Natural Organic Compounds for Application in Organic Farming

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Abstract: Chemical fertilizers, pesticides, and fungicides are widely used in agriculture to improve crop yields. Most of the compounds used are synthetic, and their overuse causes environmental pollution and human health problems. Currently, several countries are working to reduce the use of agrochemicals. Organic agriculture is now emerging as a sustainable alternative to traditional agriculture using environmentally friendly strategies such as the application of organic fertilizers from plant and animal waste and pesticides based on plant extracts and microbials. However, the availability of commercial biopesticides and organic fertilizers is very limited because there are certain barriers to the commercialization of biological products. These barriers include small available quantities of raw materials and strict registration laws requiring toxicological tests and other studies that are expensive and time consuming. The objective of this review is to provide details about the various organic fertilizers and pesticides that do not have the same disadvantages as synthetic compounds in terms of persistence and toxicity.

1. Introduction

Modern agriculture requires good quality control to produce foods. Agrochemicals are compounds that are widely used in agriculture to control weeds, diseases or pests in crops. Their mode of operation is repulsion, prevention, mitigation or destruction of weeds and/or pests and diseases. Based on their purpose, agrochemicals can be classified into insecticides, herbicides, bactericides, fungicides, miticides, molluscicides, nematicides, wood preservatives, and rodenticides. Depending on the chemical structure of the agrochemicals, they can be classified into organochlorines, organophosphates, carbamates, chlorophenols, and synthetic pyrethroids [1]. According to the World Health Organization (WHO), agrochemicals can be classified according to their toxicity depending on the median lethal dose (LD_{50}) for rats (Table 1) [2].

Table 1. Classification of pesticides by toxicity.

WHO Class	LD$_{50}$ for Rats (mg kg^{-1} Body Weight)	
	Oral	Dermal
Ia Extremely hazardous	<5	<50
Ib Highly hazardous	5–50	50–200
II Moderately hazardous	50–2000	200–2000
III Slightly hazardous	Over 2000	Over 2000
U Unlikely to present acute hazards	5000 or higher	

The use of agrochemicals in agriculture helps increase crop yields to meet the demands of the growing human population. However, continuous and non-judicious application of agrochemicals can cause chronic health problems in humans and can destroy the environment and biodiversity [3–6]. Depending on the chemical structure, some agrochemicals are persistent in the environment and can accumulate in cattle meat, vegetables, and fruits that are eaten by humans [7–12]. In this context, numerous initiatives have emerged worldwide to decrease agrochemical use in agriculture. In Europe in particular, there is a plan to reduce the use of agrochemicals by approximately 50% by 2025 [13,14]. As mentioned previously, synthetic fertilizers are used to meet the growing demands of the world's population. For example, in China, there has been overuse of synthetic fertilizers, causing environmental pollution. Hence, the central government of China launched the 'Action Plan for the Zero Increase of Fertilizer Use' (APZIFU) in 2015 to stop the overuse of synthetic fertilizers by 2020 [15–17].

Organic agriculture can be described as a form of agriculture that uses sustainable natural resources and strategies such as the application of biofertilizers, biological pest control, and crop rotation. Thus, organic farmers use natural pesticides and fertilizers, which differs from traditional agriculture using synthetic fertilizers, pesticides, and growth regulators to improve crop yields and hormones and antibiotics to increase meat and milk production in animals [18].

Considering the problems caused to the environment and human health by the overuse of synthetic agrochemicals, we present some alternatives involving sustainable and ecofriendly materials, some of which are readily available.

2. Organic Matter Fertilizers

The enormous amounts of chemical fertilizers applied to increase crop production has polluted the water, soil, and air at a large scale. In turn, this has increased consumers' mistrust concerning the quality and safety of food production [19]. Organic farming has been promoted to restore soil health and fertility status through the addition of organic matter. This is a common practice among farmers because it improves physical, chemical, and biological soil properties, in addition to supplying plants with nutrients [20]. Farmers need to return to traditional methods using crop residues and animal waste such as manure.

Some of the sources of organic manure are provided below:

2.1. Crop Residues

Crop residues are materials (non-photosynthetic plants) left on cultivated soils after crops have been harvested. They are considered an effective measure against erosion because they can improve soil structure, increase the soil organic matter content, reduce evaporation, and fix CO_2 in the soil. Moreover, they can be used in the production of biofuel [21,22].

The usual practices of crop management include (1) disposal in landfills and (2) the incineration of these residues under minimally controlled conditions, which aggravates air pollution, in terms of increasing the emissions of particulate material, as well as increasing CO_2 emissions [23,24].

An improvement to this practice corresponds to the use of this biomass to generate energy in a sustainable way [24,25].

Moreover, the incorporation of these residues, as green manure, can provide nitrogen to the soil, through biological nitrogen fixation, increasing the supply of N to subsequent crops, allowing the reduction of chemical fertilizer applications [26,27]. In general, most used green manure comes from legumes, although its exclusive use is not very advantageous because it provides a short period of supply of N due to its rapid decomposition (3–4 weeks), so it is not very suitable for application to crops that have a very long crop cycle [28]. In this sense, the effect of the use of green manure from legumes and non-legumes, independently and in combination, has been studied to improve the yield of various crops [27,29–31]. In this way, the incorporation of green manure improves the chemical, biochemical, and microbiological characteristics of the soil [27,32]. Considerable research has been done regarding the improvement in bacterial communities of soils undergoing treatment with green manure, finding that its application increased the diversity of the bacteria during decomposition [27,33–35]. On the other hand, the use of certain green manures has allowed the control of weeds and nematodes, without affecting the crop yield, allowing these fertilizers to be used as biofumigants [36–39].

2.2. Animal Manure

Animal manure is used to fertilize crops and grasslands, leading to a relevant reduction in the use of N fertilizer. The availability of animal wastes is projected to rise in future decades, specifically in developing countries [40,41]. The numerous organic manures of animal origin include bird manure (specifically poultry manure), bovine manure, sheep manure, and pig manure, among others. The availability and use of such manures for crop production depend on the geographical area, manure price, extent of manure production, and management [42–44]. Marta et al. [45] studied the influence of the application of animal manures in reducing the toxicity of soils contaminated with heavy metals, finding that their application corresponds to a good alternative of phytoremediation.

2.2.1. Bird Manure

In bird manure (or bird guano), uric acid is the main source of nitrogen. This compound is an important, inexpensive, commercially available type of fertilizer [46]. For instance, seabird guano has been extensively studied because soils (ornithogenic soils) that receive it exhibit high concentrations of nutrients such as NO_3^- and NH_4^+, and the biota that live in and around these soils is supported largely or wholly by seabird excrement. Seabird guano normally contains 8–21% nitrogen by mass, primarily in the form of uric acid (~80%), protein (~10%), ammonia (~7%), and nitrate (~0.5%) [47]. However, the application of untreated manure could trigger a risk of vegetable contamination since manure may harbor bacteria such as *Escherichia coli*, *Listeria monocytogenes*, *Salmonella spp.*, and other pathogens that might taint soil, irrigation water, and plants [48].

Poultry (chicken, *Gallus gallus domesticus*) manure or poultry litter is a very good source of nutrients that can be integrated into most fertilizer plans. The nutrient composition of poultry manure varies with the bird species, feed ratio, quantity of litter droppings, manure management procedure, and type of waste. Overall, the main components of this kind of waste are nitrogen, phosphorous, and potassium [49].

2.2.2. Bovine Manure

Bovine manure, or cattle manure, has been used as a fertilizer supplement in agriculture, specifically in horticulture. Studies have revealed that the average characteristics of cattle manure expressed as percentages of dry matter are as follows: 1.034 ± 0.029 for density, 2.40 ± 1.84 for ammonia N, 2.04 ± 0.86 for organic N, 41.51 ± 5.53 for C, and 11.74 ± 4.73 for the C/N ratio [50]. Compared to mineral N fertilizers, bovine manure (farmyard manure and slurry) is slightly less effective for crops, but it has been determined that it increases soil organic carbon (SOC) and soil N, helping long-term soil fertility maintenance [51].

2.2.3. Sheep Manure

In Mediterranean countries, sheep manure is habitually utilized as an organic fertilization source. Studies have demonstrated that recycling this type of organic matter in poor soils, which occur extensively in these territories, can improve the soil structure and, in the long term, increase fertility [52, 53]. In this sense, sheep manure is a promising amendment for improving soil structure, microbial activity, water use efficiency, and crop performance, but remains poorly explored due to the lack of availability [54]. Elouear et al. [55] studied the application of sheep manure to contaminated soil. They found that sheep manure decreased Cd, Pb, and Zn concentrations in plant tissues (alfalfa, *Medicago sativa* L.). In this way, sheep manure was effective in the immobilization of metals in soil contaminated by mine activities. This amendment could reduce metal toxicity and metal uptake by plants with a low risk of leaching into groundwater.

One of the main disadvantages of animal manures is the increased volume of organic material production. Commercial poultry production can encounter complications in the disposal of waste. One solution is to recycle waste through the age-old process of composting as a traditional field fertilizer. Nevertheless, in some regions, this has triggered environmental problems such as ground water pollution by phosphorus [56]. Another factor to consider is the content of heavy metals in cattle manure, which could come from animal feed. These heavy metals in soil, water, and plants can bioaccumulate in the environment and subsequently in humans [50].

2.2.4. Pig Manure

Pork farms produce a large amount of pig manure. It is estimated that each pig can produce about 28 kg of manure per day. Pig manure is rich in inorganic and organic nutrients and possesses similar properties to mineral fertilizers. Its chemical composition depends on the conditions of the farm, the age and type of the animals, and their diet and condition [57]. However, effects of long-term pig manure applications on denitrification have been intensively studied in paddy soils, showing that denitrification activities were significantly raised due to pig manure application increasing the amount of total organic carbon and microbial biomass carbon. Some studies reported that organic matter provided favorable micro-sites for denitrification, and applications of pig manure could generate favorable conditions for denitrification [58]. Due to the nutrient imbalance (N:P ratio of this manure is <4:1), eutrophication processes can occur in water courses due to the loss of P from the soils because of leaching and runoff processes. For this reason, the use of this waste is recommended in croplands with P deficits [59]. On the other hand, prolonged application of pig manure significantly increases the concentration of antibiotics and the abundance of antibiotic resistance genes (ARGs) [58].

2.2.5. Urine

Urine contains all the macronutrients (N, P, and K) required for fertilizer production [60]. Human urine is a valuable fertilizer, although its value is underestimated, and it is underutilized [61]. This waste product is a rich source of diverse nutrients that has been utilized since ancestral times to increase the development of plants, particularly leafy vegetables, and is commonly obtainable at no cost [62]. The reuse of human urine is receiving attention as an alternative fertilizer because it contains nutrients such as nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg). Approximately 75–90% of N is excreted as urea and the remainder is in the form of either ammonium or creatinine. The urea/ammonium ratios in urine and synthetic fertilizers are comparable; that is, 90–100% of N in urine is in the form of either urea or ammonium, as demonstrated in fertilization assays [63]. Pradhan et al. [64] reported that urine has been successfully used to fertilize cucumbers, corn, cabbage, wheat, and tomatoes. Overall, the amount of N in wood ash is low/none; consequently, ash could represent a suitable supplement to urine fertilizer. In addition, Pradhan et al. [63] used human urine as a fertilizer in cabbage cultivation in comparison with industrial fertilizer. The results showed that urine achieved the same fertilizer value as industrial fertilizers. This study demonstrated

that insect damage was lower in urine-fertilized-associated soil than in industrial-fertilized plots but was more extensive than in nonfertilized plots. On the other hand, Pradhan et al. [65] revealed that the use of urine can increase the yield of red beets. Furthermore, the microbial and chemical qualities were comparable to those in mineral-fertilized products.

2.3. Compost, Vermicompost, and Biochar

One of the most important management strategies for solid organic waste is composting, which is a process that involves the biooxidative decomposition of organic matter [66–68]. Composting can produce high-quality products that are effective for application in agriculture, due to its cost-effectiveness, easy operation, and environmental friendliness [69,70]. In this sense, the composting of cattle manure has a variety of agricultural benefits, such as decreasing the mass and water content, inhibiting pathogens, killing weed seeds, and producing stable and spreadable organic matter [71]. For example, in Spain, farmers use a substitute approach for cattle manure management through composting on intensive livestock farms to obtain a healthier useful agricultural product [72].

The quality of the compost depends on factors such as the presence of inappropriate materials, such as glass or plastic, which can affect the concentration of heavy metals, electrical conductivity, and decomposition rate, among others [73]. Within the composting process, greenhouse gases (GHGs) are produced, such as nitrous oxide (N_2O), methane (CH_4), and ammonia (NH_3) [74]. Although the generation of these GHGs is lower than when using livestock manure to improve the yield of certain crops [75], GHG emissions from compost can be reduced using chemical additives (salts of PO_4^{3-}, Mg^{2+}, superphosphate, gypsum, etc.) that promote chemical reactions in the compost substrate in relation to the renewal processes of N; physical additives (biochar, zeolites, bentonites, sand, soil, etc.), which adsorb or change the physical factors of the compost; and microbials (ammonia-oxidizing bacteria, etc.), i.e., microorganisms that affect the renewal processes of N [74].

Another composting strategy corresponds to vermicomposting wherein certain species of earthworms are used to accelerate the process of waste degradation and produce manure. The use of epigean earthworms is preferred, which are associated with the accumulation of organic matter on the soil surface and have been intensively cultivated in captivity. *Eisenia fetida*, *E. fetida Andrei*, and *Lumbricus rubellus* have been found to be efficient in this regard [76]. This technique is faster than composting because the organic material passes through the earthworm gut. The worm manure is rich in microbial activity and plant-growth regulators. Furthermore, this product is fortified with pest-repellent elements. The vermicomposts are rich in nitrogen and phosphorus, with high levels of humic acid, and excellent stability and maturity. Thus, vermicomposting can biodegrade organic matter and recover valuable nutrients from diverse organic wastes [77,78]. In addition, it serves to reduce the concentrations and availability of heavy metals [79–83]. On the other hand, certain organic pollutants can be accumulated in the body of worms, so their content in vermicompost is significantly reduced [83]. In recent times, vermicomposting has been used to attenuate the release of ARG and human pathogenic bacteria (HPB), present in organic wastes, such as excess activated sludge (EAS) and some animal manures. Huang et al. [84] found that worms decreased the abundance of ARG and HPB, but sludge vermicompost was still ARG and HPB enriched. Cui et al. [85] studied the influence of vermicomposting on the ARG present in EAS, finding that its attenuation varied between 31%–99%, depending on the type of tested genes. On the other hand, the presence of certain pollutants, such as tetracyclines in low concentrations, can improve the growth of earthworms, increasing the rate of decomposition of organic matter, enhancing the level of humification in the vermicompost [86].

Another strategy of organic waste management corresponds to biochar, produced by the thermal decomposition (300–1000 °C) of biomass, which improves the low fertility of soils, increases crop yields, relieves plant stress, immobilizes heavy metals, and sequesters carbon to mitigate global warming [87–89]. Besides, biochar can retain NH_3, NH_4^+, and NO_3^- present in animal manure [90]. On the other hand, it is a method to immobilize persistent organic pollutants and pesticides [89,91]. In this sense, one way to mitigate the application of ARG corresponds to the transformation of pig

manure into biochar, which when used as an amendment, presented ARG levels much lower than the amendments of composted pig manure [92]. Other types of biochar used as an amendment are effective in reducing antibiotic abundances, ARG, and HPB, ensuring the safety of vegetables, protecting human health [93].

3. Bio-Pesticides

The continuous application of insecticides has caused some insects to develop resistance. Besides, the continuous use of synthetic insecticides causes ecological disturbance by affecting non-targeted insects. Furthermore, prolonged indoor spraying of insecticides may cause respiratory problems for inhabitants, particularly children [94].

3.1. Plant Essential Oils

As an alternative to synthetic pesticides, the use of plant essential oils has increased. There are several examples of plant essential oils being used as pesticides (see Table 2).

Table 2. Some typical compounds extracted from plants used as pesticides.

Name of Organic Pesticide	LD$_{50}$ for Rats (mg kg^{-1} Body Weight)	WHO Class [2]	Plant Genera	Reference
Allicin	60	II	*Allium*	[95]
Allyl sulfide	2980	III	*Allium*	[96]
Carvacrol	810	II	*Anabasis, Carum, Cinnamomum, Mentha, Ocimum, Origanum, Thymus, Zea*	[95]
Cinnamaldehyde	1160 (guinea pig)	II	*Cassia, Cinnamomum, Lavendula, Pogostemon*	[95]
Citronellal	5000	U	*Citrus, Corymbia, Cymbopogon*	[97]
Citral (Geranial + Neral)	4960	III	*Citrus, Cymbopogon, Eucalyptus, Lavendula, Lippia, Ocinum, Piper, Thymus, Zingiber*	[98]
Eucalyptol (1,8-Cineole)	2480	III	*Alpina, Artemisia, Blumea, Cinnamomum, Curcuma, Eucalyptus, Eugenia, Laurus, Lavendula, Lippia, Mentha, Ocinum, Piper, Psidium, Rosmarinus, Salvia, Syzygium, Zingiber*	[95,98]
Eugenol	2680	III	*Acorus, Ageratum, Alpina, Cinnamomum, Citrus, Cymbopogon, Eugenia, Lantana, Laurus, Lavendula, Myristica, Nicotiana, Ocimum, Pimpinella, Piper, Pogostemon, Syzygium*	[98]
Limonene	4600 (lowest published lethal dose)	III	*Anethum, Apium, Carum, Chenopodium, Cinnamomum, Citrus, Coriandrum, Croton, Cuminum, Cymbopogon, Eucalyptus, Hyptis, Lavendula, Lippia, Mentha, Myristica, Nicotiana, Ocimum, Origanum, Pimpinella, Piper, Rosmarinus, Salvia, Syzygium, Valeriana*	[95]
Linalool	2790	III	*Artemisia, Cinnamomum, Citrus, Coriandrum, Cymbopogon, Eucalyptus, Laurus, Lavendula, Mentha, Myristica, Ocimum, Origanum, Rosmarinus, Salvia, Syzygium, Thymus, Zingiber*	[95]

Table 2. *Cont.*

Name of Organic Pesticide	LD$_{50}$ for Rats (mg kg^{-1} Body Weight)	WHO Class [2]	Plant Genera	Reference
Menthol	3180	III	*Mentha, Thymus*	[95]
Nicotine	1 (lowest published lethal dose, human)	Ia	*Erythroxylum, Nicotiana*	[95]
Pulegone	150 (mouse, intraperitoneal)	II	*Bystropogon, Mentha, Origanum*	[95]
Thymol	980 (mouse = 1800)	II	*Anabasis, Carum, Lavendu/a, Ocimum, Origanum, Thymus*	[95,98]
Zingiberene	5000 (as ginger oil, with 29% α-Zingiberene)	U	*Zingiber*	[99,100]

Plant essential oils are obtained from the nonwoody parts of plants, specifically the foliage. The most used extraction methods are steam trapping or hydrodistillation [101,102].

The predominant functional groups in these compounds are alcohols, aldehydes, ketones, and simple hydrocarbons. Most essential oils are complex natural mixtures that can contain between 20 and 60 components. They are largely characterized by two or three components present at high concentrations (20% to 70%) that generally determine the biological properties of essential oils. The major components present at high concentrations are monoterpenes (C$_{10}$) and sesquiterpenes (C$_{15}$) and some related phenols (cinnamates and phenylpropenes). Within the predominant group, the monoterpenes are cyclic, saturated or unsaturated, including aromatic structures as well as bicyclic and acyclic structures [98,103].

Pesticides derived from plants volatilize quickly and show short persistence times and low vertebrate toxicity, so they present less risk to the environment and animals [98,101,104]. For example, Isman and Machial [98] extensively reviewed the use of pesticides based on plant essential oils. The essential oils with the highest reported bioactivity against insects and other pests are cinnamon oil (cinnamaldehyde), clove oil (eugenol), lemongrass oil (citronellal, citral), mint oil (menthol, pulegone), oregano oil (carvacrol), thyme oil (thymol, carvacrol), and rosemary oil (eucalyptol).

Batish et al. [101] extensively reviewed the characteristics of the essential oil produced from *Eucalyptus*, finding that 1,8-cineole is the most important component conferring its pesticide properties. *Eucalyptus* oil has been proven to present insecticidal, antifungal, antimicrobial, herbicidal, acaricidal, and nematicidal properties, as well as low toxicity.

Brahmi et al. [105] studied the contact and fumigant toxicities of essential oils from *Mentha pulegium* L. and *Mentha rotundifolia* (L.) against *Rhyzopertha dominica* (F.). They found that contact toxicity resulted in the mortality of *R. dominica* after 96 h (2.0 μL/mL) compared with untreated controls. The stronger activity shown by *M. rotundifolia* essential oil is due to its primary components of carvone and 1,8-cineole. Fumigant activity demonstrated that *M. rotundifolia* essential oil was the more toxic. After 96 h of treatment using a dose of 2.0 μL/mL, *M. rotundifolia* essential oil showed 44.3% fumigant activity compared with *M. pulegium* essential oil (39.2%).

Mansour et al. compared the toxicity of essential oils extracted from *A. cepa, C. cyminum, Matricaria camomilla, O. basilicum, O. vulgare, Pelargonium radula,* and *Petroselinum sativum* with the toxicity of commercial insecticides (Carbosulfan, Fenitrothion, Fenvalerate, and Methomyl) against *Schistocerca gregaria*. It was found that among these essential oils, *A. cepa* oil was the most toxic (LD$_{50}$ = 1.11 mg/L and LC$_{90}$ = 1.42 mg/L), followed by that of *P. sativum* (LD$_{50}$ = 1.34 mg/L and LC$_{90}$ = 1.61 mg/L). The oils from *C. cyminum, P. radula, M. chamomilla, O. basilicum,* and *O. vulgare* presented LD$_{50}$ values that ranged between 1.54–1.59 mg/L and LD$_{90}$ values between 1.84–1.91 mg/L. In some of these essential oils, the presence of biologically active compounds such as carvacrol, caryophyllene, p-cymene, linalool, and thymol was verified by GC/MS. In the case of insecticides, fenitrothion was the most toxic (LD$_{50}$ = 0.33 mg/L), followed by carbosulfan and

methomyl (LD$_{50}$ = 1.2 mg/L), while fenvarelate was the least toxic (LD$_{50}$ = 1.48 mg/L). Surprisingly, it was observed that the oil from *A. cepa* was more toxic than methomyl. Finally, combinations of essential oils, or essential oils and insecticides or mixtures of insecticides were tested, and three types of interactions were revealed: potentiation, addition, and antagonism [106].

Pavela et al. [107] studied the efficacy of essential oils obtained from 18 aromatic plant species against *Tetranychus urticae* applied via fumigation at a concentration of 15 μL/L. Essential oils from *Ocinum basilicum* (LC$_{50}$ = 0.6 μL/L), *M. spicata* (LC$_{50}$ = 1.3 μL/L), and *O. compactum* (LC$_{50}$ = 12.5 μL/L) showed the highest acute toxicity in *T. urticae* females. These essential oils presented fertility inhibition of 80%. In addition, the fumes of the essential oils obtained from *M. arvensis*, *M. pulegium*, and *O. majorana* inhibited oviposition by more than 80%. Other essential oils from *C. aurantifolia*, *Lavandula latifolia*, *P. graveolens*, and *Thuja occidentalis* inhibited oviposition by between 70% and 80%. The ovicidal effect presented a high efficiency (over 50%) when essential oils from *M. spicata*, *M. arvensis*, and *M. pulegium* were applied.

Qasem and Abu-Blan [108] studied the effect of the application of extracts from common weeds in the treatment of pathogenic fungi in plants (*Alternaria solani*, *Helminthosporium sativum*, *Rhizoctonia solani*), showing that extracts of nettle-leaved goosefoot (*C. murale*), London rocket (*Sisymbrium irio*), and sickleweed (*Falcaria vulgaris*) severely inhibited the growth of *A. solani*. Moreover, the extracts obtained from scarlet pimpernel (*Anagallis arvensis*), hawksbeard (*Crepis aspera*), sowthistle (*Sonchus oleraceus*), and Syrian thistle (*Notobasis syriaca*) were very toxic to *H. sativum*, while the Persian buttercup (*Ranunculus asiaticus*) extract was the most toxic to all three species of fungus.

Thomidis and Filotheou [109] used essential oils from *O. basilicum*, *O. vulgare*, *R. officinalis*, *R. officinalis* 'Prostrates', and *S. officinalis* against *Pilidiella granati* (a plant pathogenic fungus). The in vivo experiments showed that only the essential oils of *O. basilicum* and *O. vulgare* presented effectiveness against the fungus. The analysis of these essential oils revealed many compounds, including carvacrol, eucalyptol, linalool, and thymol.

Toledo et al. [110] evaluated the effects of essential oil from Negramina (*Siparuna guianensis*) plants against the green peach aphid *Myzus persicae*. They found that this essential oil caused mortality in *M. persicae* (LC$_{95}$ = 1.0 mg/cm^2) and presented repelling action at low concentrations (0.14 mg/cm^2). Besides, the application of Negramina essential oil did not affect *Coleomegilla maculata* and *Eriophis connexa*, two natural enemies of *M. persicae*. The major compounds found in this essential oil were β-myrcene and 2-undocanone. In this way, Negramina essential oil has potential to be used in integrated pest control programs.

Xin et al. [111] studied the effects of the application of a *Sophora flavescens* extract, available commercially in China as *S. flavescens* alkaloids (SFAs) and found that its application increased the yield of tomato plants and improved the taste of the fruit. Moreover, it served as an insecticide against caterpillars and aphids.

Zapata et al. [112] used essential oil obtained from the leaves of *Laurelia sempervirens* against greenhouse whitefly (*Trialeurodes vaporariorum*) and found that it is a highly toxic and powerful fumigant that acts very rapidly. Moreover, it is also toxic against *Encarsia formosa*, a pathogen that is used commercially to control whitefly, so the application of this essential oil is not compatible with whitefly control by *E. formosa*.

Toxicity to Animals

Considering how beneficial essential oils may be and their wide use in the flavoring, preparation, and preservation of foods, fragrances, and aromatherapy products [113,114], they can be expected to be safe for mammals. In this context, most essential oils exhibit a low acute toxicity of approximately 2 g/kg for dermal or oral application [115].

On the other hand, it has been found that some essential oils, such as those from *S. sclarea* and *Melaleuca quinquenervia*, cause the secretion of estrogen, which can induce estrogen-dependent cancer. Pulegone, which is found in the essential oils of mint species, can cause cancer and has been shown

to be very toxic to rats (LD$_{50}$ = 150 mg/kg). Methyleugenol is a carcinogenic compound present in *Laurus nobilis* and *M. leucadendron* essential oils. D-Limonene, a constituent of *Citrus* essential oils, is carcinogenic in male rats. Estragole, a compound present in *A. dracunculus* and *O. basilicum* essential oils, has shown carcinogenic properties in rats and mice. Other oils may contain photosensitizing molecules such as cyanin, flavins, hydrocarbons and porphyrins, which can cause skin disorders, such as cancer or skin erythema. Within this group, compounds such as psoralen, a photosensitizing molecule present in the essential oil of *Citrus bergamia*, can induce skin cancer after forming covalent DNA adducts under solar light or ultraviolet A [98,103].

3.2. Homemade Pesticides

Most biological pesticides can be made at home. They are based on compound properties that can affect insects or pathogens by preventing their approach to a plant or acting as an irritant that repels pests and diseases. There is limited literature regarding the specific preparation of pesticides based on natural products. In this context, we present some household preparations for traditionally used pesticides.

3.2.1. Ginger

Ginger (*Z. officinale*) has been traditionally used in agriculture for the treatment and/or prevention of tomato moth (*Tuta absoluta*) infestation. A preparation of the alpha-zingiberene compound for use against *T. absoluta* from the essential oil of ginger has been patented [116]. It is also possible to apply ginger extracts to other plants such as potato (*Solanum tuberosum*) and aubergine (*S. melongena*). In addition, ginger has been used against fungal pathogens such as *Botryodiplodia theobromae*, *Colletotrichum camelliae*, *Curvularia eragrostidis*, *Fusarium udum*, *Pestalotiopsis theae*, and *Sclerotinia sclerotiorum* because of its zingiberene content [117]. Ukeh et al. [118] investigated the repellent activity of ginger and alligator pepper (*Aframomum melegueta*) against maize weevil (*Sitophilus zeamais*), finding that multi-component blends of these essential oils could be used as control agents in the pest control of stored products.

3.2.2. Nettle Tea

Nettle (*Urtica dioica* L.) is a perennial plant belonging to the Urticaceae family. It blooms in summer, and its leaves and stems have trichomes containing a fluid that causes blisters on the skin. The compounds responsible for this irritant action are acetylcholine, serotonin, and histamines. This plant is considered a weed in intensive agriculture [119]. However, since ancient times, nettle has been used in medicine for the treatment of rheumatic conditions and urinary tract infections and as an analgesic and anti-inflammatory. In addition, nettle is used for its histamine desensitization, anti-platelet aggregation, antioxidant, and immunomodulatory activities, among many other medicinal uses [119–121]. Moreover, it has been used in the production of textile fibers and biomass [119].

Nettle tea is a traditional preparation of fresh nettle in a proportion of 20% *w/v* with water that is placed in a semicovered container that allows air flow and that is left to ferment for 10 to 15 days with periodic stirring of the mixture. At the end of the period, the nettle tea should be filtered and kept in a cool and dark place. It is recommended to apply nettle tea every 10 days in the afternoon on the leaves of plants with a sprinkler at doses between 15% *v/v* for fruit vegetables and 20% *v/v* for leafy vegetables. This pesticide is effective in controlling aphids and mites, and the leaf waste can be used as fertilizer [122].

3.2.3. Garlic

Garlic (*A. sativum*) is used in food preparation. It has also been used as a medicinal plant for over 4000 years for its antiseptic, antiinflammatory, antioxidant, cardioprotective, and anticancer activities. The major organosulfur compounds responsible for the antimicrobial activity of garlic are ajoenes, allicin, alliin, allyl sulfide, and 1,2-vinyldithiin [123–125].

For example, Gong et al. [126] studied the effect of 2% raw garlic straw extracts against root-knot nematodes (*Meloidogyne incognita*) in tomato, resulting in the inhibition of the nematodes and increasing the tomato yield. Jess et al. [127] investigated the potential use of garlic oil to control *Megaselia halterata* (Diptera: Phoridae) in commercial mushroom production, finding that garlic solutions at low level concentrations (0.1–20%) successfully repelled adult female *M. halterata*.

A typical recipe for a garlic solution is to use 25 g of chopped garlic in 10 L of water. This solution is applied to the soil and plants and is effective against fungi, bacteria, and insects (mites, aphids, Lepidoptera larvae, and small bedbugs) [122].

3.2.4. Onion

Onion (*A. cepa*) has been used in food and for the treatment of many diseases. Similar to garlic, onions contain organosulfur compounds responsible for their antimicrobial activity [123]. Mfarrej and Rara studied different essential oils as natural pesticides. They found that mixing 5 mL onion oil, 75 mL vinegar, and 75 mL water was an effective repellent for grasshoppers, bees, flies, spiders, and ants, with a degradation time of 1 h 30 min [128].

To make a liquid pesticide based on onion, macerate 100 g of onion, add 10 L of warm water, and apply the mixture to the soil or plant. In addition, a fermented onion slurry can be made using 500 g of bulb, stalk, or ground plant material in 10 L of water that is allowed to ferment for 10 days, stirring frequently. It should be diluted in 10 parts of water before use. These pesticides made with onions are not recommended for use on peas and small beans because they stop their growth [122].

Garlic and onion can be used together to produce an infusion or fermented slurry. For the preparation of an infusion of garlic and onion, add 75 g of chopped garlic and onion to 10 L of warm water, and allow the mixture to soak as tea. Subsequently, the preparation is applied to the plants and soil and is effective against mites, aphids, and fungal diseases. A fermented slurry of garlic and onion is prepared by fermenting 500 g of bulb, husk, and stalk tissues of onions and fresh garlic in 10 L of water with stirring for 1 or 2 weeks. The product is diluted in 10 parts of water and is applied to the soil around plants and trees, protecting them against fungal diseases and insects, especially carrot fly (*Chamaepsila rosae*). If used in conjunction with nettles, the bimaculate spider (*T. urticae*) can be controlled on strawberries [129].

3.2.5. Nicotine

Nicotine is the main psychoactive ingredient in tobacco leaves and is the basic element of cigarettes responsible for their psychopharmacological effects [130]. It has been used as a pesticide since the 15th century [131]. Nicotine is a nonsystemic insecticide that binds to the cholinergic acetylcholine nicotinic receptor (nAch) in the nerve cells of insects, producing continuous firing of this neuroreceptor [132].

Nicotine can be obtained from powdered tobacco leaves, extracts from tobacco plants, waste from the tobacco industry, aqueous extracts of cigarette butts, and can also be synthesized [132–135].

Reuben et al. [133] studied the effect of the application of tobacco leaf powder snuff at 3% *w/w* against cowpea weevil (*Callosobruchus maculatus* L.) on stored cowpea (*Vigna unguiculata* L.) grains, finding that this treatment protected the stored grains better than other tested botanicals.

Dieng et al. [135] studied the effect of using a pesticide solution manufactured using cigarette butts against *Aedes aegypti* and observed insecticidal activity against its larvae.

Leaves dried in the shade under diffuse light should be used to make a tobacco (*Nicotiana tabacum* L.)-based powder. The finely ground powder is sprinkled on the grains to be protected and can be used to produce dilutions with calcium carbonate as required [133,136]. To prepare a liquid insecticide based on nicotine, it is necessary to add five cigarette butts to half liter of water for 24 h. The obtained liquid is subsequently filtered and applied to plants [137].

3.2.6. Clove

Clove (*S. aromaticum*) is a native spice from Indonesia that is very rich in flavonoids, hydroxycinnamic acids, hydroxybenzoic acids, and hydroxyphenyl propene and has a high content of eugenol. The use of its essential oil in agriculture for controlling *Reticulitermes speratus*, *Leptotrombidium imphalu*, *A. aegypti*, *Anopheles dirus*, *Solenopsis invicta*, *Vespula pensylvanica*, and *Polistes dominulus* has been reported [138]. Essential clove oil can be obtained by steam distillation. Once clove oil is obtained, a few drops are mixed in a cup of water, and the mixture is sprayed on plants. A formulation containing between 5% and 10% clove essential oil is very effective against the agricultural pests mentioned above [138]. Plata-Rueda et al. [139] studied the effect of terpenoid constituents of clove essential oil against granary weevil (*S. granarius* L.). They determined that the primary compounds in clove essential oil were eugenol (27.1%), caryophyllene (24.5%), caryophyllene oxide (18.3%), 2-propenoic acid (12.2%), α-humulene (10.8%), γ-cadinene (5.01%), and humulene oxide (4.84%). The application of clove essential oil and terpenoids (eugenol, caryophyllene oxide, α-humulene) showed marked toxicity against *S. granarius*. Insects decreased their breathing rate and reduced their mobility on treated surfaces.

3.2.7. Rue

Plants belonging to the *Rutaceae* family have long been used in African and American cultures for medicinal and esoteric purposes. *Ruta graveolens* has been extensively used by the Mapuche culture for the removal of bad spirits, whereas *R. bracteosa* is used for the treatment of stomach disorders and seizures [140]. *R. graveolens* has been extensively used in Mexico in infusions for the empirical treatment of stomach ailments, wounds, snake bites, fever, headaches, cough, nervousness, flu, inflammation, toothaches, earaches, and body aches [141]. *R. chalepensis* is commonly known as fringed rue. Its extracts and essential oil show biological activities associated with abortive, anthelmintic, emnagogic, and spasmolytic properties and depressant activity in the central nervous system. In addition, it has been used as a repellent and an insecticide [142].

A decoction of rue can be made by mixing 100 g of leaves and fresh rue flowers in 1 L of water and boiling the mixture for 5 to 10 min. The solution is then filtered and diluted 1:5 with water. It is applied directly to plants and serves to control aphids and mites [129].

3.3. Effective Use of Fungi in Agriculture

Fungi are a widely diverse group with a high species number and numerous unidentified species. Nowadays, fungi with an agricultural use increase day-by-day and have innumerable emerging applications with an optimal result to control pests and environmental safety of crop production. Entomopathogenic fungi present a myco-biological option to control pests, where the fungi colonize the insect body in different development stages (i.e., eggs, larvae, nymphs or adults) [143,144]. Entomopathogens have several advantages compared with traditional agrochemicals, i.e., lower costs, increased efficiency, safety for beneficial organisms (i.e., pollinators, aqueous fauna, birds), decreased chemical residues in the environment and changes in the agricultural practices the help to preserve the biodiversity of the land [145–148].

The effectiveness of fungal use varies by the pests species and at least two conditions: (1) fungi applied as an aqueous solution of conidia have a short shelf life and are sensitive to UV radiation; (2) 2–3 weeks is required to kill the pests; (3) the environment has to be free of fungicide (for 2 weeks); (4) the growth of conidia requires a specific relative humidity; and (5) there is a shortage of commercial preparations with entomopathogenic fungi [149]. The formulations to achieve effective applications are innovative to ensure the conidia or microorganisms are intact or alive; if the fungi die, it is impossible control the pest or disease.

The most important genera of entomopathogenic fungi are *Beauveria*, *Verticillium*, *Metarhizium*, *Nomuraea*, *Paecilomyces*, and *Hirsutella*. *Beauveria* has four species that are used to kill insects; this fungus

is grown in soil around the world and is a pathogen of several insect species [149]. Pests infected with *Beauveria* were covered with a white mycelium and emerged through a cut in the exoskeleton section to attack a wide quantity of species such as termites, whitefly, malaria mosquitoes, coleoptera or beetle, etc. [150,151].

Verticillium genera have two important species, *V. lecanii* and *V. chlamydosporium*. *V. lecanii* controls nymphs and adults of different aphids such as *M. persicae*, *Aphis gossypii*, *Brevicoryne brassicae*, and *T. vaporariorum*; a variety of strains have been tested to infect aphids, including the effects of additives to improve virulence [152,153].

The genus *Metarhizium* is the most studied with three entomopathogenic species (*M. anisopliae*, *M. album,* and *M. flavoviride*). *M. anisopliae* is effective to control the green beetle (*Hylamorpha elegans*), a native Chilean species but is a pest on many crops (cereals, fruits, and fodder); in wheat seedlings, losses of 80% have been reported [154,155].

Paecilomyces fungi have two important species and both are effective to kill nematodes. *P. fumosereus* causes the sick "yellow muscardine" in whitefly (*Bemisia sp.* and *Trialeurodes sp.*), the major pest in greenhouses [149].

The future in myco-control emerged as a novelty strategy to reduce pests in crops with less effect on the environment; integrated pest management (IPM) involves biological options as a solution for sustainable agriculture.

4. Commercialization

At present, there are few commercial biopesticides based on essential oils. Some examples are presented in Table 3.

Table 3. Some organic commercial pesticides based on essential oils.

Commercial Name	Active Ingredients	Pest or Disease Control
Ant Out ®	Clove oil (20%), Cottonseed oil (40%)	Ants, spiders, silverfish, crickets
BioRepel ™	Garlic oil (10%)	Aphids, leaf hoppers, thrips, white flies
Bonide ® All Seasons Horticultural & Dormant Spray Oil	Mineral oil containing petroleum distillates	Aphids, bean thrips beet leafhopper, black scale, brown almond mite, California laurel aphid, caterpillar eggs, citrus red scale, citrus yellow scale, coconut mealybug, codling moth, European apple sawfly, fungus gnats, grape leafroller, greenhouse whitefly, leafminer, leafroller, mealybug, mites, oleander scale, psyllids, red-banded leafroller, scale, silverleaf whitefly, spider mite, spinach leafminer, sweet potato whitefly
Bonide® Neem Oil Concentrate	Neem oil	Black spot, powdery mildew, rust, spider mites, aphids, whiteflies
Garlic Barrier ® AG+	Garlic juice (99.3%)	Ants, aphids, armadillos, armyworm, beetles, birds, caterpillar eggs, deer, grasshopper, leafhopper, leafminer, loopers, mealybug, mites, rabbits, sawflies, whitefly, wirewom
Monterey Fruit Tree Spray Plus	Pyrethrin (0.25%), Neem oil (70%)	Powdery mildew, downy mildew, rusts, leaf spots

Table 3. *Cont.*

Commercial Name	Active Ingredients	Pest or Disease Control
Organic JMS Stylet-Oil	Paraffinic oil (97.1%)	Aphids, armyworm, beet leafhopper, black scale, brown almond mite, caterpillar eggs, citrus red scale, citrus yellow scale, fall armyworm, grape leafhopper, leafhopper, leafminer, leafroller, mealybug, mites, oleander scale, omnivorous leafroller, potato leafhopper, bean jassid, powdery mildew, psyllids, red-banded leafroller, scale, silverleaf whitefly, spider mite, spinach leafminer, sweet potato whitefly.
Pest Out ®	Cottonseed oil (40%), Clove oil (20%), Garlic oil (10%)	Aphids, mites, thrips.
QL Agri ® 35	Quillaja Saponaria extract (35%)	Ectoparasite and endoparasite nematodes, control of mites and insects in different crops such as vines, citruses, tomatoes, apples, cherry trees, and walnuts.

Most commercially available organic pesticides are based on petroleum-based oils and essential oils in addition to certain inorganic salts. These salts ensure that the durability of the product will be greater than when fresh plant extracts or fermented slurries such as those described above are used. Some barriers to the commercialization of new products have been identified: (i) There are deficiencies in the quantity of available raw materials. While the cost of raw materials is low, most promising essential oils are obtained from plant species that are difficult to grow or exhibit low yields of essential oils. In addition, the physiological variability of plants at different stages of development should be considered. In this regard, it is necessary to streamline crop production and industrialize the production of essential oils to ensure adequate quality control and availability of these products in the market. Additionally, (ii) there are strict registration laws requiring toxicological tests and studies, especially in nontarget organisms. Although there has been much research on the effectiveness of biopesticides, there is no collaboration between the companies that produce these extracts at a large scale and the research centers, so the studies are very limited [101,115,156,157].

On the other hand, the development of agrochemicals based on fungal species or strains has increased due to the major attention by the organic farming community and safe food production. Initially, organic crop production faced huge obstacles due to the scarce availability of agrochemicals appropriated for this farming production. Nowadays, the market of agrochemicals for organic farming has increased considering different formulations and producers, and the bioactivity of the microorganisms is better than in the past.

Table 4 lists some formulations authorized for use in organic farming to control disease.

Table 4. Some biopesticides based on microorganisms authorized in organic farming.

Commercial Name	Active Ingredients	Pests or Disease Control
Baciforte ® SC[a]	*Bacillus subtilis* strain 55, 0.1% *w/v* (1×10^9 CFU[b]/mL)	*Pseudomonas syringae* and *Clavibacter michiganensis* pv. *michiganensis* in tomatoes
Bacifruit ® SC	*B. subtilis* strain C110, 0.1% *w/v* (1×10^9 CFU/mL)	*Botrytis cinerea* in tomatoes, lettuce, blueberry, raspberries, peppers, and table wine

Table 4. *Cont.*

Commercial Name	Active Ingredients	Pests or Disease Control
Trichoforte ® WP[c]	*Trichoderma atroviridae* strain TC (0.1% *w/w*), *T. atroviridae* strain T10 (0.1% *w/w*), *T. harzianum* strain TF (0.1% *w/w*), *T. harzianum* strain TA (0.1% *w/w*) (0.1% *w/w* = 1×10^9 CFU/g)	In tomatoes, useful to control *B. cinerea*: foliar disease, *F. oxysporium*: root disease and *Phytium spp.*: damping-off disease. In walnuts, control *Phytophthora cinnamomi, P. citrophthora, P. cactorum*: roots disease.
Trichofruit ® WP	*T. atroviride* strain TC (0.1% *w/w*) and *T. atroviride* strain T10 (0.1% *w/w*) (0.1% *w/w* = 1×10^9 CFU/g)	Useful to control *B. cinerea* in fruits of table and grape wine, and blueberry
Conbiol 4 ® WP	*P. lilacinus* strain Patagonia (4% *w/w*), *B. bassiana* strain Portezuelo (4% *w/w*), *M. anisopliae* strain Tierra del Fuego (4% *w/w*) and *Arthrobotrys oligospora* strain Josefina (4% *w/w*) (4% *w/w*=1×10^9 CFU/g)	Useful to control eggs and youth nematodes in citruses (*Tylenchulus semipenetrans*), grape wine nematodes (*Meloydogine incognita, Xiphinema index, X. americans, Pratylenchus thornei, Paratylenchus vanderbrandei*), and coleopthera (*Naupactus xanthographus*).
Inbiol ®	*M. anisopliae* (1×10^{12} CFU/mL) and *B. bassiana* (1×10^{12} CFU/mL)	Useful to control *Pseudococcus viburni* in table and grape wine, citruses, avocados, coffee, bananas, apples and pears.
Radiobacter ® G 84	*Agrobacterium radiobacter* strain K84	Useful to control *A. tumefasciens* in blueberry, raspberry, almond, peach, apricot, cherry and plum trees. Prevent infection in the roots of seedlings and nursery plants.
Rhizobius ®	*Rhyzobius lophanthae*	Effective to control *Aspidiotus nerii, Hemiberlesia lataniae, H. rapax, Aonidiella aurantii, Lepidosaphes ulmi*.

a: SC: Suspension Concentrate, b: CFU: Colony-forming unit, c: WP: Wettable powder.

5. Conclusions

The overuse of synthetic fertilizers and pesticides in conventional agriculture has become relevant in recent years due to the growing demand for food worldwide, but it also poses environmental problems. In this context, several countries have set deadlines for the reduction and/or elimination of these substances in agriculture due to environmental and human health problems. Therefore, alternatives have been sought to support sustainable agriculture free of agrochemicals and chemical fertilizers. Within the context of these alternatives, organic farming utilizes manures from animal waste and byproducts of plant and animal origin by adopting strategies to transform organic waste into organic manures such as composting or vermicomposting. Other relevant practices include crop rotation and prioritizing the use of biodegradable pesticides that do not accumulate in the environment. These benefits from organic farming are of importance in new food and agriculture policies whose models contribute to food security, self-sustainability, and forms of recycling.

Despite the benefits of natural fertilizers and pesticides, certain aspects such as the content of heavy metals present in animal manures, the toxicity of essential oils to nontarget organisms, and their possible carcinogenic and/or mutagenic activity should be considered. In this context, composting, vermicomposting, or biochar should be preferred strategies.

Currently, there are very few available organic pesticides based on essential oils, petroleum-based oils, and inorganic salts. There are some barriers to the commercialization and intensive use of biopesticides and organic manures due to strict legislation. Furthermore, the large-scale manufacturing of these products is an obstacle because of the lack of collaboration between research centers and industries dedicated to the production of organic manures and biological pesticides. On the other hand, the raw materials required for the manufacturing of these products are mostly low in price, but they are often characterized by seasonal variability and availability as well as limited production. In this context, the use of plant extracts as pesticides at the domestic level emerges as a viable alternative for the owners of small farms, obtaining these extracts by using both traditional and modern scientific knowledge.

The use of fungi and strains as biopesticides has the potential to be a more robust alternative than synthetic pesticides because these microorganisms have complex interactions with the pests that are to be controlled, so that the development of resistance by the pests is lower. Although they have disadvantages, in terms of storage, and may be sensitive to environmental conditions. Besides, biopesticides based on microorganisms can be quite expensive compared to synthetic pesticides. They often do not work as quickly and they have to be applied more frequently, making them a tough sell in some markets. However, they constitute a strategy to make modern agriculture a sustainable activity, without affecting ecosystems or human beings, the main consumers of this activity.

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