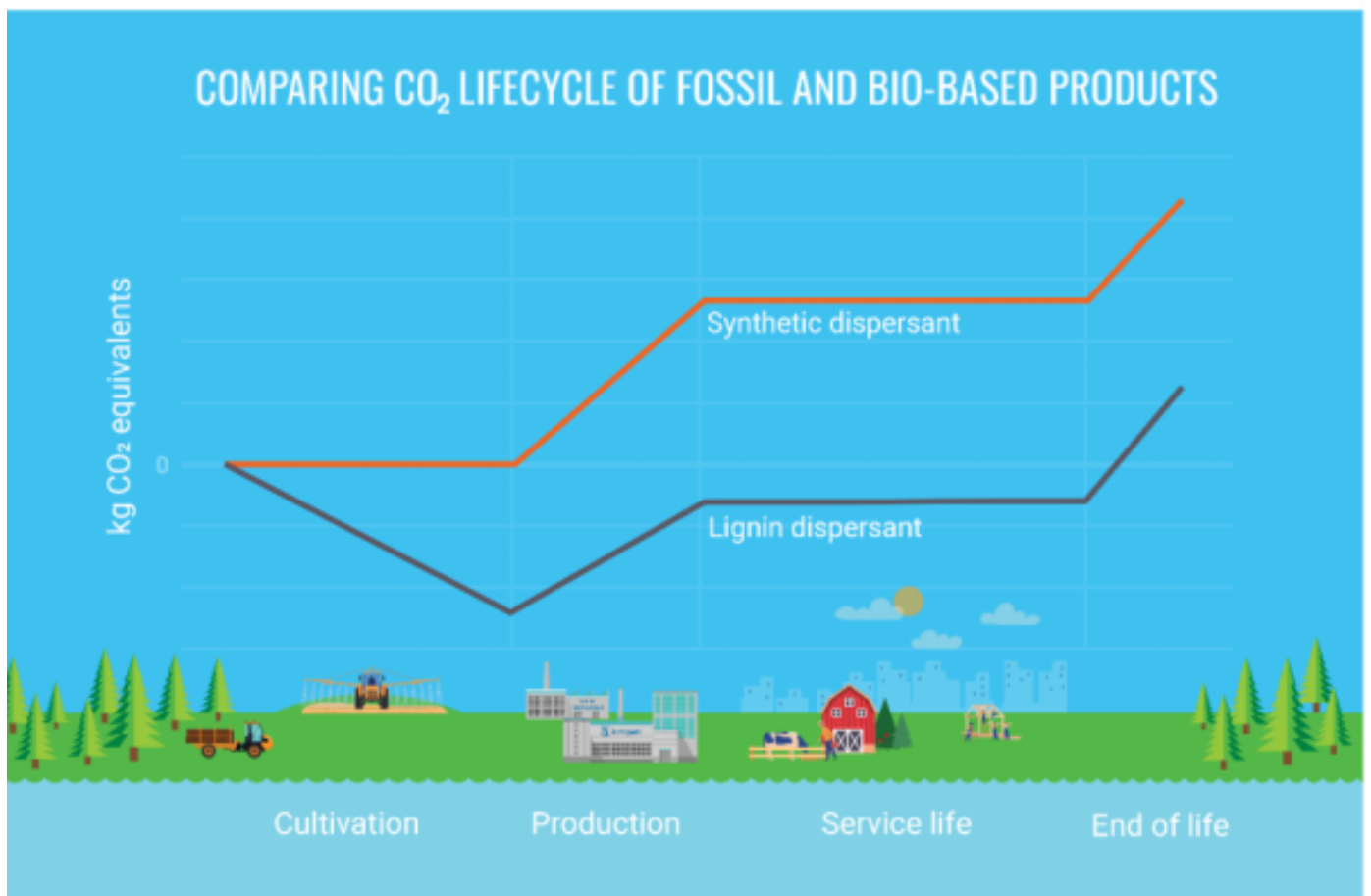


Fig. 19 Comparison is carried out by the Norwegian Institute for Sustainability Research using life cycle analysis methodology according to the ISO standards 14040/44. The model substance used as a standard synthetic dispersant is polycarboxylate and compares the lignin dispersant reduction in kg of CO<sub>2</sub> from cultivation, to negative CO<sub>2</sub> in production and during service life of the biopolymer<sup>96</sup>.

### 1.3.9 Sophorolipid

A surfactant is a surface-acting, or 'wetting' material added to two immiscible liquid phases to create a colloidal suspension (emulsion). Molecules of surfactant aggregate in the form of micelles which reduces the surface tension, or interfacial free energy of the system. Sophorolipids are glycolipids and have a hydrophobic fatty acid tail and a carbohydrate head of the glucose disaccharide sophorose, making ideal surfactants with diverse applications due to the hydrophilic and hydrophobic components (Fig. 20, Fig. 21)<sup>97</sup>. Decreasing the surface tension of water (72 mN/m) to surface tension values of ~35 mN/m has been recorded for sophorolipids, the amphiphilic nature of the molecule produces an antimicrobial action, whereby reducing the surface tension, pathogen membrane permeability is also disrupted<sup>98,99,100,101</sup>.

Sophorolipids are derived naturally from the species *Candida*<sup>97,102</sup>. Most surfactants are petroleum-based and are among the most ubiquitous contaminants in aquatic systems<sup>103,104</sup>. The range of naturally produced biosurfactants synthesised by living cells has increased in recent years with a commercial interest in the diversity of applications, although application in the agricultural industry is still rare and not typically associated with foliar fertilisation as depicted in Fig. 20<sup>105,106</sup>.

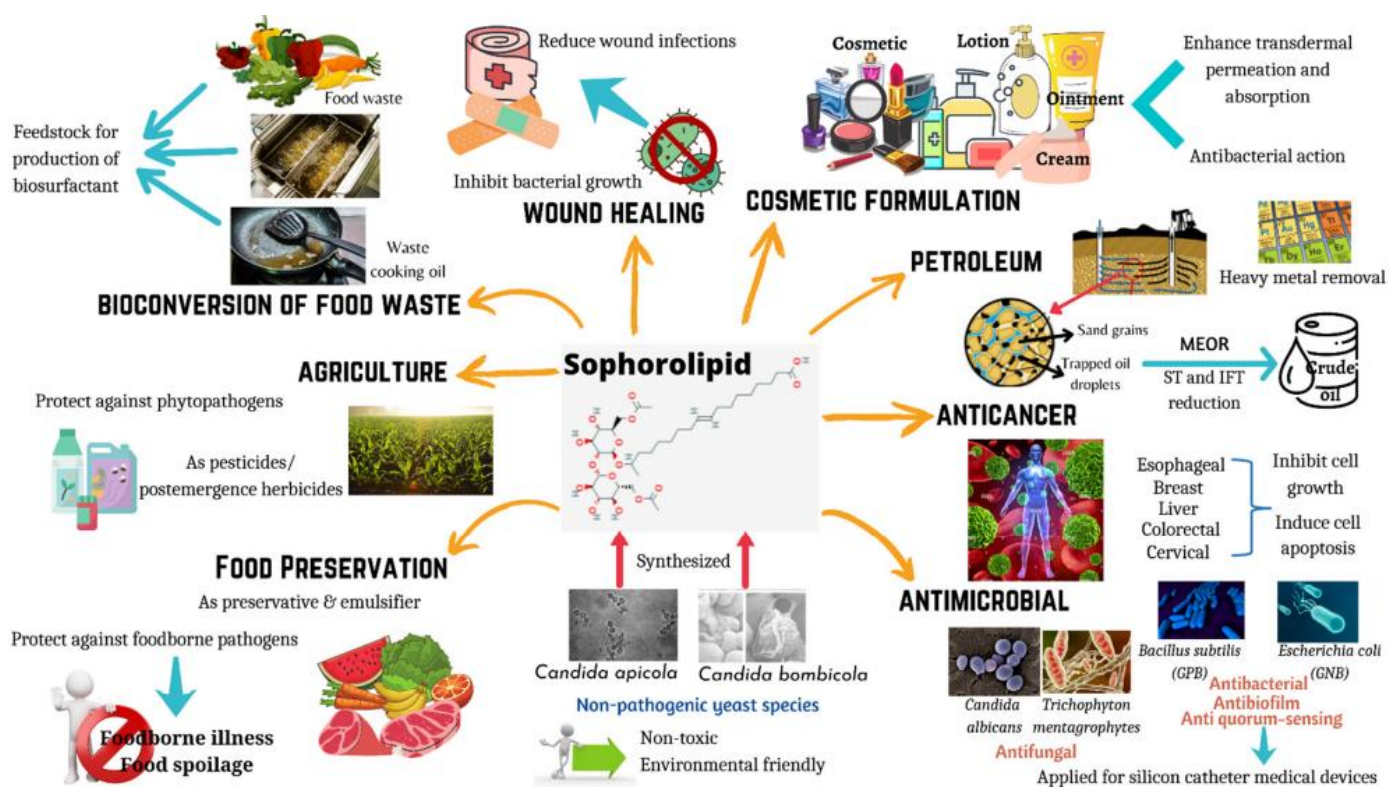


Fig. 20 Potential of sophorolipid application use, sophorolipids are bio-based antimicrobial formulating agents for applications in a diversity of applications, including food, health and agriculture<sup>107</sup>.

Many raw material co-formulants are approved by the Food Standards Agency (FSA) as additives and E numbers for colours, preservatives, antioxidants, stabilisers, thickeners, and natural/synthetic chemicals suitable for food use, do not also comply with FPR regulations<sup>49,108</sup>. Agricultural products in Europe are now 43

required to be FPR compliant and state definitive chemical use for agriculture<sup>49</sup>. This has led to the dossiers from suppliers, registering and aligning with FPR compliance designed for fertiliser use, and opportunities for novel adjuvants to perform properties designed and suited for formulation purposes in fertiliser products.

Commercial biosurfactants that are naturally synthesised by living cells offer a diverse chemical portfolio, scalability of production and benefits of environmental protection and increased, or total biodegradability<sup>106</sup>. Biosurfactant use in agricultural applications is still limited<sup>105</sup>. The class of sophorolipids, synthesised from *Starmerella* yeast clade are highly biodegradable, with up to ten-fold less toxicity association than petroleum-derived, synthetic surfactants. Unlike rhamnolipid biosurfactants produced by *Pseudomonas aeruginosa*, sophorolipids are produced from non-pathogenic derived yeast<sup>103,109</sup>. As a commercial alternative, high yields can be produced in bioreactor cultures at low-temperature fermentation and low energy consumption, offering scalability and associated cost-effective alternatives to conventional surfactants with no harmful by-products or process auxiliaries<sup>97,103</sup>. In a 2020 review of sophorolipid use in agriculture, Celligoi *et al.* deduced sophorolipids have great potential and capacity in the field of agriculture; where the molecules were found to enhance the solubility and mobility of plant nutrients<sup>98</sup>. Previously, Sieverding in 2015 recorded greenhouse and field trials of soy, wheat, barley and tomato that were successful in enhancing the yield of these agricultural crops by 690 kg/ha compared to 490 kg/ha when only using fungicide. The tests were applied on the seeds and the aerial part of the plants and sophorolipid addition at a concentration of 0.1-0.5 %wt for an increase in fruit, rooting of seeds and seeds<sup>98,110</sup>.

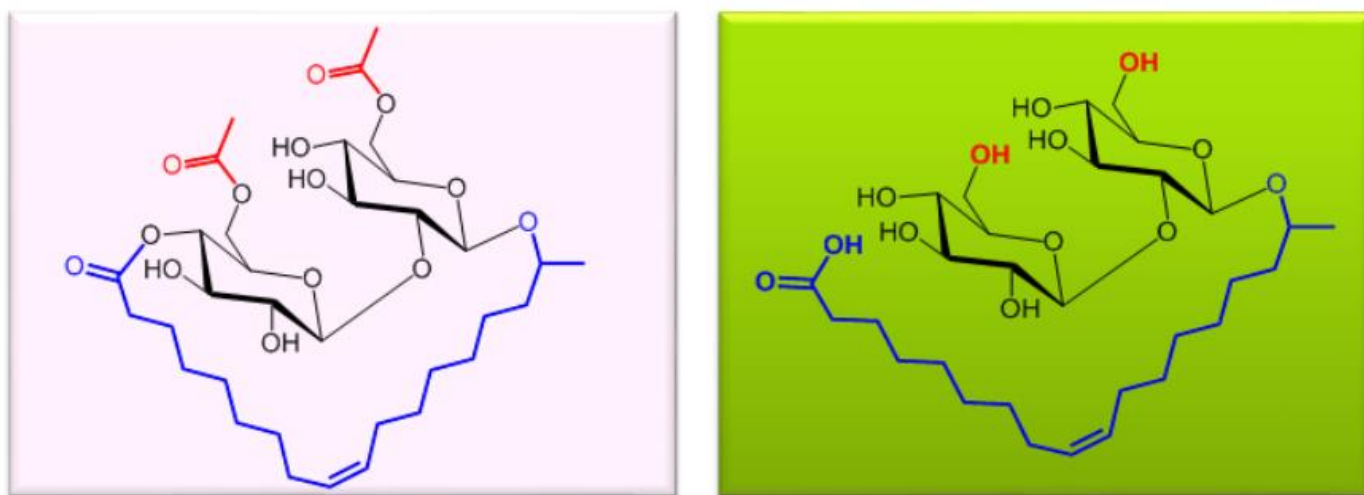


Fig. 21 Sophorolipids are glycolipids with a dimeric carbohydrate sophorose linked to the hydrophobic tail through a glycosidic bond. The lactonic sophorolipid (left) and acidic sophorolipid (right) show the mixture of the two glycolipids made from the partial hydrolysis of the water-insoluble lactone form<sup>97</sup>.

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## 1.4 Formulation requirements for foliar application

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Foliar fertilisation is a useful tool for plant leaf absorption of water and nutrients, facilitating the efficacy of sustainable and productive management of crops. Foliar application has been the focus of many controlled environments and field research. The fundamental requirement of an effective foliar nutrient spray is for the active ingredient, or nutrient supplied for plant metabolism by penetrating the leaf cuticle. The absorption of nutrient solutions by plant surfaces may also occur by cuticle cracks or imperfections, stomata, trichomes, or lenticels, whilst the cuticle and the epidermal structures influence the transpiration pathway, the conductance of ions of solution essential for plant growth<sup>7</sup>.

The physico-chemical properties of spray solutions impact factors of spray retention, leaf wetting, spreading, and rate of penetration. Two components can be categorised in plant nutrition formulations; the active ingredients, considered to be the nutritional components and or biostimulants, and the adjuvant(s). Foliar fertiliser application timing and including a surfactant to reduce the surface tension and increase the surface area of foliar uptake are both important for uptake of nutrients and their translocation by leaves<sup>111</sup>.

Without the inclusion of a surfactant, biocide, dispersant, or thickening agent, formulations are not optimised for the physical and chemical properties required for foliar nutrient uptake to be optimised and could cause phytotoxicity, scorch, or acute toxicity of the raw materials intended as a plant fertiliser.

The stabilisation of colloidal dispersions by naturally occurring polymers has been an interest of study since ancient Egyptian black and red inks were made from inorganic and organic material<sup>112</sup>. Naturally occurring polymers such as egg albumin, casein from milk or gum Arabic were used to sterically stabilise carbon black particles for pencil moulds, dispersed with water as 'instant' ink<sup>113</sup>. There is already significant scope for using naturally derived thickening agents, such as clays and gums in agricultural formulations as a replacement for the use of acrylic latex dispersions. Synthetic, acrylic thickening systems are currently predominantly used for commodity, cost-effectiveness and long-term storage stability in suspension concentrate formulations.

Typically, thickening and dispersing agents must work harmoniously to achieve a viscosity suitable not only for functional transference and application at end use but also for stability. With predominant formulation concentrations of carbonates and oxides from insoluble nutrient sources (Table 4), the water-based suspension concentrate range has a predominant alkaline range of pH 7-12. The solids loading for inorganic nutrient sources can be as much as 900 g/L and therefore suspended using a minimum quantity of adjuvants and water as a solvent to achieve a 1 litre and 1kg equivalent formulation. For global transportation, a homogenised suspension must withstand temperature extremes of the continents from Europe, Asia, Latin America, America, and Canada, typically a range of 0°C or below to 50°C.

For a viscosity that is stable under storage conditions and yet can flow as a liquid, anionic polyacrylates are sodium salts of polyacrylic acid, with low molecular weight and are used as part of the thickening and dispersing system in foliar nutrient sprays. For current acrylic dispersants, typical pH ranges are 7-9 with a viscosity of 50-400 cP and active w/w of non-volatile solids 38.0-42.0 %.

Implementing Green chemistry is a type of pollution prevention, which in this study concerns a fundamental change in the intrinsic nature of the feedstock for the product's environmental outcome. By designing and redesigning chemical alternatives for sustainable agriculture, the prevention and elimination of marine microplastic pollution implement an active industrial approach to pollution prevention as opposed to end-of-pipe control.



Table 4 Common nutrients for macro and micro supply in fertiliser adapted from Fernández *et al.*<sup>114</sup>.

	Nutrient	Plant available ion	Raw material sources	Important functions
1°	Nitrogen	$\text{NO}_3^-$ , $\text{NH}_4^+$	Urea, ammonium sulphate, ammonium nitrate	Component of proteins, chlorophyll, genes
	Phosphorous	$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^{2-}$	Phosphoric acid, potassium phosphate, ammonium phosphate, calcium phosphate	Energy transfer, metabolism, and constituent of genes
	Potassium	$\text{K}^+$	Potassium sulphate, potassium chloride, potassium nitrate, potassium carbonate, potassium phosphate, potassium hydroxide,	Osmotic and ionic regulation, enzyme function, carbohydrate and protein metabolism
2°	Magnesium	$\text{Mg}^{2+}$	Magnesium sulphate, magnesium chloride, magnesium nitrate, magnesium oxide, magnesium hydroxide,	Chlorophyll component and enzymatic reactions
	Calcium	$\text{Ca}^{2+}$	Calcium chloride, calcium carbonate, calcium hydroxide, calcium propionate, calcium acetate	Cell division and membrane integrity
	Sulphur	$\text{SO}_4^{2-}$	Magnesium sulphate, ammonium thiosulphate	Constituent of proteins, amino acids, and vitamins, necessary for the production of plant oils
Micro/ Trace	Iron	$\text{Fe}^{2+}$	Iron sulphate, iron chelates, iron complexes (lignosulfonates, glucoheptonates)	Component of cytochromes (respiratory enzymes, ferredoxins for N fixation and photosynthesis)
	Zinc	$\text{Zn}^{2+}$	Zinc sulphate, zinc oxide, zinc chelates, zinc organic complexes	Necessary for enzyme systems, Nucleic acid synthesis, metabolism of auxin (plant hormone)
	Manganese	$\text{Mn}^{2+}$	Manganese sulphate, manganese nitrate, manganese carbonate, manganese chelates,	Enzyme component, photosynthesis
	Copper	$\text{Cu}^{2+}$	Copper sulphate, copper oxide, copper chelates	Enzyme components, grain production, photosynthesis
	Boron	$\text{H}_3\text{BO}_3$	Boric acid, borax, sodium octoborate, B-polyols	Cell wall, cell division, pollination, fruit and seed set
	Molybdenum	$\text{MoO}_4^{2-}$	Sodium molybdate	Normal assimilation of N, N fixation, reduction of nitrate to ammonia, and chlorophyll



### **1.4.1 Dispersion of insoluble raw materials**

Effective dispersion of insoluble carbonates and oxides commonly used as a nutrient source for fertilisation (Table 4) is a more complex substitution for biodegradable alternatives than the widely known sources of natural thickening agents such as gums, clays and silicas. Microplastics can be characterised as functionalised polymers for increasing the efficiency and efficacy of fertilisers, pesticides and herbicides<sup>32</sup>.

Dispersing agents, currently polyacrylate used in YaraVita foliar fertilisation formulations provide many benefits to foliar formulation, design, and application. Dispersing agents can give multiple design functions such as wetting, or lowering the surface tension, homogenisation of inorganic material, and coating films of nutrient source secured onto the leaf surface, offering a more permanent nutrient source patch for longer foliar feeding times than a comparable liquid ionic solution.

### **1.4.2 Storage stability testing: viscosity and rheology**

Acrylic swelling or thickening systems are effective at increasing the viscosity and stability of suspended particles, however, are not considered biodegradable. A thickening system without a dispersing agent would cause a gel-like formulation, which would not be practicable or successful as an agricultural form for a foliar nutrient spray. YaraVita foliar nutrient sprays are a highly concentrated liquid of active nutrient source at quantities up to 900 g/L of active nutrient solid, no greater than 50 µm in particle size, suspended and dispersed. Suspension and dispersion parameters are that the product must be stable at a wide range of temperatures suitable for global transportation as a standard. Accelerated storage stability of samples at temperatures of 0°C, 20°C and 45°C are standard ISO 9001 procedure, so that sediment of the active nutrient sources does not form and therefore prevent the risk of blockages of agricultural spray equipment such as nozzles, booms, and sprays.

A viscosity that is liquid but pourable and pumpable for farmers to use at ease on the farm, before diluting at a typical 200 l/ha water rate prior to the application via spray boom or knapsack are physical properties of YaraVita suspension concentrate formulations. To achieve a higher nutrient concentration in the same amount of volume as a liquid solution, dispersion and suspension are parameters to be considered for the solid, insoluble particles. To measure these parameters, viscosity, rheology, and storage stability are representative indicators. A typical suspension concentrate would have a viscosity ranging from 1500-4000 cP, dependent on active nutrient solids loading in the formulation, dispersant ability, and stability thickening. The type of rheology that must be considered is like paint, thixotropic shear, so that when the viscous material is pumped, agitated, or moved, the product shear thins and can be spread effectively through farming equipment and ultimately on the leaf surface.

Accelerated storage stability over an 8-week period, enables evaluation in the laboratory of the temperature stresses the chemical formulations are likely to endure across the globe, from 0°C to 45°C and ensures optimal warehouse storage, transportation, and ease of use for the consumer, whilst enabling a 2-year shelf life for incorporation of the product for up to two farming seasons.

### 1.4.3 Wettability

The term ‘wettability’ in this research refers to the liquid-to-surface intermolecular interactions of adhesion. Different degrees of wettability are determined for plant surfaces of the leaf, fruit, and species when in contact with water droplets, as shown in Fig. 22 and Fig. 23<sup>7,115,116</sup>.

The cuticle has two suggested pathways for the permeation of water, ions, and polar compounds. One for hydrophilic and one for lipophilic substances. Because of different plant species, growth rates, and organs, the topography and chemistry of the cuticle, including polarity and hydrophobicity have an impact on the

effectiveness of foliar sprays. In the contact angle of droplets of water, glycerol and diiodomethane was used to determine the surface free energy and polarity of peach surfaces, identifying higher surface free energy and dispersion for the trichome network, where the cuticle has a lower surface free energy and higher surface polarity Fig. 22, Fig. 23<sup>7,88,115,116</sup>. This highlights the importance of reducing the contact angle, or surface tension, for greater wettability, surface contact and area with the plant topography. This is typically achieved by adding a synthetic polymer, or surface-active agent (surfactant)<sup>117</sup>.

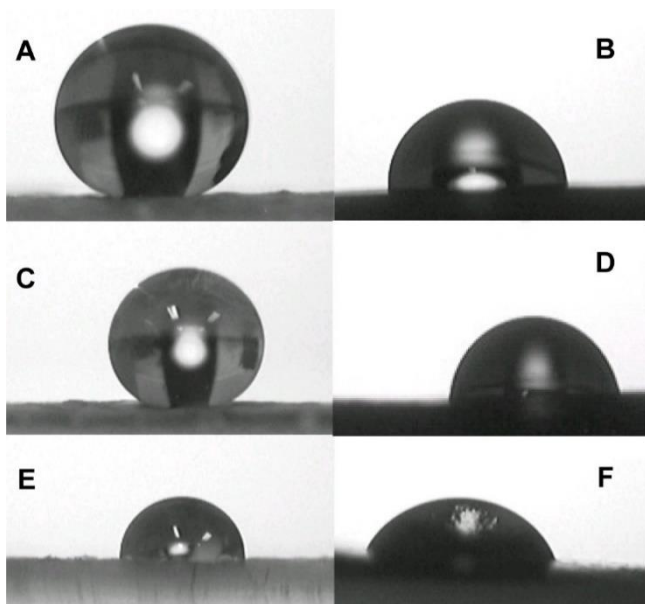


Fig. 22 Contact angle measurements on intact, adaxial *Eucalyptus* (A, C, E) leaf surfaces and pepper fruit surfaces (B, D, F). Drops of: (A, B) water, (C, D) glycerol, and (E, F) diiodomethane<sup>115,116</sup>.

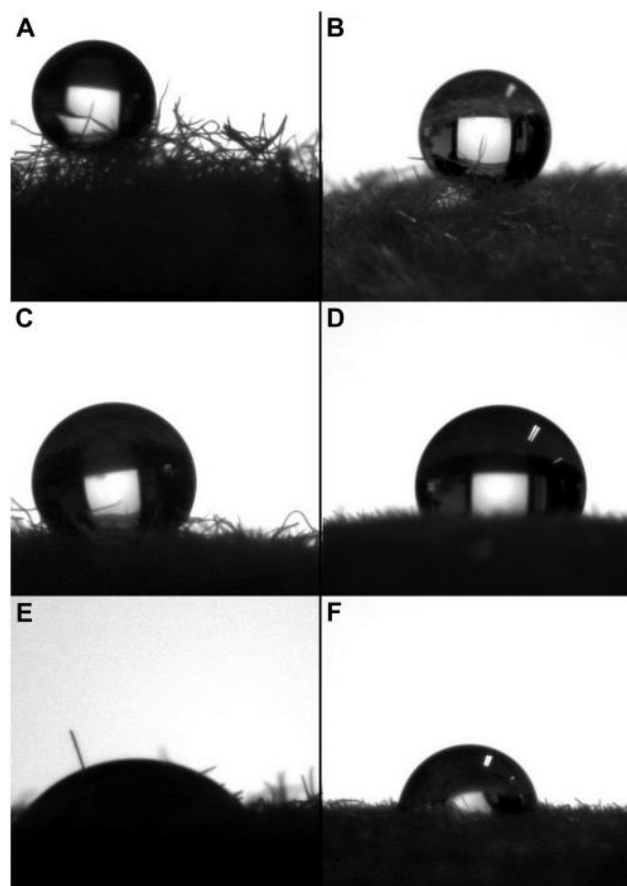


Fig. 23 Contact angles of intact peach surfaces and water (A), glycerol (C), and diiodomethane (E) and of shaved peach surfaces and water (B), glycerol (D), and diiodomethane (F)<sup>115,116</sup>. Estimation of the solubility parameters of model plant surfaces and agrochemicals is a valuable tool for understanding plant surface interactions.

#### 1.4.4 Cost and commodity

The definition of sustainability from the US Society of Agronomy in 1989 states:

*“Sustainable agriculture is one that, over the long term, enhances environmental quality and the resources base on which agriculture depends; it provides for basic human food and fibre needs; is economically viable, and enhances the quality of life for farmers and society as a whole”* <sup>118</sup>.

The stability and multifunction of polymers have enabled them to assist and exist in a multitude of products used in everyday life, with approximately 320 million tons produced annually, of which half is produced for single use (Table 5)<sup>8,84</sup>. The breakdown and accumulation of plastics have proved a challenge in society for waste management and environmental protection. Plastics do not readily biodegrade, they persist in the environment, eluding waste management systems and present particles in marine environments, leading to a chemical hazard in marine ecosystems<sup>84</sup>. As large quantities of plastic accumulate, UV radiation fragments disintegrated plastic into pieces less than 5 mm in size, defined as microplastics, and further categorised in size as small (<1 mm) and large (1-5 mm), according to the European MSFD Technical Subgroup on Marine Litter<sup>85</sup>. Typical microplastics found to accumulate and remain in the environment are primarily polyolefins (polyethylene (PE), polypropylene (PP)), polyethylene terephthalate, or thermoplastic polyester (PET)<sup>3</sup> (Agarwal, 2020). Other water-insoluble polymer particles are polystyrene (PS), nylon (PA), poly (vinyl chloride) (PVC), polyethylene-propylene copolymer (PEP), and polyacrylates (PAK)<sup>3</sup>.

To reduce the reliance of PLFs on fossil fuels and petrochemical-derived feedstocks, developing novel PLFs from renewable, bio-based feedstocks offers a solution to make PLFs more sustainable for the future. In a 2022 technical report, the Royal Society of Chemistry (RSC) evaluates innovation using degrade under control or triggered processes and the opportunity to increase technical performance, such as stability testing, biodegradability, and formulation function<sup>8</sup>. Offering such solutions reduces the risk of microplastics and provides improvement on the recyclability of substrates.

Market	Global polymer market value (\$ billion)	Global polymer volume (million tonnes)	Average estimated unit value (\$/kg)
Commodity plastics	420 <sup>69</sup>	320 <sup>69</sup>	1.31
PLFs	125.2	36.3	3.56

Table 5 Comparison of values, volumes and unit values for plastics and PLFs<sup>8</sup>.

In the last decades, human health and the environment are social agendas of importance. Where alternatives to plastics in the environment exist, government policy and social adoption can drive change and in turn improve environmental and health protection from future microplastic abundance. As the demand for sustainability from policy and consumers grows, biopolymer research, development and competitive supply could challenge the competitive price levelling of new, biodegradable solutions to the current, inexpensive polymers available<sup>12</sup>. Proposed actions for establishing collaboration between academia, industry, and policy are identified by the RSC and indicate a positive contribution to applying green chemistry principles to proactive industrial solutions<sup>8</sup>. The goals are to explore the emerging need, innovation, and exploration of PLFs biodegradability and stability testing for a sustainable future in addressing PLF research and policy.

The approach in this study is to consider the Green Chemistry Principles originally addressed by Paul Anastas and John Warner in 1998. Applying knowledge of the industry to implement a significant change in formulation chemistry is an essential step forward for applying Green Chemistry. Sourcing biodegradable alternatives to the current processing of synthetic, primary microplastic polymer use is a response to increased volumes of production at Yara Pocklington by 30%, incorporating up to 60 tonnes of polyacrylate raw material used in the last year due to increasing demand for fertiliser.

In the 70's, solarisation was an advancement from methyl bromide applications for eliminating weeds and pests before sowing. The term solarisation is used for covering and reconditioning the soil with a polymeric film. The polymeric films used as a commodity were very transparent to visible light, for soil heating, and opaque to infrared radiation, preventing heat loss at night. Although polymeric films historically derived from olefins offered a very affordable, commodity material, there was the disadvantage of the waste cost incurred with the removal and disposal of the films after 4-6 weeks of use after germination. Environmental pollution from synthetic polymer films is not limited to the inability to biodegrade, but also problems arising from the pollution and law violations from burning after use<sup>32</sup>. Whilst the technique of solarisation is commonly still used, advances in green chemistry have led to the development of biodegradable films made of natural polymers. Advantages are aligned with the Green Chemistry Principles:

- Eliminating the use of non-biodegradable polyolefin material
- Ensuring polymers are manufactured from renewable feedstocks of which common input materials for the biodegradable films are glycerol, polyvinyl alcohol, and alginates.
- The materials from renewable feedstocks are chosen to biodegrade under aerobic and anaerobic conditions and do not persist in the environment by breaking down into innocuous degradation products<sup>119,120</sup>.

In general, agricultural, and biological feedstocks can be excellent alternative feedstocks to non-renewable petrochemically derived feedstocks. Critically, concerns about biological feedstocks include seasonal supply and land and energy use. However, the alternative feedstocks are not limited to agricultural products. Agricultural waste, biomass and non-food-related bioproducts are often lignocellulose-derived materials that provide a significant structure for a wider range of renewable feedstocks<sup>5</sup>.

### 2.1 Equipment



Consumables: Burette, glass beakers, pipettes, funnels, spatulas, measuring cylinders weighing boats

Two decimal place balance

White Elec. Inst. Co. Ltd. Torsion balance

Calibrated oven and fridge; 45°C and 0°C, respectively.

DV2T Brookfield viscometer (Fig. 24)

IKA RW20 overhead stirrer; 288 – 2400 rpm (Fig. 25)

Fig. 24 DV2T Brookfield viscometer



Fig. 25 IKA RW20 overhead stirrer

### 2.2 Dispersants and formulations

NB The technical data on the polymers provided is gathered from TDS and SDS data. Supplier names are excluded as proprietary information of Yara UK.

#### Water

In this study the solvent used in all formulations for this study, ranging from 20-30% w/w content and literature value of 72 m/Nm, generic tap water used ~pH6-7.

#### Polyacrylate liquid RM1 2695

This is a low-viscosity dispersing agent most suited to dispersing inorganic pigments and micronutrients in waterborne systems. The 2695 dispersant consists of an ammonium salt of an acrylic copolymer in water and appears straw-coloured with a pH of 7.5. It is most effective due to its compatibility with glycols.

### Polyacrylate liquid RM2 UL2

A sodium polyacrylic acid dispersing agent with low molecular weight, between 1,000 and 3,000 Dalton. The Brookfield viscosity is 20-70 cps with a solids content of 40-42%. This dispersing agent is used in all sample evaluations as it is known to be stable and effective as a non-ionic surfactant.

### Sophorolipid liquid RM3 Breakthru SF420

A 100% bio-based surfactant, indicating intended use as a wetting agent. It is an adjuvant based on sophorolipids produced in a sustainable manner by fermentation.

### Lignosulfonate Hybrid liquid RM4 PPEM9565/PPEM9566

Surface tension 65-70 (mN/m). Structure is confidential to supplier.

### Yucca plant extract liquid RM5 Surf

Yucca extract is a natural surfactant or wetting agent. Yucca schidigera contains saponins, a soapy, steroidal-like substance that acts as a natural spreader/sticker for horticultural and agricultural use.

### Lignosulfonate soluble powders - RM6 Ultrazine NA, RM7 Borresperse NA, RM8 Ufoxane 3A, RM9 Vanisperse CB

Sodium lignosulfonate > 93% water < 7% dispersing agent recommended for dispersant use in agrochemicals, dyestuff and carbon black. Complete solubility and a pH of 7.1-9.5, pH (10% Solution)  $9.0 \pm 0.5$ . Density of 500 - 630 kg/m<sup>3</sup> and Safety Data Sheet states 'expected to be biodegradable'. Table 6 identifies properties of the lignosulfonates.

<i>Product name</i>	<i>Molecular weight</i>	<i>Degree of sulphonation</i>
<i>Vanisperse CB</i>	Low	Low
<i>Ufoxane 3A</i>	High	Low
<i>Ultrazine NA</i>	High	Standard
<i>Borresperse NA</i>	High	Standard

Table 6 Properties distinguishing differences in the degree of sulphonation, molecular weight and polarity of the sodium lignin sulfonates.



Fig. 26 Properties distinguishing differences in the degree of sulfonation, molecular weight and polarity of the sodium lignin sulfonates.

### Glycerine liquid RM10

Colourless, odourless viscous liquid, with dispersion, antimicrobial, and antifreeze properties often used as a humectant.

### Benchmark samples

Samples of known, standard, control formulations were prepared (3 x 250 ml), filled and sealed with a cap. Samples were tested at the same time as the prepared experimental formulations for comparison. Samples of the experimental formulations using the biodegradable dispersants, and a standard formulation using polyacrylates as a control were kept in storage under each of the following temperature conditions:

- Fridge at 0°C
- Lab Cupboard at ambient room temperature (approximately 20°C)
- Storage oven at 45°C

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## 2.3 Experimental methods and procedure

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### 2.3.1 Dilution of dispersant candidate material

Solutions of 20 % w/w concentration of each candidate dispersant were diluted using deionised water in 100 ml volumetric flasks, labelled, and fully dissolved. For each experiment, candidate dispersants were added into a 50 ml B-Class burette. Alongside the burette, an overhead stirrer was set up at 1000 RPM for 30 seconds to provide constant agitation to homogenise the mixture after each dispersant addition. The zinc oxide and water mixtures were made and clamped beneath the overhead stirrer and burette. For each candidate dispersant, aliquots of 0.5 ml or 1.0 ml were added to the mixture to determine the demand for dispersant by the zinc oxide and water mixture.

### 2.3.2 Formulation mixture

A 1-litre formulation of foliar fertiliser suspension concentrate product, YaraVita Zintrac 700 was made in a 2-litre beaker. Monoethylene glycol from Helm, 99.8% (100 g) and acrylic dispersant Acriflow UL2 from 40% w/w minimum and 3500 molecular weight maxima from Witton (15 g) were added to generic Yorkshire water tap water from Yara (600 g) and mixed using an IKA WR20 mixer at 550 rpm. Potassium hydroxide from Norkem 90% (2 g) and Yara untreated technical grade urea 46% w/w N (39 g) were included and mixed at 1,100 rpm for 30 minutes to ensure a homogenised mixture was reached at room temperature. Norkem Zinc oxide 99.9% (876 g) was added slowly to incorporate in the mixture and the mixing rate increased every 15 minutes by 100 rpm to a final mixing rate of 1,500 rpm over an hour. Acrylic thickener from Coatex 30% w/w minimum (25.6 g) is a polymer added for thickening and with the formulation pH at 9, the acrylic thickener was activated and swelled to increase the viscosity of the mix within a minute. Lastly, anti-foam (1.80 g) and Promex CHS3 bactericide (1.70 g) were added to finalise the formulation before a weight-based water correction finalised the formulation to density 1.73 g/cm<sup>3</sup>.



Fig. 27 Formulation mixture using IKA RW20 overhead stirrer (Fig. 25)

### 2.3.3 Surface tension

A platinum-iridium ring torsion balance was used to measure surface tension. All measurements were done in triplicate at ambient temperature ( $20 \pm 2^\circ\text{C}$ ) and pressure (1 atm) and the average of three readings were reported for each of the independent experiments at 1% w/w concentration.



### 2.3.4 Storage stability

Formulations of standard YaraVita Zintrac were made as a benchmark to compare test formulations of the varying naturally derived polymers. Each formulation made was decanted into three 250 ml bottles and kept individually at 0°C, 20°C and 45°C for 8-weeks<sup>121</sup>. Using YaraVita Zintrac as a control, each week, the samples were checked visually for syneresis and using a spatula to gently stir the sample to detect sedimentation, lumps, or abnormalities in the formulation. Viscosities and comments were recorded and tabulated.

### 2.3.5 Dispersant demand

For dispersant demand testing, a mixture (proprietary – not disclosed) using the same ratio of zinc oxide to water in the benchmark formulation YaraVita Zintrac, was used to determine the efficacy of candidate dispersants at 20% w/w active dispersant content. A burette was used to add the dispersant 20% w/w solution at 0.5 ml or 1.0 ml aliquots whilst under constant agitation for 30 seconds at 1000 RPM using the overhead stirrer. After 30 seconds, a viscosity reading was recorded before adding the next aliquot until 50 ml of the 20% w/w dispersant solution was added.

### 2.3.6 Phytotoxicity assessment

Assessments are made seven days after spraying. This allows maximum scorch development to take place. Record all assessment data on Phytotoxicity Assessment Data Sheet QSFA 080 (Appendix 7.1.3) and count all the leaves in each pot (total leaf count).

Classify the leaves into one of four categories:

- no scorch
- slight scorch
- moderate scorch
- severe scorch

Recording the total number of leaves in each category. Using the total leaf count figure, the percentage of leaves falling into each category can be calculated for each pot in percentage terms. Statistical appraisal can then be conducted on these percentage figures for slight, moderate, and severe scorch using the Fisher Significance Test (FST).

Scorch categories are defined as follows:

**SLIGHT** Where a few individual spray droplets have produced scorch in droplet-sized areas.

**MODERATE** Where two or three spray droplets have joined together to produce larger areas of scorch, but in very discreet, spaced-out areas of the leaf.

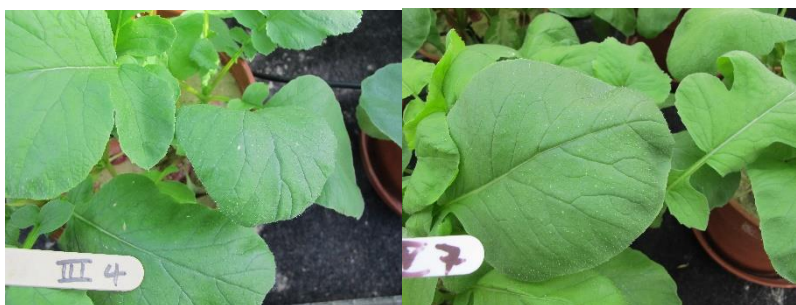
**SEVERE** Where there are bigger areas of scorch caused by several spray droplets joining together, or widespread numbers of scorched areas across the leaf. It should be immediately obvious that leaves in this category would be unacceptable to any grower. If in doubt, classify the scorch as severe.

When the data is reported, it is the severe scorch results section that is of greatest significance. This phytotoxicity score would result in a fail of the spray treatment. In certain trials, there may be background

levels of severe scorch resulting from the growing environment pre-spraying. Therefore, always compare the severe scorch levels in treated plants over and above that found in the standard control untreated plants.

Certain formulations tested may produce other problems on the leaf besides the conventional brown necrotic spotting, known as scorch and described above in point 7 (d). The most likely deviant form of scorch is "black pitting" in which pin-head sized dots of black tissue reaction develop on the leaf. These may be more prevalent on the undersurface of the leaf. The black pitting should be assessed into the following categories as defined below:

SLIGHT	Less than 5 black pits per cm <sup>2</sup> of leaf.
MODERATE	Equal to 5 - 10 black pits per cm <sup>2</sup> of leaf.
SEVERE	Greater than 10 black pits per cm <sup>2</sup> of leaf.



Examples of slight scorch



Examples of moderate scorch



Examples of severe scorch

Fig. 28 Percentages are calculated for the number of leaves in each black pitting scorch category against the total number of leaves per pot.

### 3.1 Introduction

Green Chemistry Principles were applied in this study to achieve the same function of polyolefins in formulation chemistry for PLFs in nutrient spray solutions. In addition, the environmental outlook for the end-of-life cycle of the polymer substrates through the biodegradation journey to the point of assimilation was considered.

The Green Chemistry Principles from Anastas and Warner most relevant to this study have been<sup>5</sup>:

1. It is better to prevent waste than to treat or clean up waste after it is formed.

Critically, by preventing the direct placement of non-degradable polymers into PLFs, or other industrial-scale raw materials and products, it is possible to prevent one direct source of marine litter widely documented<sup>15,16,85</sup>. Marine litter of microplastics less than 5µm in size are present and accumulating in marine ecosystems posing a threat to the marine life food web and the wider scale impact this has on further ecosystems outside of the oceans. It is far easier to limit this problem by preventing such waste, especially in direct, primary use systems such as is explored in agriculture in this study, than the global clean-up required at the end of the raw material/products' functional use, where persistence in the environment is predicted to be tens of hundreds of years<sup>2,3</sup>.

7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.

In this study, the aim was not only to prevent the use of PLFs that are not biodegradable from non-renewable feedstocks but to replace them with a feedstock source that is replenishable and more sustainable for the future<sup>32</sup>. Technical and cost challenges are considered; however, sustainability is addressed concerning an approach to the outlook and projections for food security and agricultural forecasts.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

Of 120 current bulk formulations, one-third are water-based liquid suspension concentrates containing PLFs with the potential for substituting with biodegradable alternatives. Chemicals selected for their potential of replacing currently sourced PLFs must be biodegradable, and they should also be functional during their lifetime, in a comparative way to existing polymer use in industry for the most practicable transition to a closed-loop life cycle. In the industry of agriculture, it is well documented that polymers, more specifically, fossil fuel based microplastics, used in agricultural products currently do not have waste streams available, and polymer fragments from their life after use are an environmental problem that is not currently addressed after the end of their useful life cycle. From literature reviews, the chemicals chosen for alternative use to polyolefins as PLFs are chosen on their known characteristics to best formulate within modified foliar nutrient sprays as effective dispersants

and wetting agents that are environmentally less hazardous and renewable for the future, with consideration for their design to break down into innocuous degradation products after use.

### 3.2 Dispersant demand

The most standard formulations of YaraVita foliar suspension concentrates interchange or combine the use of the dispersants polyacrylate liquid RM1 2695 and polyacrylate liquid RM2 UL2, producing a dispersed formulation compatible with the active and adjuvant components. However, when considering the stated biodegradability, Table 7 shows the poor biodegradability of these polymers derived from crude oil. To improve the biodegradability of products designed for agricultural applications, alternative polymers purported to possess greater biodegradability were selected, as indicated in Table 7.

#### 3.2.1 Biodegradability reference table

Polymer	State	Polymer Reference	Active composition (% w/w)	Biodegradability (Safety Data Sheet)
Polyacrylate	Liquid	RM1 2695	40	Very persistent
Polyacrylate	Liquid	RM2 UL2	40	Very persistent
Sophorolipid	Liquid	RM3 Breakthru SF420	50	Readily biodegradable (> 99% after 28 days) OECD 301 C
Lignosulfonate hybrid	Liquid	RM4 PPEM9565	45	Inherently biodegradable OECD Test Guideline 301D
Lignosulfonate hybrid	Liquid	RM4.1 PPEM9566	40	Readily biodegradable OECD Test Guideline 301D
Yucca plant extract	Liquid	RM5 Surf	50	Readily biodegradable
Modified sodium lignosulfonate	Solid	RM6 Ultrazine NA	100	Expected to be biodegradable
Modified sodium lignosulfonate	Solid	RM7 Borresperse NA	100	Expected to be biodegradable
Modified sodium lignosulfonate	Solid	RM8 Ufoxane 3A	100	Expected to be biodegradable
Modified sodium lignosulfonate	Solid	RM9 Vanisperse CB	100	Expected to be biodegradable
Glycerine	Liquid	RM10 Glycerine	99.5	Readily biodegradable

Table 7 Preliminary indication to the compatibility of polymers as dispersing agents based on technical and safety data sheets.

Investigating the polymer alternatives as dispersing agents involved a screening test of formulating YaraVita Zintrac using only the formulation ratios of zinc oxide and water to avoid any adjuvant polymer effect of dispersion. The dispersant demand test involves gradually adding an aliquot that can be dispersed homogeneously in the mixture for 30 seconds, recording the viscosity at each input until the viscosity reached the lowest value on the viscometer (below 1000 cP), indicating the solids had been dispersed into a liquid form, effective for formulation dispersion. For the standard control dispersants, RM1 and RM2, the viscosity was found to increase after the initial dispersant quantity of 0.5 to 1.0 ml were added. For this reason, experiment aliquots were added until 50ml of each dispersant at 20% w/w concentration was added to capture any similar occurrences.

In the dispersant demand test, RM5, yucca extract and RM10, glycerine required dispersant quantities too great to be economically viable or practical, and with the potential risk of having to reduce the elemental nutrient active content concentration to achieve a flowable liquid. This was in part to be expected as the properties of these candidates are tailored toward humectant (glycerine) and wetting properties (yucca extract). The remaining dispersants show comparable economically viable dispersion abilities, with the modified lignosulfonates and lignosulfonate hybrid candidate materials indicating the most comparable to the effective dispersion of polyacrylate standards. Typically, it took less than 10 ml of 20% w/w dispersant for all materials to effectively disperse the zinc oxide water mixture (Appendix, 7.1). Four of the candidates were selected as the most effective at dispersing the zinc oxide and water mixture, as shown in Fig. 29.

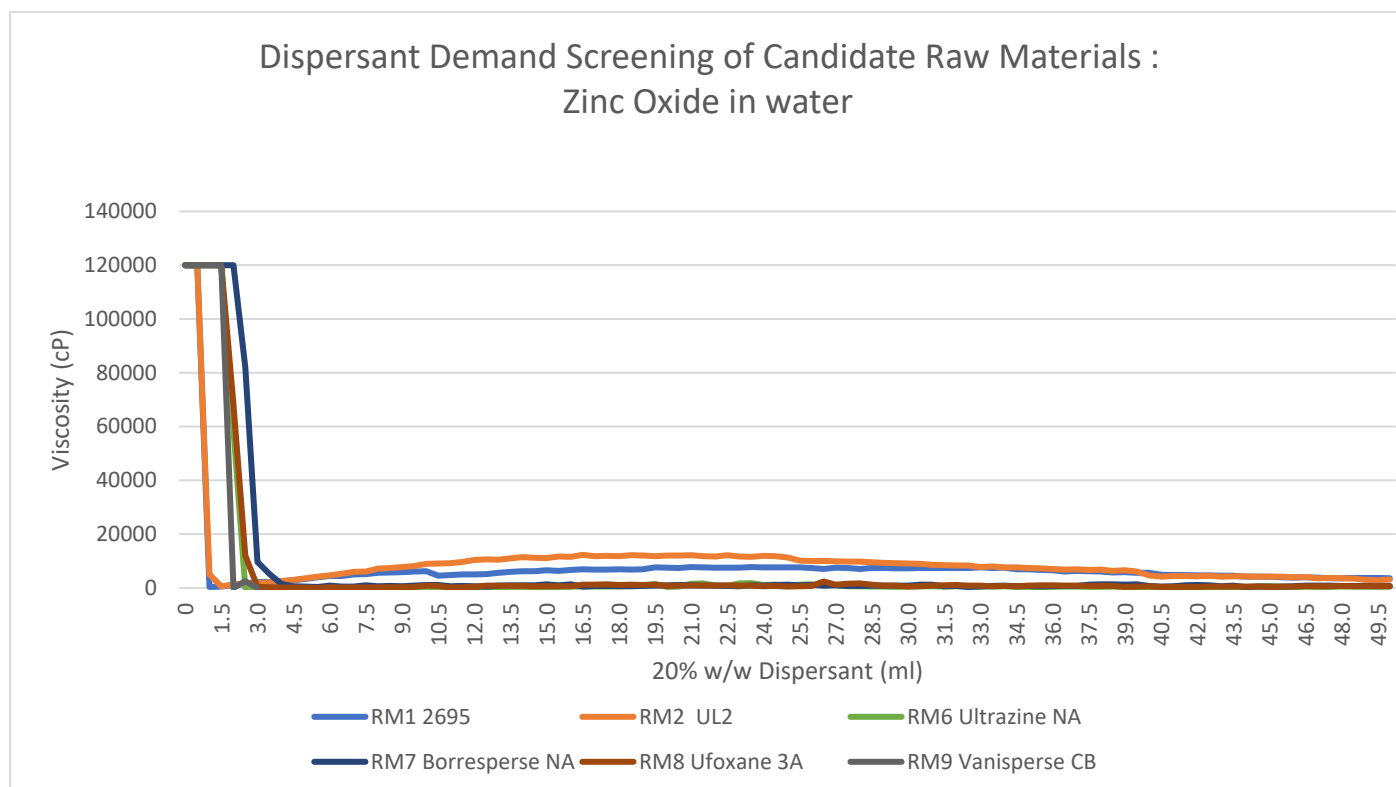


Fig. 29 Dispersant demand test screening candidate biodegradable dispersants against the standard control dispersant polymer and nutrient source, zinc oxide used in the benchmark formulation YaraVita Zintrac.

These materials were in the lignosulphonate category of polymers and were the most effective when compared to the benchmark standard controls. These raw materials come as powder dispersants and the presence of modified and unmodified hydroxyl groups assist in dispersing the zinc oxide particles to prepare a formulation. At the 20% w/w concentration, the lignosulfonates responded effectively as a dispersant at increased volume than the original polyacrylate dispersants and showed greater consistency as a dispersant over time in comparison to the polyacrylate benchmarks which increased in viscosity after the volume of 4 ml was added.

There are slight differences in dispersant demand between the lignosulfonates indicating polarity, molecular weight, and degree of sulfonation affect the dispersion of zinc oxide particles in water. RM9, Vanisperse CB shows the least amount of dispersant required for the dispersant demand test and is the most hydrophobic, with low molecular weight and low degree of sulfonation. The lignosulfonate that required more dispersant was RM7, Borresperse NA, the more hydrophilic, higher molecular weight with a greater degree of sulfonation.

For dispersant demand testing, the results conclude that lignosulfonates are comparable to the standard control raw materials currently used in YaraVita formulations in dispersant demand of zinc oxide in water and would be the most suitable candidates for an alternative biodegradable dispersant alternative.

### 3.3 Surface tension

Surface tension is of critical importance for a foliar-applied fertiliser, for retention on the leaf surface in challenging weather conditions, and to increase the droplet surface area contact with the leaves of the crops (Fig. 30). A 1% w/w dispersant active in water solvent, was chosen to be used to determine the efficacy of the selected raw materials as wetting agents to lower the surface tension of water content in the formulations. 15 is representative of the typical dilution for a foliar suspension concentrate formulation, where 2 L of product would be diluted into 200 L of water. The active concentrations of each candidate material were diluted from the data compiled in Table 7.

All biodegradable dispersants performed better than the standard control polyacrylate dispersants, with a surface tension lower or equal to 63 mN/m (Fig. 31). Yucca plant extract, RM5 had the lowest surface tension, with the sophorolipid RM3 following closely with 40 mN/m. This indicates there is a strong disruption of these molecules to the Van der Waals and hydrogen bonds in the solution, although the data does not disclose the specific structure of the molecules, it is expected that there is a strong surfactant effect where the hydrophilic and hydrophobic tails form micelles, interrupting the bonds forming between water molecules at the air: water surface layer and reducing the density of water molecules near the surface.

The results indicate the addition of the biodegradable surfactants at a 1% w/w minimum could significantly improve the wetting properties and critically reduce the surface tension of the formulated product. Increasing nutrient dispersion and reducing the likelihood of phytotoxicity on the leaf surface using biodegradable surfactants can add increased value in comparison to the current YaraVita Zintrac acrylic adjuvants. The polymers identified as suitable agents for reducing the surface tension of water had the opposite characteristics when compared to the dispersant demand test. Therefore, as an additional coformulant, it could be considered to add the biodegradable polymer alternatives for specific functions in the formulations.



Fig. 30 A demonstration on a leaf surface of the addition of 5% w/w surface acting (wetting) agent using Polyacrylate liquid RM1 in water (right) versus the high surface tension of water (left).

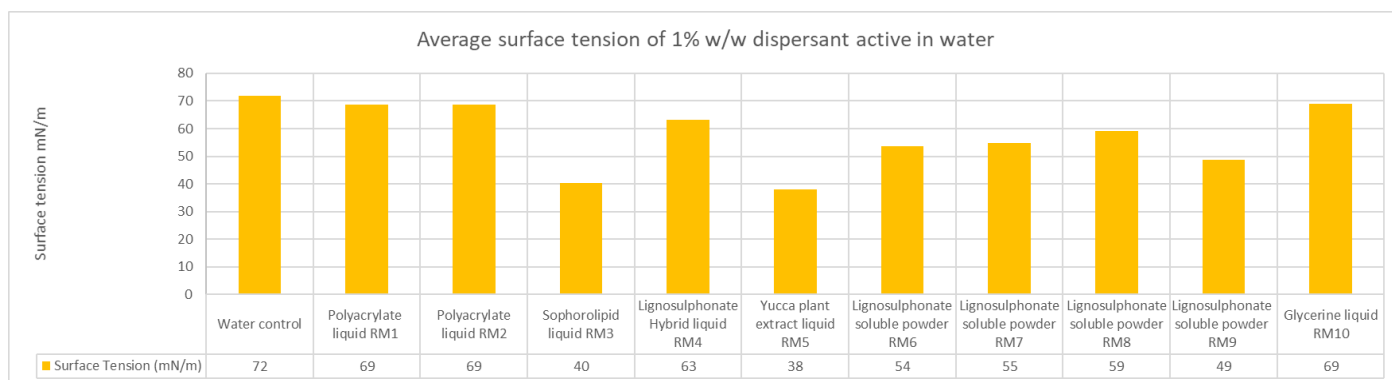


Fig. 31 A bar chart showing the relative surface tension of dispersant raw materials at 1% w/w concentration in water in comparison to water with the highest surface tension of 72 mN/m as the control.



### 3.4 Stability studies

The stability of the co-formulants selected was studied under different environmental temperatures. The study was carried out by changing the quantity of the dispersant while keeping other parameters of the formulation constant. The test formulation for zinc oxide suspension concentrate formulation is referenced in Table 8.

#### 3.4.1 Biodegradable zinc oxide-based formulation

Ingredient	Role	Concentration (wt%)	Concentration (g/L)
water	Solvent	42.98	q.s. 1L
Xanthan gum	Natural rheology modifier	0.15	25.00
Optigel	Natural rheology modifier	0.15	25.00
Lignosulfonate	Dispersant	0.8-1.0	15.00-30.00
Glycerine	Anti-freeze	5.73	100.00
ZnO	Micronutrient source	49.97	872.00
Biodegradable surfactant	Wetting agent	0.06	1.00
Biodegradable defoamer	De-foamer	0.06	1.00
Na propionate	Preservative	0.06	1.00

Table 8 Formulation of the 40% w/w zinc content, using the most favourable candidate biodegradable polymers.

Storage samples were inspected weekly, over an 8-week period, recording sample conditions over time. Settlement of insoluble nutrient content can be detected using a spatula, where viscosity is recorded to numerically gauge the consistency and stability of the formulation over time after allowing each sample to acclimatise to room temperature. The following observations would be considered as the sample failing the 8-week storage stability test:

- Hard or sticky settle
- Excessive syneresis
- Excessive viscosity increase or decrease

- Solidification
- Skinning
- Formation of lumps
- Gas evolution
- Microbial growth/spoilage
- Freezing

The 8-week storage test is the most rigorous test used to measure the stability of formulations, although it is a long period for assessment it provides the most accurate profile and prediction of the product stability over time at different thermal conditions. In suspension concentrate formulations, multiple factors such as coagulation and gravity change the thickening and dispersant structure over time so it is important to identify such changes in instability and visually record any physical separation of the formulation, typically visible as a liquid syneresis or felt as a solid sedimentation using a spatula<sup>121</sup>.

Suspension concentrates sample formulations of RM6 and RM8, performed best from the storage stability criteria, with no syneresis visible and a small range of viscosity change. The modified sodium lignosulfonates with high molecular weights and moderate hydrophilicity and hydrophobicity acted as stable dispersants in the formulation using biodegradable materials. RM8 performed the 8-week storage stability test with a smaller range of viscosity change, indicating greater stability at 1500-2000 cP than the standard formulation range of 2200-3200 cP.

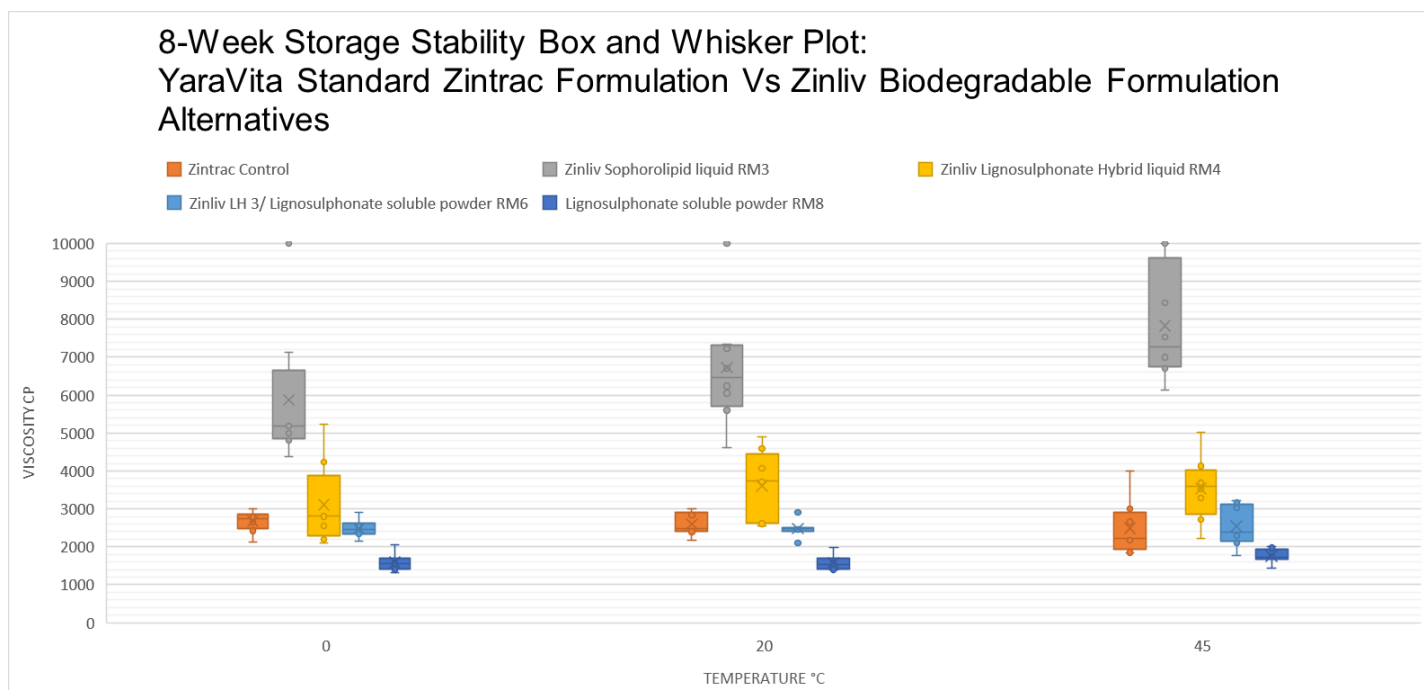


Fig. 32 Box and Whisker plot<sup>121</sup> to show the viscosity margins of each product across an 8-week accelerated storage stability at temperatures of 0, 20 and 45°C. The locality, spread and skewness of the samples in their temperature ranges is shown. A positive result is to match the benchmark viscosity of the Zintrac control sample (orange) within a range of 1000 – 3000 centipoises, this is a typical viscosity to match the shear and pump rates of the thixotropic fertiliser used by operators and customers for foliar fertiliser transportation and dilution.

From a batch formulation, three 250 ml samples were separated and kept at three temperatures: 0°C, 20°C and 45°C. Viscosities were recorded at the same time once a week for a period of eight weeks (appendix, 7.4). At 0°C from Fig. 32, the spread of data is greatest in RM3 and RM4 and indicated that the formulation is likely to increase over time in cold conditions. This indicates that RM3 and RM4 are not as effective at dispersing zinc oxide particles in a suspension concentrate form as the standard control polymer. RM6 had a lower spread of viscosity throughout the eight-week period, an indication that at 0°C this formulation is stable as a suspension concentrate formulation. RM8 performed similarly to RM6, however the viscosity locality was lower than the standard control.

In comparison to the benchmark formulation of YaraVita Zintrac, RM8 and RM6 show good locality of viscosity within the time frame and across the temperature ranges. This indicates that the accelerated storage stability would provide suitable stability over time at a variety of conditions for two years in real time for stock management and customer use of the product. Both raw materials RM6 and RM8 have a high molecular weight and identify to the polymers of the standard control formulation which also have high molecular weights. For further studies and factory trials, RM8 had lower sulfonation and showed the greatest consistency and suitability for a stable formulation that can effectively disperse zinc oxide slurry, and provide wetting properties greater than water and surpassing the benchmark standard control polymers

used that do not biodegrade. RM8 therefore is identified as the most suitable candidate to trial a formulation of zinc oxide nutrient using natural and biodegradable components that are approved by the organic registered body in Europe<sup>83</sup>.

RM3 is commercially targeted as a surfactant that has good wetting capabilities, which was indicated in the results in Fig. 31. for surface tension as one of the best-performing candidate biodegradable polymers. Although the material responded well as a wetter, for the properties not disclosed of this material, the biopolymer did not perform in a consistent range of viscosities. Properties were not disclosed for this candidate raw material, though identifies the properties are not optimised for dispersant demand at a range of temperatures in a standard formulation. The viscosities were significantly higher for RM3 than the benchmark sample, indicating a challenge for commercial use in varying climates around the globe for pumping and pouring of a product for agricultural use. RM4 performed more consistently at the range of temperatures and although properties of the commercial material are not fully disclosed, the results correlate with the lignosulfonate content in this material and the positive results seen in RM6 and RM8, which are also lignosulfonates and identified as the most suitable candidates in this study.

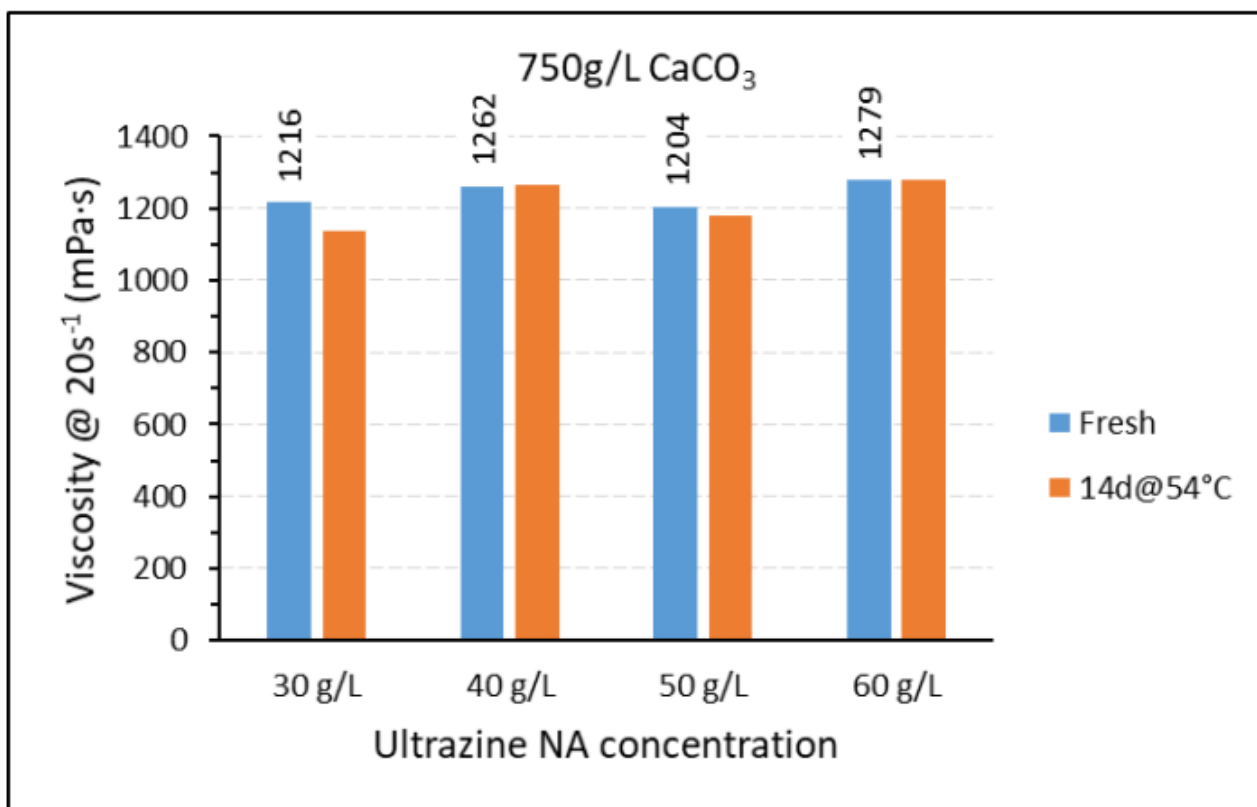


Fig. 33 Graph showing increasing modified lignosulfonate RM6 Ultrazine NA concentration and related viscosity of a formulation containing 750 g/L calcium carbonate as the active micronutrient source.

### 3.4.2 Other polymers and micronutrient sources

To make formulations that used biodegradable dispersants, it was important to consider other polymer co-formulants used in the formulation. Storage stability testing and anti-foam testing using an ISO9001 raw material procedure were used to change the acrylic polymer, biocide and de-foamer polymers too.

A new formulation using the same concentration wt% of YaraVita Zintrac was developed based on the 'Zinliv' formulation in Table 8. This formulation was developed over time by initially changing the dispersant and thickening system based on the existing ratios of YaraVita Zintrac 700, until a ratio suited to using natural thickeners and the screened biodegradable dispersants performed in the desired viscosity range. After a successful thickening and dispersant system was created between ratios of natural thickening agents xanthan gum, optigel clay and the candidate dispersant materials, a series of samples were made up to determine the optimal range of dispersant addition. After raw material approval, the biodegradable biostat sodium propionate and defoamer were added to finalise the formulation designed to be suitable for use in organic farming by the organic body FiBL, which approved all materials in the formulation as natural and suitable for use in organic farming<sup>83</sup>.

YaraVita supplies a range of suspension concentrate products primarily based on carbonates and oxides as micronutrient sources. As zinc oxide is typically easy to disperse due to a relatively small molecular mass of 81.38 g/mol, other candidate nutrient sources were then trialled. Calcium carbonate has a greater molecular mass of 100.09 g/mol, and greater still is the molecular weight of manganese carbonate at 114.95 g/mol. The atomic radius of manganese and calcium is greater than zinc, respectively. This indicates that as the atoms are typically greater in weight and radius, naturally the molecules become increasingly more difficult to disperse. As seen in Fig. 33, increasing the concentration of the lignosulfonate from 30 g/l to 60 g/l did not decrease the viscosity relative to addition. To prevent waste and conserve costs, further tests were carried out to find the minimum amount of dispersant required to formulate new biodegradable formulations based on existing YaraVita products. The products considered were based on existing YaraVita formulation nutrients from the raw materials zinc oxide, manganese carbonate and magnesium hydroxide (brucite), with optimal dispersant quantities, found to be 15 g/l, 20 g/l and 30 g/l, respectively (costs are not disclosed due to NDA).

### 3.4.3 Phytotoxicity assessment and testing

As a final crop safety test, a phytotoxicity comparison was carried out to determine the sensitivity of radish leaves to the final formulation consisting of the chosen lignosulfonate from the series of screening tests. Due to the overall results, RM8 Ufoxane 3A, was used as the candidate dispersant in the formulation to trial against the standard control, YaraVita Zintrac 700 in a glasshouse safety trial on radishes. Radishes are a very sensitive crop and any phytotoxicity or challenges with the formulation are typically very visible on the large, quickly growing radish leaves. For the turnover of tests, radishes have a typical growth period of 4-5 weeks until foliage growth is ready for harvesting and analysis.

Comparison between products at the same rate of application identified a significantly greater phytotoxicity for YaraVita Zintrac at a rate of 2 l/ha in the % of slight scorch identified on final radish foliage. For moderate scorch, the rates of 1 l/ha and 2 l/ha were similar for both products, Zintrac in comparison to Zinliv showed significantly higher scorch at the higher rate of application at 3 l/ha. There were no significant differences between any rate of application for foliage categorised as severe scorch. As a final recommendation, Zinliv in this study reduces the % of scorch in comparison to YaraVita Zintrac on harvested radish leaves.

	Treatment	Application Rate (l/ha)	Water Rate (l/ha)	RADISH EXPO F1-PHYTOTOXICITY ASSESSMENTS					
				Slight Scorch (%)	FST	Moderate Scorch (%)	FST	Severe Scorch (%)	FST
1	Control	0	200	0.00	C	0.00	D	0.00	A
2	Zintrac-1	1	200	0.00	C	0.00	D	0.00	A
3	Zintrac-2	2	200	44.21	A	7.01	BC	0.00	A
4	Zintrac-3	3	200	35.76	B	19.43	A	0.00	A
5	ZinLiv-1	1	200	3.23	C	0.00	D	0.00	A
6	ZinLiv-2	2	200	34.10	B	4.99	CD	0.00	A
7	ZinLiv-3	3	200	34.48	B	10.78	B	0.00	A
	FST=Fisher Significance Test								

Table 9 Phytotoxicity assessment statistical data from YaraVita ISO 9001 procedure on glasshouse safety testing, reference images for defining scorch are used to determine the severity of phytotoxicity on the leaf and scored to produce data for statistical data to compare the safety profile of test formulations.



Fig. 34 Photographic result of the final test formulation, MagLiv magnesium carbonate active nutrient formulation designed for organic use. The image shows the most extreme case of the experiment where a spreading pattern at 3 times the recommended agronomic application rate is applied, showing the product to be safe on harvested radish leaves. Visual record are kept to detect phytotoxicity from reference images.

From the results, the formulation containing the lignosulfonate dispersant RM8 resulted in lower phytotoxicity. Although it is not possible to determine if RM8 was the cause in the reduction of slight scorch, Zinliv is a formulation composed of ingredients that are considered natural and biodegradable and is aligned with regulations and registered bodies as a product suitable for use in agriculture. In general, the polymers that are biodegradable alternatives to synthetic polymeric adjuvants in foliar fertiliser have a beneficial impact on the test safety crop, wetting properties and a comparable dispersant demand and storage stability to the benchmark control.



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## 4.0 Conclusion

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To eliminate the use of persistent or non-biodegradable polymers where suitable biodegradable alternatives exist, progression has been aligned to Green Chemistry principles in agriculture<sup>5</sup>. Utilising renewable feedstocks, preventing the use of non-biodegradable plastics and using biodegradable alternatives where commercially available and economically viable, are sustainable starting points for renewing PLF industries, with a particular focus on direct, application in the environment for agricultural use and efficacy. As an industry, agriculture aims to optimise nutrient uptake and efficacy of the fertiliser applied to increase yield and profit, whilst adhering to consumer environmental concerns and enforcement of regulatory affairs. Organic farming has become a more profitable area of agriculture and fertiliser for use in organic farming can be optimised for micronutrient use efficacy with suitable co-adjuvants in formulations, provided those formulants are from renewable feedstocks and of biodegradability certified and accepted by standardised organic international bodies<sup>83</sup>.

In this research, the candidate material sourcing of lignosulfonates and sophorolipids was considered as renewable source-derived raw materials. These materials were tested in comparison to existing petroleum-derived polymers as candidate alternatives for effective function in foliar nutrient fertiliser, storage stability, and surface tension, based on reviews of biodegradation studies and physical lab studies. After successful practical screening in modified formulations, the co-adjuvants were screened for crop safety by product application on radish leaves to ensure no phytotoxic damage. **The formulations upheld chemical composition, crop safety testing and functionality to the standard existing YaraVita formulations currently available. By offering a solution for sustainable farming, YaraVita foliar nutrient sprays that do not contain microplastics offer a biodegradable product, suitable for organic farming.** Compositions of the redeveloped formulations align with the Green Chemistry Principles, preventing microplastic waste directly applied on the farm, designed with optimal chemical properties during their functional useful lifetime and designed for biodegradation after a useful lifetime, by using renewable feedstocks of naturally derived polymers.

The raw materials and co-formulants are compliant with one of the world's leading institutes in the field of organic agriculture, the Research Institute of Organic Agriculture (FiBL) and offer a practice for future sustainable farming to be adopted as part of a new product range in the world's leading fertiliser companies<sup>83</sup>. Though not limited to organic farming practices, organic farming often incurs premiums for specialised raw material selection which is often passed to the supplier and the consumer product, though at large volumes and commercialisation, these costs can be reduced. Produced from the staple and large volume products of the pre-existing YaraVita foliar active nutrient range, the range of products designed for organic use have been formulated with the intention of improving biodegradability and use in organic farming. The sourcing of renewable feedstocks and clean synthesis of biodegradable polymers is part of the green chemistry research process. How can legislation guide activity in the environment for the future of agriculture to consider and implement significant parameters of biodegradability for soil and marine

fragmentation of chemical agricultural deposits? Further to the literature reports on the biodegradability of the nutrient or active components and co-adjuvants used in foliar nutrient spray formulation chemistry, OECD is a standard method that can verify the ultimate degradation of the complete formulation composition for industrial certification as a good standard of responsible industry practice<sup>78</sup>. In anticipation of future legislation concerning the environmental considerations of industry, selecting co-formulants that meet such criteria as individual components is a proactive decision by suppliers, consumers, and industries, before policy and legislation.

### 5.1 Next steps

From the safety trials on radish crops, it would be interesting to determine if the new formulation which uses biodegradable polymer alternatives has a positive impact on dry biomass weight and nutrient uptake. In the case of the zinc oxide formulation, zinc in the leaf and fruit of the crop could be measured after harvest. By taking the dry weight of the harvest and grinding the biomass, digesting the material in acidic conditions, and filtering and diluting the contents for analytical chemistry analysis. One method for identifying wavelengths specific to micronutrients such as Zn, would be by Inductively Coupled Plasma -Optical Emission Spectroscopy (ICP-OES) analysis where key micronutrient content can be correlated to the foliar fertiliser application. This comparison could identify if polymers and formulations that are of natural origin have a positive correlation to the nutrient use efficiency of crops in comparison to synthetic polymeric adjuvants from petrochemical feedstock.

The studies in this research were predominantly focused on zinc oxide as the raw material for finding polymer alternatives that are biodegradable. YaraVita has a diverse portfolio focused on supplying micronutrient content for most elements that are critical for the metabolic processes used in plants for optimum health and yield. Now that there are found to be suitable polymer alternatives that have a biodegradable life cycle, it is possible to implement them in the suspension concentrate range for continuous improvement aligned with sustainability and regenerative farming. With further implementation, the biodegradable polymers approved in this study for agricultural use could be tailored to each formulation for improving carbon footprint of raw materials and the life cycle assessment of products manufactured.

### 5.2 Biodegradability

The next steps would be to demonstrate OECD biodegradability tests for revised formulations in comparison to that of the original suspension concentrate formulations, to account for the mixture of the individually selected adjuvants. Biodegradation can be challenging to replicate under laboratory conditions, taking into consideration the diversity, efficiency and complex natural microbial communities and their catabolic pathways. It is however necessary to compose and utilise standards for biodegradation to calibrate the environmental outcomes of industrially produced materials and avoid the introduction of persistent materials in the environment.

With the potential of using biodegradable polymers as a suitable alternative to current, approved non-renewable and non-biodegrading polymers, there is a great scope for companies like Yara to adopt more sustainable practices in chemical formulations. With the example of the possible swap for the dispersant, wetting and thickening agents in formulations, there is greater scope to ensure microplastics do not enter waste systems or the environment as microplastics. Agriculture has currently undergone a rigorous change with the adoption of the Fertilising Products Registration (FPR) EU 2019/1009<sup>49</sup>. Compliance for raw materials used in formulations destined for agricultural use is more stringent, with the materials having to not only be REACH and EU REACH compliant as chemicals themselves but also registered for the designated

use in agriculture on the ECHA uses dossiers<sup>1,14</sup>. In the future stringent regulations on the nature of biodegradation could determine the persistence of formulants in the environment, especially where it is possible for biodegradation studies to be part of the LCA for manufacturers to make informed choices on the persistence and sustainability of raw material selection.

### **5.3 Sustainable Agriculture**

Following on from the perspective of sustainability, there is potential for carbon footprint data to contribute to the TDSs provided for raw materials. To adopt Green Chemistry, enhance crop production and do so sustainably, assessing the LCA of every component in fertiliser is a critical step to taking progressive steps and launching initiatives to reduce CO<sub>2</sub> emissions<sup>96</sup>.

. Agriculture is a global industry with an indirect and direct carbon footprint across operations from mining operations to the supply chain, manufacturing process and transport to consumer.

A goal target for the UN Sustainable Development Goals is to achieve sustainable management and efficient use of natural resources by 2030<sup>65</sup>.

By using sustainable raw materials that can be assimilated at the end of useful life, prevention, and reduction of waste by adopting sustainable practices in formulation chemistry is a critical sustainability goal met, superseding local country policy and averting the use of microplastics for responsible consumption and production<sup>24</sup>.

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## 7.0 Appendix

### 7.1 Viscosity table of dispersant demand test

Viscosity table of dispersant demand test recorded viscosities of incremental additions of candidate raw materials to disperse a zinc oxide and water slurry with 20% w/w active content concentration of the dispersant (excluding glycerine and yucca extract).

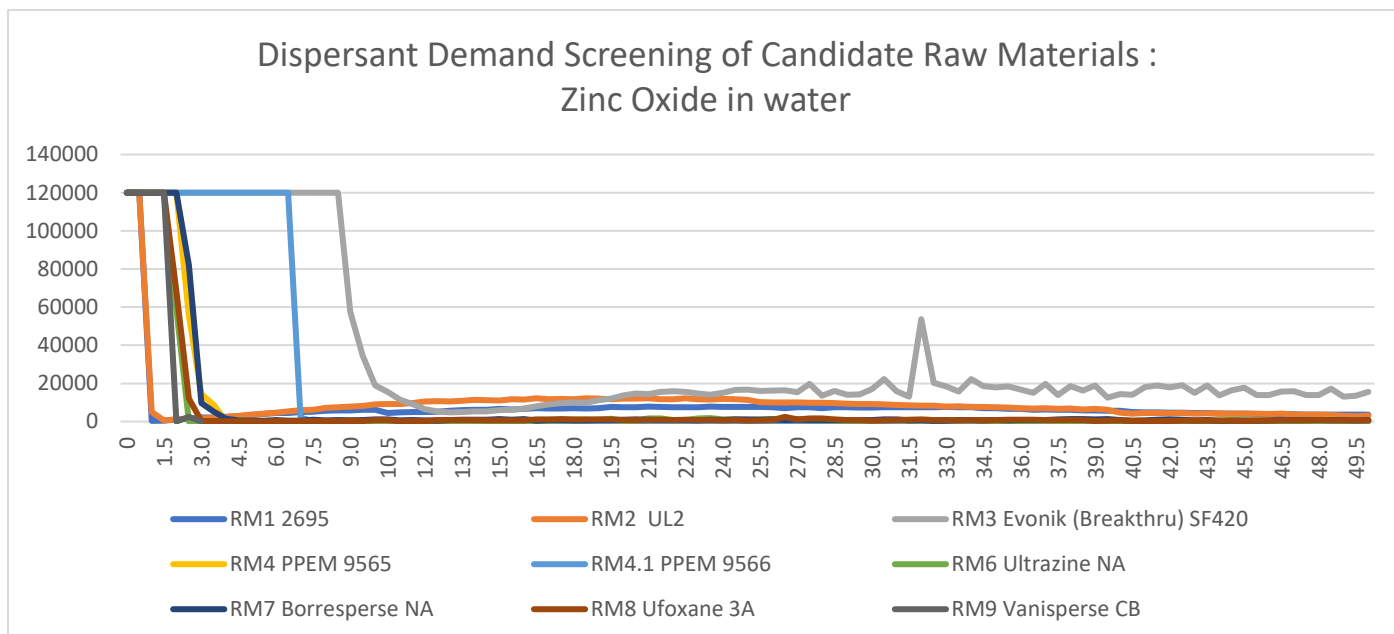
Solution added 20% w/w (ml)	Viscosity (cP) (1 RPM; Spindle 63; Brookfield DV2)								
	RM1 2695	RM2 UL2	RM3 Evonik (Breakthru ) SF420	RM4 PPEM 9565	RM4.1 PPEM 9566	RM6 Ultrazine NA	RM7 Borresper se NA	RM8 Ufoxane 3A	RM9 Vanisper se CB
0	120000	120000	120000	120000	120000	120000	120000	120000	120000
0.5	120000	120000	120000	120000	120000	120000	120000	120000	120000
1.0	360	5040	120000	120000	120000	120000	120000	120000	120000
1.5	480	600	120000	120000	120000	119900	120000	120000	120000
2.0	1080	1200	120000	120000	120000	58920	120000	68280	0
2.5	1440	1680	120000	55560	120000	0	82000	12000	2520
3.0	2160	1680	120000	14400	120000	0	9720	360	0
3.5	2160	2040	120000	8640	120000	0	5160	240	
4.0	2520	2480	120000	240	120000	240	1440	120	0
4.5	2880	3000	120000	720	120000	120	600	120	
5.0	3360	3600	120000	120	120000	120	480	120	360
5.5	3960	4200	120000	480	120000	120	360	0	
6.0	4440	4680	120000	240	120000	120	840	240	480
6.5	4440	5280	120000	240	120000	240	480	120	
7.0	5040	6000	120000	120	1980	360	480	240	240
7.5	5160	6120	120000	360	210	240	960	120	
8.0	5640	7200	120000	360	180	240	600	240	360
8.5	5760	7440	120000	480	20	360	720	240	
9.0	5880	7800	57630	720	20	360	600	240	480
9.5	6120	8160	34560	480	20	360	840	360	
10.0	6240	9000	18840	480	20	360	1080	840	720
10.5	4560	9120	15480	360	20	240	1080	720	
11.0	4800	9230	11520	120	20	240	600	120	480
11.5	5040	9720	9120	120	20	240	720	240	
12.0	5040	10440	6480	120	20	240	600	360	480
12.5	5160	10680	5400	600	20	240	480	840	
13.0	5640	10560	4800	600	20	240	840	840	720
13.5	6000	10920	4920	720	20	360	960	720	

14.0	6240	11400	5280	600	20	360	960	720	360
14.5	6240	11160	5290	240	20	240	960	600	
15.0	6600	11040	6000	720	20	360	1320	600	360
15.5	6360	11640	6240	840	20	360	960	600	
16.0	6720	11520	6840	560	20	480	1320	600	600
16.5	6960	12240	8040	600	20	480	480	1200	
17.0	6840	11760	9000	600	20	480	720	1200	360
17.5	6840	11880	9600	720	20	520	720	1320	
18.0	6960	11760	10080	960	20	600	600	1080	600
18.5	6840	12120	9840	960	20	780	600	1200	
19.0	6960	12000	11160	600	20	980	720	1080	600
19.5	7680	11760	12000	360	20	1440	840	1200	
20.0	7560	12000	13680	460	20	360	960	720	720
20.5	7440	12000	14640	960	20	480	1080	840	
21.0	7800	12120	14400	840	20	1560	960	840	480
21.5	7680	11760	15600	960	20	1680	840	960	
22.0	7560	11640	15960	360	20	840	840	840	360
22.5	7560	12120	15480	480	20	720	720	960	
23.0	7560	11640	14640	840	20	1680	600	840	360
23.5	7800	11520	14100	600	20	1800	960	840	
24.0	7680	11880	15000	720	20	1080	840	600	600
24.5	7680	11760	16560	600	20	1200	1080	720	
25.0	7680	11280	16800	720	30	840	1200	480	600
25.5	7680	10200	16080	840	30	1200	960	600	
26.0	7440	10080	16180	600	40	1320	1080	720	600
26.5	7080	10080	16320	840	40	960	840	2400	
27.0	7560	9960	15360	720	50	1080	960	1200	600
27.5	7440	9840	19680	720	50	600	720	1560	
28.0	7080	9840	13560	840	60	600	720	1680	600
28.5	7440	9600	16080	840	60	480	840	1200	
29.0	7440	9360	14040	720	60	480	840	840	600
29.5	7320	9240	14280	840	60	360	840	840	
30.0	7320	9120	16920	480	70	480	840	480	480
30.5	7440	9000	22320	600	60	600	1200	600	
31.0	7440	8640	15840	480	50	600	1200	840	720
31.5	7440	8520	12960	600	50	480	600	960	
32.0	7440	8400	53640	600	50	600	720	1080	1680
32.5	7440	8400	20280	600	40	600	360	840	
33.0	7680	7800	18360	600	50	600	480	840	1080
33.5	7440	8040	15720	600	60	480	720	600	

34.0	7560	7680	22320	720	60	600	840	720	840
34.5	6960	7680	18600	720	60	360	600	600	
35.0	6960	7440	17880	720	60	360	720	840	600
35.5	6720	7320	18480	480	70	240	600	960	
36.0	6600	7080	16680	480	70	360	720	960	1080
36.5	6120	6840	15120	600	70	480	720	900	
37.0	6360	6960	19680	480	80	480	720	840	1080
37.5	6240	6720	13800	600	70	360	1200	720	
38.0	6120	6840	18600	600	60	360	1320	720	1200
38.5	5760	6360	16200	480	70	480	1320	720	
39.0	5880	6600	18840	360	90	360	1200	360	720
39.5	5640	6120	12480	480	70	240	1320	480	
40.0	5640	4680	14400	480	80	240	720	600	840
40.5	4920	4200	14000	480	50	240	480	360	
41.0	4800	4440	18120	480	60	120	600	360	840
41.5	4800	4440	18960	600	60	0	960	360	
42.0	4680	4320	17880	480	70	0	1080	360	960
42.5	4680	4560	19080	360	70	120	960	480	
43.0	4560	4200	15000	480	80	120	600	480	720
43.5	4560	4320	18840	720	70	120	840	480	
44.0	4200	4320	13680	840	80	120	360	480	600
44.5	4200	4200	16440	960	80	600	480	480	
45.0	4200	4200	17760	600	90	600	480	360	480
45.5	3960	4200	13800	720	80	240	480	480	
46.0	3840	3960	13800	600	80	240	600	480	720
46.5	3960	4080	15720	360	70	480	840	600	
47.0	3840	3600	15960	760	80	360	840	600	840
47.5	3600	3720	13920	840	90	360	840	600	
48.0	3600	3600	13800	840	60	480	720	720	720
48.5	3720	3480	17280	960	50	480	720	600	
49.0	3720	3000	12960	720	60	480	720	600	720
49.5	3720	2880	13560	840	70	480	600	600	
50.0	3600	3120	15480	840	60	480	720	600	720



## 7.2 Candidate raw materials evaluated for dispersant demand



In the graph for dispersant demand screening, a zinc oxide and water mix were used to test the candidate raw materials. Effective dispersion is compared to the standard control polymers used in YaraVita suspension concentrate formulations. Lignosulfonate biodegradable polymer alternatives were analysed for efficacy in dispersing the mixture.

## 7.3 Surface tension data

Surface tension data recorded in triplicate for the raw material candidate selection property of wetting ability, reducing the surface tension of deionised water in a 1% w/w addition.

Raw material 1% w/w solution	Surface tension (N/m)			
	Replicate 1	Replicate 2	Replicate 3	Average
Water control	0.072	0.072	0.072	0.072
Polyacrylate liquid RM1	0.069	0.068	0.069	0.069
Polyacrylate liquid RM2	0.069	0.068	0.071	0.069
Sophorolipid RM3	0.041	0.039	0.040	0.040
Lignosulfonate Hybrid liquid RM4	0.063	0.063	0.062	0.063
Yucca plant extrac RM5	0.038	0.038	0.038	0.038
Lignosulfonate soluble powder RM6	0.055	0.054	0.053	0.054
Lignosulfonate soluble powder RM7	0.054	0.056	0.056	0.055
Lignosulfonate soluble powder RM8	0.058	0.058	0.059	0.059
Lignosulfonate soluble powder RM9	0.049	0.049	0.050	0.049
Glycerine RM10	0.069	0.069	0.070	0.069

## 7.4 8-Week storage stability results

Table of 8-Week Storage Stability Results for standard control formulation YaraVita Zintrac vs organic trial product Zinliv using hybrid lignosulfonate raw material 4.

Date/Week	Temperature °C	Standard formulation Viscosity (cP)		Comments
		Zintrac Control	Zinliv RM4	
17/06/21 Week 1	0	3010	4230	
	20	3000	4910	
	45	4000	5020	
24/06/21 Week 2	0	2860	2860	
	20	2920	4070	
	45	3000	3700	
02/07/21 Week 3	0	2829	2800	
	20	2829	3759	
	45	2659	3519	
09/07/21 Week 4	0	2130	2849	
	20	2489	3719	
	45	2270	3689	
14/07/21 Week 5	0	2789	5239	
	20	2479	4589	
	45	2170	4129	
17/07/21 Week 6	0	2679	2109	
	20	2459	2609	
	45	2190	3289	
02/08/21 Week 7	0	2419	2559	
	20	2180	2649	
	45	1830	2719	
12/08/21 Week 8	0	2639	2190	
	20	2399	2559	
	45	1850	2230	

Table of 8-Week Storage Stability Results for standard control formulation YaraVita Zintrac vs organic trial product Zinliv using hybrid lignosulfonate raw material 5.

		Standard formulation Viscosity (cP)		
Date/Week	Temperature °C	Zintrac Control	Zinliv RM5 Surf	Comments
06/05/21 Week 1	0	3050	8250	
	20	2900	8700	
	45	2400	9200	
17/05/21 Week 2	0	2900	7000	
	20	2720	9000	
	45	2000	9000	
28/05/21 Week 3	0	2800	7700	
	20	3480	8000	
	45	1880	7700	
04/06/21 Week 4	0	2810	6400	
	20	2680	8400	
	45	3670	8600	
11/06/21 Week 5	0	2300	6600	
	20	2400	7430	
	45	1620	9520	thicker at the bottom -sedimentation
17/06/21 Week 6	0	2630	6040	
	20	2380	8740	
	45	1600	8910	
24/06/21 Week 7	0	2380	6490	
	20	2380	7600	
	45	1560	12000	thicker at the bottom- sedimentation
02/07/21 Week 8	0	2629	7128	
	20	2399	12000	thicker at the bottom- sedimentation
	45	1720	7128	

Table of 8-Week Storage Stability Results for standard control formulation YaraVita Zintrac vs organic trial product Zinliv using hybrid lignosulfonate raw material 4.

		Standard formulation Viscosity (cP)		
Date/Week	Temperature °C	Zintrac Control	Zinliv RM4 lignosulfonate hybrid	Comments
16/11/20 Week 1	0	2780	2200	
	20	2670	1750	
	45	2810	1850	
23/11/20 Week 2	0	3080	1640	
	20	2970	1890	
	45	3220	2210	
30/11/20 Week 3	0	2640	1700	
	20	2730	1490	
	45	2760	1430	
10/12/20 Week 4	0	2840	1700	
	20	2840	1440	
	45	2780	1410	
17/12/20 Week 5	0	2680	1680	
	20	2660	1480	
	45	2600	1450	
23/12/20 Week 6	0	2600	1820	
	20	2650	1420	
	45	2640	1120	Soft settle
30/12/20 Week 7	0	annual leave	annual leave	
	20	annual leave	annual leave	
	45	annual leave	annual leave	
06/01/20 Week 8	0	2600	1610	
	20	2820	1330	
	45	2600	1370	Soft settle (formulation could require more thickener)

Table of 8--Week Storage Stability Results for standard control formulation YaraVita Magtrac vs organic trial product Magliv using hybrid lignosulfonate raw material 4.

Date/Week	Temperature °C	Standard formulation Viscosity (cP)		Comments
		Magtrac Control mg hydroxide	Magliv Mg hydroxide RM4 lignosulfonate hybrid	
26/11/20 Week 1	0	3300	5870	
	20	3270	5560	
	45	4930	5200	
03/12/20 Week 2	0	5000	4610	
	20	3970	4630	
	45	3400	4200	
10/12/20 Week 3	0	4330	5040	
	20	3930	4660	
	45	3420	4430	
17/12/20 Week 4	0	4260	4450	
	20	4050	4410	
	45	3650	4430	
24/12/20 Week 5	0	4020	4310	
	20	4000	4420	
	45	3640	4460	
31/12/20 Week 6	0	annual leave	annual leave	
	20	annual leave	annual leave	
	45	annual leave	annual leave	
07/01/21 Week 7	0	4200	4640	
	20	3840	4510	
	45	4130	4800	
14/01/21 Week 8	0	4400	4730	
	20	3960	4460	
	45	4230	4800	

Table of 8--Week Storage Stability Results for standard control formulation YaraVita Magtrac vs organic trial product Magliv using hybrid lignosulfonate raw material 6.

Date/Week	Temperature °C	Standard formulation Viscosity (cP)		Comments
		Magtrac Control Mg carbonate	Magliv Mg carbonate RM6 Ultrazine NA	
26/11/20 Week 1	0	2600	8090	
	20	-	-	Result not recorded
	45	2419	7488	
03/12/20 Week 2	0	1810	6809	
	20	-	-	Result not recorded
	45	2080	-	Result not recorded
10/12/20 Week 3	0	2429	7058	
	20	-	-	Result not recorded
	45	2320	6209	
17/12/20 Week 4	0	annual leave	annual leave	
	20	annual leave	annual leave	
	45	annual leave	annual leave	
24/12/20 Week 5	0	annual leave	annual leave	
	20	annual leave	annual leave	
	45	annual leave	annual leave	
31/12/20 Week 6	0	2449	5259	
	20	-	-	Result not recorded
	45	2879	4299	
07/01/21 Week 7	0	2539	4289	
	20	-	-	Result not recorded
	45	4059	3249	
14/01/21 Week 8	0	2200	4569	
	20	2270	4569	
	45	4319	3939	

Table of 8-Week Storage Stability Results for standard control formulation YaraVita Magtrac vs organic trial product Magliv using hybrid lignosulfonate raw material 4.

Date/Week	Temperature °C	Standard formulation Viscosity (cP)		Comments
		Magtrac Control MgOH	Magliv MgOH RM4 lignosulfonate hybrid	
26/11/20 Week 1	0	3300	5870	
	20	3270	5560	
	45	4930	5200	
03/12/20 Week 2	0	5000	4610	
	20	3970	4630	
	45	3400	4200	
10/12/20 Week 3	0	4330	5040	
	20	3930	4660	
	45	3420	4430	
17/12/20 Week 4	0	4260	4450	
	20	4050	4410	
	45	3650	4430	
24/12/20 Week 5	0	4020	4310	
	20	4000	4420	
	45	3640	4460	
31/12/20 Week 6	0	annual leave	annual leave	
	20	annual leave	annual leave	
	45	annual leave	annual leave	
07/01/21 Week 7	0	4200	4640	
	20	3840	4510	
	45	4130	4800	
14/01/21 Week 8	0	4400	4730	
	20	3960	4460	
	45	4230	4800	

Table of 8-Week Storage Stability Results for standard control formulation YaraVita Mantrac vs organic trial product Manliv using hybrid lignosulfonate raw material 6.

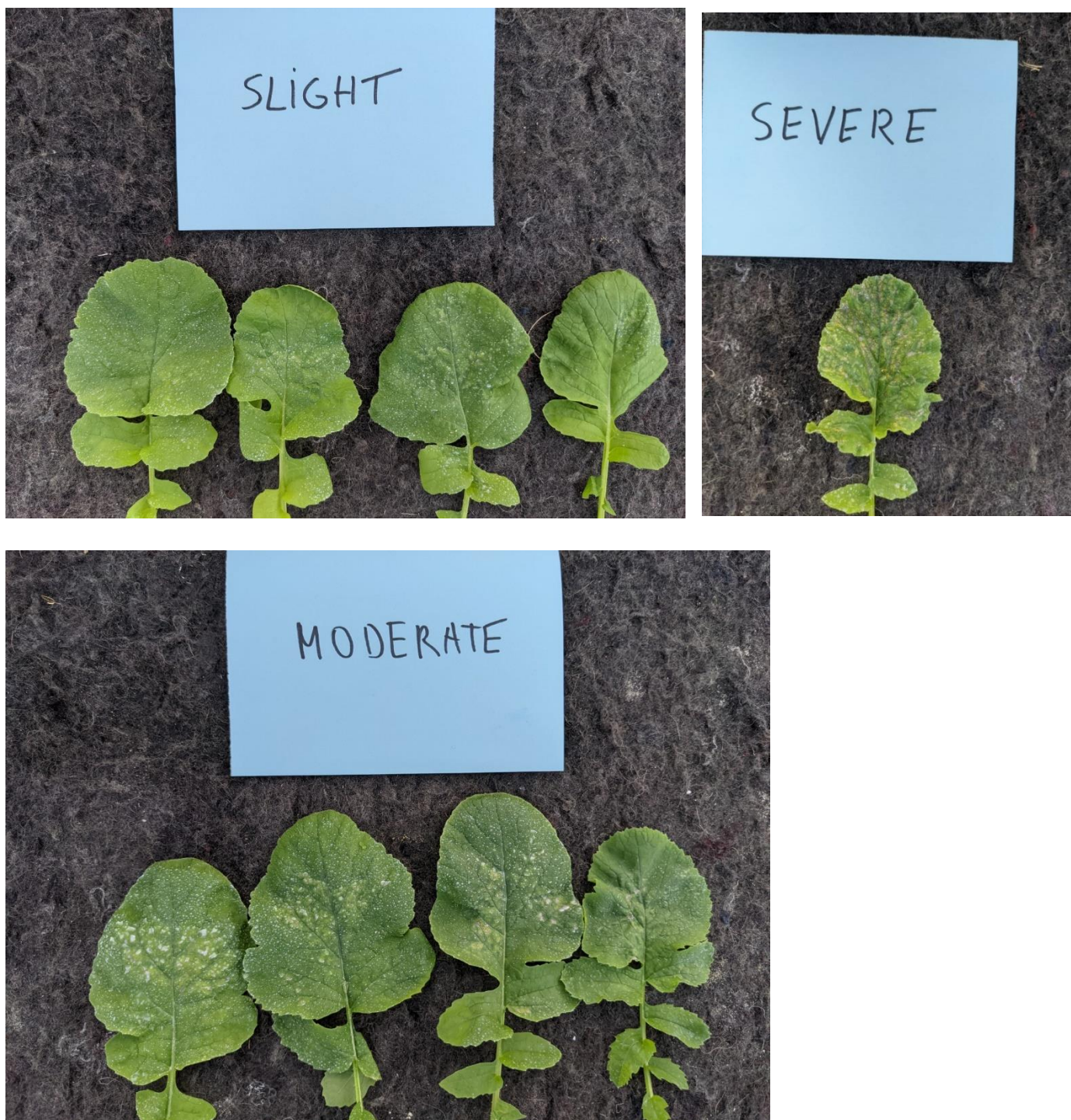
Date/Week	Temperature °C	Standard formulation Viscosity (cP)		Comments
		Mantrac	Manliv Mn carbonate F3670	
23/02/22 Week 1	0	4399	5000	
	20	4949	5469	
	45	5209	5199	
28/02/22 Week 2	0	3829	3319	
	20	4559	4119	
	45	4639	4019	
08/03/22 Week 3	0	5049	3459	
	20	4889	4409	
	45	4619	3999	
13/03/22 Week 4	0	3419	2607	
	20	4529	3304	
	45	4779	3417	
20/02/20 Week 5	0	2890	2959	
	20	3829	3089	
	45	4799	2919	
31/12/20 Week 6	0	2917	2917	
	20	3450	3450	
	45	4500	4500	
07/01/21 Week 7	0	3309	2539	
	20	3869	2769	
	45	4199	4059	
14/01/21 Week 8	0	3019	2679	
	20	3399	2230	
	45	3209	2850	



## 7.5 Phytotoxicity assessment data sheet: QSFA 0801 issue N° 01: for R&D purposes

TRIAL CODE					DATE				
REP I	TOTAL	SLIGHT	MODERATE	SEVERE	REP II	TOTAL	SLIGHT	MODERATE	SEVERE
1					1				
2					2				
3					3				
4					4				
5					5				
6					6				
7					7				
8					8				
9					9				
10					10				
11					11				
12					12				
TRIAL CODE					DATE				
REP III	TOTAL	SLIGHT	MODERATE	SEVERE	REP IV	TOTAL	SLIGHT	MODERATE	SEVERE
1					1				
2					2				
3					3				
4					4				
5					5				
6					6				
7					7				
8					8				
9					9				
10					10				
11					11				
12					12				

## 7.6 Glasshouse safety trial visual reference categories of phytotoxicity



Radish leaves were harvested at the end of demonstrations to show the effects of phytotoxicity and categorise according to ISO 9001 procedure. The glasshouse safety trial visual reference categories of phytotoxicity are slight, severe, and moderate.