



Article

# Humic and Acetic Acids Have the Potential to Enhance Deterioration of Select Plastic Soil-Biodegradable Mulches in a Mediterranean Climate

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Abstract: The perceived variability of plastic soil-biodegradable mulch (BDM) degradation has generated concerns about its functionality and sustainability, especially in climates and regions where biodegradation may be limited. This study evaluated the effects of surface-applied products (compost tea, dairy-based compost, humic and acetic acids) on the surface deterioration and visible degradation of three plastic BDMs (BASF 0.6, Novamont 0.6, and Novamont 0.7) and one cellulose paper mulch (WeedGuard Plus) in a Mediterranean climate. Deterioration was monitored for 10 months, and degradation was evaluated 6- and 12 months following soil incorporation. Deterioration varied between the two years of the study; however, the average deterioration for WeedGuard Plus reached 100%, BASF 0.6 and Novamont 0.6 achieved  $\geq$ 80%, while Novamont 0.7 reached  $\geq$ 70%. Application of humic and acetic acids increased BASF 0.6 deterioration, but only humic acid increased Novamont 0.7 deterioration. Scanning electron microscopy of mulch surfaces demonstrated evidence of microbial colonization; however, the surface-applied products did not enhance microbial counts. In-soil degradation of BDMs was inconsistent, but faster degradation occurred overall for starch- and polybutylene adipate-co-terephthalate (PBAT)-based BDMs. Future studies should continue to explore on-farm strategies to enhance in-soil degradation to meet the production system's goals.

Keywords: biodegradation; mesh bag study; plastic pollution; plasticulture; biodegradable mulch



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# 1. Introduction

Plastic agricultural mulches have been a staple in specialty cropping systems for many decades to enhance the yield and quality of numerous crops. Despite the horticultural benefits of plastic mulch, there is a price with its use. Plastic mulch has a short operational lifetime that is generally one growing season, after which it is removed and disposed. The primary polymeric components of most plastic mulches are low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) [1,2], collectively referred to as polyethylene (PE). These plastic polymers are derived from non-renewable, petroleum-based feedstocks that are nondegradable [3]. Poor management of used plastic mulch can have long-term consequences that negatively impact society, as residual non-degradable plastic in soil has the potential to become a source of pollution in terrestrial and aquatic systems [3,4]. To alleviate the economic, environmental, and waste management challenges associated with the absence of sustainable disposal pathways for PE mulch, soil-biodegradable mulches (BDMs) have been created to serve as an alternative mulching material in cropping systems.

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BDMs were developed during the early 1980s, but their wide adoption was limited due to low and unpredictable rates of biodegradation in soil [1,2]. Advancements in technology and research have led to the development of new and promising formulations of biodegradable polymers that can be used to manufacture more reliable BDMs. As the global use of plastic mulch continues to rise, there is also a growing market for BDMs in the United States. Unlike PE mulch, BDMs are designed to be tilled into soil at the end of the growing season. Alternately, BDMs can be removed and composted on-farm after use [5], but the labor costs associated with removal would offset the potential economic gains of BDM use. Once incorporated into soil or compost, the residual BDM fragments are metabolized by microorganisms and converted into carbon dioxide, water, and microbial cell biomass under oxic or aerobic conditions [2,6]. BDMs have the potential to reduce the amount of plastic waste generated as well as eliminate the labor cost of PE mulch removal and disposal.

To be a viable alternative for PE mulch, BDMs should provide similar crop production benefits and achieve 100% biodegradation after tillage [7]. Many field studies have demonstrated that BDM performance is comparable to PE mulch in terms of weed management, soil temperature modification, soil moisture conservation and crop yield enhancement [6]. However, there is still considerable uncertainty about the degradability of BDMs and the effect they can have on soil health and subsequent crop production if BDM fragments do not degrade within a few years and instead accumulate in soil [8,9]. To ensure the performance and integrity of BDMs in specialty cropping systems, standards have been established. ASTM D6400 outlines the standardized tests and specifications to confirm that a BDM is biodegradable under industrial composting conditions [10]. Higher temperatures in compost (60–70 °C) help accelerate the metabolic rate of microbial communities, which increases enzymatic activity, thereby facilitating the biodegradation process [8]. However, under in vivo or in situ soil conditions the rate of BDM biodegradation by microorganisms can differ, as biodegradation is directly influenced by temperature. For this reason, the European standard EN 17033 has been issued to ensure that BDMs are truly biodegradable in field conditions [11,12]. EN 17033 requires that  $\geq$ 90% biodegradation of the polymeric feedstock is achieved in aerobic conditions at 20-28 °C within 2 years of being incorporated into natural topsoil from an agricultural field or forest site. However, EN 17033 applies only to the polymeric feedstocks and does not consider the minor additives incorporated in the manufacturing and extrusion processes of the final mulch.

BDMs are currently composed of 75 to 95% by mass of polymeric feedstocks [7]. The feedstocks may be bio- and/or fossil-fuel based; however, commercially available BDMs are typically a blend of both feedstocks with a biobased composition of approximately 10 to 50%. The remaining percent by mass is generally composed of additives such as plasticizers, fillers, ultraviolet stabilizers, and nucleating agents that aid manufacturing and enhance mulch mechanical properties [6,7]. This creates a mulch that is more flexible and durable, thereby improving its ease of application as well as on-farm use. Laboratory tests utilize plastic polymers in powder form that is more susceptible to degradation compared to plastic film fragments that would occur under field conditions [5,12,13]. Therefore, it is not guaranteed that BDMs will achieve  $\geq$ 90% biodegradation under conditions that differ from the laboratory tests [9].

The biodegradation rate of BDMs under field conditions is influenced by soil temperature and moisture, as well as soil microorganism activity, community composition, and size [8,14,15]. These environmental factors can differ across weather, climate, soil type, and production practices (e.g., tillage, compost application, cover cropping, etc.) [16,17]. Biodegradation is also dependent on environmental weathering and the polymeric composition of the mulch, with greater weathering leading to enhanced embrittlement and faster biodegradation once incorporated into soil [16]. In general, higher temperatures and greater soil microorganism activity have shown to promote faster rates of BDM biodegradation under aerobic conditions [18–20]. However, the individual constituents and their relative proportion in a BDM can be affected adversely by temperature, causing the mulch

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constituents in the final mulch product to degrade at different rates [18,19]. Thus, BDM functionality and biodegradation potential can vary between field sites, the crops grown, and years [5,15,21].

Studies analyzing the long-term impact of BDMs on soil quality are limited. Short-term (<4 years) field studies demonstrate that BDMs do not have an adverse effect on the physical, chemical and biological properties of soil [22,23]. BDMs have also been shown to have a minimal influence on soil microbial community structure and function [24]. Changes in soil properties, function and overall health were attributed to location and the time of sampling rather than mulch type, revealing comparable effects between BDMs and PE mulch [22,23]. Field study findings by Sintim et al. [14] report that BDMs did not have detrimental effects on soil and groundwater quality after four consecutive seasons. However, to determine the sustainability of BDMs, longer-term field studies are required to determine if repeated applications could elicit unintended consequences on the environment.

Continuous applications of BDMs could pose environmental risks if mulch fragments do not achieve complete degradation or degrade too slowly under field conditions. Accumulation of mulch residues in soils could negatively impact soil quality and subsequent crop production [9]. There are concerns about slow and/or incomplete BDM biodegradation, and the concerns are greater for regions with colder temperatures and for soil moisture extremes (dry or saturated) [5,25]. Sintim et al. [5] evaluated the in situ degradation of three commercially available BDMs in two field sites that varied in environmental conditions and soil type: Knoxville, TN (humid subtropical climate and sandy loam soil; 59.9% sand, 23.5% silt, and 16.6% clay) and Mount Vernon, WA (Mediterranean climate and silt loam soil; 12.4% sand, 69.8% silt, and 16.0% clay) [5]. BDM in-soil degradation rates varied between the field sites, and 100% degradation was not observed at either location after 3 years of being incorporated in soil. However, greater BDM deterioration and in-soil degradation were observed in Knoxville, TN (61% to 83%) than in Mount Vernon, WA (26% to 63%). The authors' findings also show that BDM weathering between field sites during the growing season was greater in Knoxville, TN than in Mount Vernon, WA, which helped make the BDMs more susceptible to microbial degradation. A combination of lower soil temperatures and higher soil moisture during the nongrowing season in Mount Vernon, WA also limited microbial degradation as the soils became anaerobic or anoxic [5]. In a separate study in Lynden, WA, Zhang et al. [15] evaluated the deterioration and visible in-soil degradation of four BDMs in a raspberry (Rubus idaeus L.) production system. One year after BDM application, deterioration of all BDMs reached 91%; however, visible in-soil degradation was minimal 18 months after the BDMs were buried in soil.

These findings suggest that further studies are necessary to gain a better understanding of how commercially available BDMs perform under diverse field conditions. It also highlights a need to identify on-farm management practices that can be used to enhance BDM biodegradation in soil, particularly in locations that are predisposed to lower degradation rates. The objectives of this study were to (1) evaluate the impacts of surface-applied products (compost tea, dairy-based compost, acetic and humic acids) on mulch surface deterioration, and (2) quantify visible degradation after the application of the aforementioned products.

#### 2. Materials and Methods

### 2.1. Experimental Location and Design

The experiment was carried out at the Washington State University Northwestern Washington Research and Extension Center (NWREC) in Mount Vernon, Washington, United States of America (lat: 48°26′2″ N, long:122°23′33″ W). The field site has Skagit silt loam, characterized as a fine-silty mixed nonacid mesic Typic Fluvaquents, with pH 6.5 and 2.7% organic matter [26]. This experiment was carried out during the 2019/2020 year and was repeated in 2020/2021 in an adjacent field with the same soil type. The experimental layout was a randomized complete block split-split-plot design. The experimental site was 0.1 ha and the main plot treatments were 73 m-long raised bed plots. Split-plots

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measured 18 m-long and split-split plot size was 0.9 m. Each raised bed measured 0.61 m wide. The site was not fumigated; however, an herbicide (Spartan 4F, active ingredient: sulfentrazone at 39.6%, FMC, Philadelphia, PA, USA) was applied after bed shaping and prior to mulch application. The herbicide Weed Pharm (active ingredient: acetic acid at 20.0%, Pharm Solutions, Destin, FL, USA) was sprayed twice and Aim EC sprayed once during the growing season to manage weeds (active ingredient: carfentrazone-ethyl at 22.3%, FMC, Philadelphia, PA, USA).

## 2.2. Mulch Materials Used in Experiment

Four commercial BDMs were used as the main plot treatments, four degradation products served as the split plot treatments, and two degradation product application time intervals acted as the split-split treatments. The experiment included four replicates (Tables 1 and 2). The mulch treatments included three plastic BDMs (BASF 0.6, Novamont 0.6, and Novamont 0.7) and one cellulosic-paper mulch (WeedGuard Plus) that was used as a 100% biodegradable control [27]. Table 1 provides information on the BDM treatments such as thickness, extruder, and primary feedstock ingredients. Potentially degrading products were recommended by the mulch extruders to promote mulch surface deterioration and in-soil degradation when surface-applied to BDMs during the growing season. These products included compost tea, acetic acid and humic acid (Table 2). However, during the second-year study, compost tea was not available, therefore dairy-based compost was used as a substitute. Assigned split plot treatment areas were not sprayed to operate as a control.

**Table 1.** Soil-biodegradable mulch (BDM) treatments applied in a field study in northwestern Washington, USA.

Mulch Treatments z	Thickness (µM)	Extruder <sup>y</sup>	Primary Feedstocks
BASF 0.6	15.2	PolyExpert Inc., Laval, QC, Canada	PLA + PBAT <sup>x</sup>
Novamont 0.6	15.2	Dubois Agrinovation, Saint Remi, QC, Canada	Starch-based, PBAT copolyester
Novamont 0.7	17.8	Dubois Agrinovation, Saint Remi, QC, Canada	Starch-based, PBAT copolyester
WeedGuard Plus	254.0	Sunshine Paper Co. LLC, Aurora, CO, USA	Cellulosic

 $<sup>^{</sup>z}$  BASF, WeedGuard Plus, and Novamont mulch treatments are biodegradable based on ASTM D6400 (standard outlining tests and criteria for BDM biodegradability under industrial composting conditions) and EN 17033 (standard outlining tests and criteria for BDM biodegradability in a laboratory setting using natural topsoil from an agricultural field or forest site).  $^{y}$  Manufacturer of soil-biodegradable mulch (BDM).  $^{x}$  PLA = polylactic acid; PBAT = polybutylene adipate-co-terephthalate.

**Table 2.** Degradation product treatments surface-applied to soil-biodegradable mulches (BDMs) to enhance surface deterioration and in-soil degradation in a field study in northwestern Washington, USA.

Degradation Manufacturer Treatments		Dilution Rate	Application Rate	Key Product Ingredient(s)	
Actagro liquid humus (humic acid 10.0%)	Actagro; Osceola, AR, USA	3.8 L humic acid to 37.9 L of water	280.6 L/ha	Mixture of organic (humic and fluvic) acids with 22% derived from leonardite <sup>y</sup> and 2% soluble potash	
Weed Pharm (acetic acid 20.0%)	Pharm Solution, Inc.; Destin, FL, USA	3.8 L Weed Pharm to 7.6 L of water	280.6 L/ha	Acetic acid	
Compost tea <sup>z</sup>	Cascasde Cuts; Bellingham, WA, USA	3.8 L compost tea to 7.6 L of water	561.2 L/ha	Compost based solution with unspecified bacteria and fungi	
Compost (dairy-based)	Smit's Compost; Lynden, WA, USA	_	5 cm depth	Compost with unspecified bacteria and fungi (total nutrient analysis of dry material: 1.9% N, 0.5% P, 0.8% K, 1.7% Ca, 0.6% Mg, 0.2% Na, 0.4% S, 27.8 ppm B)	

<sup>&</sup>lt;sup>z</sup> Compost tea was utilized as a degradation treatment during the 2019/2020 study, but due to difficulties with product sourcing it was replaced with dairy-based compost during the 2020/2021 study. <sup>y</sup> Leonardite is a humic substance derived from oxidated lignite that is used as a biostimulant.

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#### 2.3. Field Plot Establishment

The mulches were established in the field on May 2019 and June 2020 using a bed shaper/mulch layer (Model 2600 Bed Shaper, Rain-Flo Irrigation, East Pearl, PA, USA) (Figure 1). Drip irrigation tape (T-Tape, Model #508-08-340, 0.2 mm, 20 cm dripper spacing, 4.23 L/min/100 m flow rate, San Diego, CA, USA) was laid simultaneously below the plastic mulch. No plants were established on the raised beds, but planting holes were added every 66 cm in 2019 to simulate a production situation. Planting holes were not added in 2020 to reduce weed pressure. In 2019, the experimental site was irrigated seven times between late July and late August for an average run time of 2 h, and in 2020 the field site was not irrigated since there was adequate moisture in the soil. Degradation products were surface-applied on a day with temperatures over 18 °C, low wind (<10 kph) and without forecasted rainfall for the following 24 h to maximize product-mulch interaction. A calibrated backpack sprayer (Bellspray Inc. d.b.a R&D Sprayers, Opelousas, LA, USA) was utilized to apply each degradation product separately and was triple rinsed between each product application. Compost tea (2019 only), humic and acetic acids were sprayed onto the surface of the mulch in the assigned split-split plots. In 2020, aged, dairy-based compost was sourced locally (Smit's Compost, Lynden, WA, USA) and applied manually to the surface of the mulch treatments at a 5 cm depth. In the first-year study, degradation products were applied in September 2019 and March 2020. For the second-year study, the degradation products were applied in September 2020 and April 2021. Application timing for spring 2021 was delayed as compost tea production was halted at the nursery where it was produced due to COVID-19 and a new treatment was sourced. The treatment was changed to dairy-based compost (1.9% N, 0.5% P, 0.8% K), which is widely accessible to growers in the region. In the spring, degradation products were reapplied to the autumn split-split plots for a combined autumn and spring application to assess if increased application frequency would influence mulch surface deterioration.



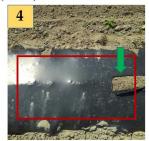
Field application of soilbiodegradable mulches (BDMs)



Weathering



Degradation product application





Monitoring of percent soil exposure (PSE) and decomposition bags

Figure 1. Methodology followed in the 2019/2020 and 2020/2021 field trials.

# 2.4. Soil Temperature and Moisture

Soil temperature and volumetric moisture sensors attached to loggers (TEROS 11, Meter Environment, Pullman, WA, USA) were established in the second and third replicate. Each logger was set at 15 min intervals. The sensors were positioned below the mulch in the center of each assigned main plot at a depth of 15 cm. The distance between the

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sensors and dripline emitters was kept at approximately 10 cm and was consistent across all treatments.

# 2.5. Scanning Electron Microscopy of BDM Mulch Surfaces

Scanning electron microscopy (SEM) was performed to observe microbial colonization of BDM mulch surface. Mulch samples were collected from each replication of BASF 0.6 and Novamont 0.6 in autumn 2019. Mulch samples were collected before degradation product application and then 48 h, 1 week, and 2 weeks after product application. Sample dimensions of  $1.5 \times 2.0$  cm were placed into tissue cassettes (Polysciences, Warrington, PA, USA) and stored in 2.5% glutaraldehyde in a 0.1 M sodium diphosphate buffer (pH 7.2) at 4 °C. After 48 h, the mulch samples were dehydrated through a dilution series of ethanol. The dilution series started at 50% ethanol (v/v). The concentration was increased every 20 min until samples were in a solution of 100% ethanol (v/v; 50%, 70%, 80%, 90%, 95%, and 2 times at 100%). Lastly, the samples were mounted on specimen stubs and sputter coated with gold/palladium (Polaron SC7640 sputter coater, Quorum Technologies, East Sussex, UK). Images were observed using a Tescan Vega 3 thermionic scanning electron microscope (Brno-Kohoutovice, Brno, Czech Republic) at an accelerating voltage of 10 kV. Secondary electron images were collected with a constant 50 μm field-of-view and constant ~50 μm pixel size. To determine if microbial cells were present on BDM surfaces, each SEM image was analyzed following a uniform set of identification criteria. A microbial cell was marked and counted if it demonstrated a full-bodied appearance, or if multiple microbial cells were visible as aggregates of ellipsoidal and/or spherical shape and comprised a size between 0.5 and 5.0 μm. To distinguish from minerals, microbial cells also had to demonstrate an intermediate brightness, as well as a uniform and smooth surface appearance [28].

### 2.6. BDM Surface Deterioration

To assess mulch surface deterioration, percent soil exposure (PSE) data were collected twice a month following the application of the mulch, from May 2019 to April 2020 and June 2020 to April 2021. The PSE measurements occurred approximately on the first and fifteenth day of each month. The PSE was rated visually in the center 1 m of each plot where 0% represented a mulch that was completely intact and 100% represented fully exposed soil. The PSE ratings were measured in 1% increments until 20% soil exposure was observed and in 5% increments thereafter [27]. The PSE regions were also photographed from the third replicate to capture the progression of mulch surface deterioration.

### 2.7. Visible BDM In-Soil Degradation

To evaluate visual in-soil degradation, one  $18 \times 8$  cm weathered mulch sample (long side in the direction of mulch laying) was collected from the top center of the raised bed in each split-split treatment region from the 2019/2020 growing season. Each sample was placed in a labeled, sealable plastic bag and stored at 4 °C for no longer than 4 days from the date of collection. Within 4 days, each mulch sample was cut into two  $5 \times 5$  cm pieces and photographed at a height between 30 and 40 cm, directly above (90° perpendicular), using a flat platform. After being photographed, each mulch sample was placed into an individual, pre-sown 12 × 12 cm nylon decomposition (1 mm mesh) bag with a corresponding labeled aluminum tag to aid with identification. Two decomposition bags were buried into each designated split-split plot at a depth of 10 cm at a 45° angle. After burial of the decomposition bags, a faba bean (Vicia faba L.) cover crop was seeded throughout the field at a planting density of 168 kg/ha. Decomposition bags were retrieved at two-time intervals. The first set of decomposition bags were retrieved approximately 6 months after burial in December 2020, and the remaining decomposition bags were collected after 12 months in June 2021. Mulch surface area was measured digitally before placing into decomposition bags and after retrieval (ImageJ, National Institute of Health, Bethesda, MD, USA) to quantify changes in visual degradation over time.

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### 2.8. Statistical Analysis

The PSE data were evaluated for assumptions of normality before using analysis of variance (ANOVA). Data were initially analyzed using the agricolae package for the split-split plot ANOVA using R (version 4.0.0) [29,30]. Once it was determined that the timing of the degradation product application did not have a significant interaction on deterioration ( $\alpha$  = 0.05), a split-plot ANOVA was performed to test the effects of the degradation products on mulch treatment PSE. A post hoc Tukey's honest significant difference test was utilized to compare means at a significance level of p = 0.05. Data for the SEM microbe quantification and remaining mulch area in the decomposition bags were analyzed as a randomized complete block design using ANOVA, as timing of product application did not influence in-soil degradation. Averages of soil temperature and moisture data were calculated using R and presented by year.

#### 3. Results

## 3.1. Soil Moisture and Temperature

Soil moisture during the 2019 and 2020 growing seasons was similar for all mulch treatments (Table 3). Average soil moisture at a 15 cm depth between May and August was  $0.18~\text{m}^3\cdot\text{m}^{-3}$  (range was  $0.10~\text{to}~0.25~\text{m}^3\cdot\text{m}^{-3}$ ). From September to December, average soil moisture was  $0.23~\text{m}^3\cdot\text{m}^{-3}$  (range was  $0.18~\text{to}~0.29~\text{m}^3\cdot\text{m}^{-3}$ ) and  $0.27~\text{m}^3\cdot\text{m}^{-3}$  (range was  $0.19~\text{to}~0.31~\text{m}^3\cdot\text{m}^{-3}$ ) from January to April. Soil temperature at the same depth was also similar between mulch treatments (Table 4). Average soil temperature was 21.2~°C from May to August, 10.3~°C from September to December, and 7.3~°C from January to April.

**Table 3.** Average soil moisture from May to April 2019/2020 and 2020/2021 at the experimental site in northwestern Washington, USA.

N.C. 1.1.		S	oil Volumetri	c Content (m <sup>3</sup> ·1	m <sup>3</sup> ) <sup>z</sup>	
Mulch	May-August		September-December		January–April	
Treatments	2019	2020	2019	2020	2019	2020
BASF 0.6	0.21	0.20	0.27	0.20	0.30	0.19
Novamont 0.6	0.20	0.10	0.26	0.20	0.30	0.28
Novamont 0.7	0.18	0.12	0.24	0.18	0.26	0.22
WeedGuard Plus	0.25	0.20	0.29	0.20	0.31	0.27

<sup>&</sup>lt;sup>2</sup> Soil temperature and volumetric moisture sensors were attached to loggers (TEROS 11, Meter Environment, Pullman, WA, USA) positioned below the mulch in the center of each assigned main plot at a depth of 15 cm.

**Table 4.** Average soil temperature from May to August 2019/2020 and 2020/2021 at the experimental site in northwestern Washington, USA.

Mulch	Soil Temperature (°C) <sup>z</sup> May–August September–December January–April					y–April
Treatments	2019	2020	2019	2020	2019	2020
BASF 0.6	21.1	23.4	10.4	11.3	7.2	7.7
Novamont 0.6	20.9	21.8	9.9	10.6	6.9	8.2
Novamont 0.7	21.6	23.3	10.1	10.4	6.7	7.7
WeedGuard Plus	18.4	19.3	9.4	10.0	6.7	7.5

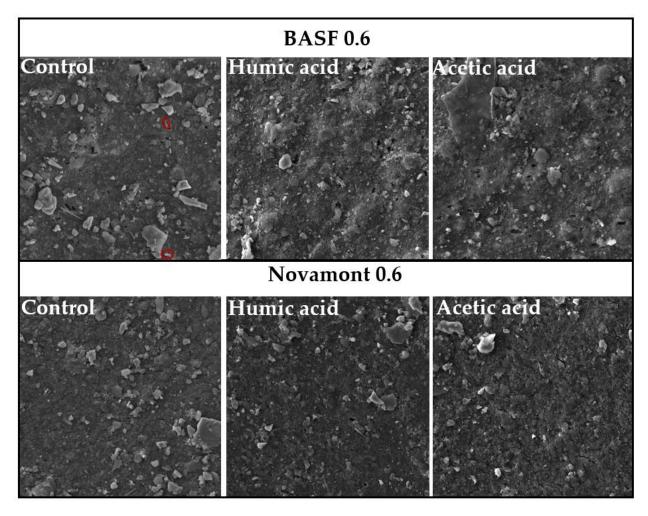
<sup>&</sup>lt;sup>2</sup> Soil temperature and volumetric moisture sensors were attached to loggers (TEROS 11, Meter Environment, Pullman, WA, USA) positioned below the mulch in the center of each assigned main plot at a depth of 15 cm.

# 3.2. Scanning Electron Microscopy of BDM Surfaces

The SEM images of BASF 0.6 and Novamont 0.6 mulch surfaces demonstrated evidence of microbial colonization before treatment application, as well as 48 h, and 1 and 2 weeks after product application (Figure 2). However, microbial quantification of mulch surfaces did not differ among mulch treatments (p = 0.10), surface-applied products (p = 0.24), and timing of sample collection (p = 0.76), nor was there an interaction among the three main

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factors (p = 0.46, Table 5). However, there was an interaction between mulch treatment and collection timing and also between the degradation product and collection timing. The microbial counts for BASF 0.6 mulch samples were higher 48 h after product application compared to the pre-application of degradation products, as well as 1- and 2-week post-product application. The average microbial counts were greater before and 2 weeks after BASF 0.6 and Novamont 0.6 samples were treated with humic acid. This is consistent with our observations regarding mulch surface deterioration of Novamont 0.6, where surface deterioration was not affected by the type of degradation product applied. While the application of humic acid to BASF 0.6 affected mulch surface deterioration, it is possible that these products may be more conducive to microbial colonization if the products are applied to the mulch surface immediately before it is tilled into the soil, to help further influence an effect on microbial colonization, activity, and the degradation processes.



**Figure 2.** Scanning electron microscopy (SEM) images of BASF 0.6 and Novamont 0.6 mulch samples before surface application (control), and 2 weeks after application of humic and acetic acids. SEM images were collected at a constant 50  $\mu$ m field-of-view and constant ~50  $\mu$ m pixel size. An example of a microbial cell is circled in green.

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**Table 5.** Microbial colonization of plastic soil-biodegradable mulch (BDM) surfaces measured before the application of degradation products, and 2-, 7-, and 14-days following product application, using split-split plot analysis of variance (ANOVA). Scanning electron microscopy (SEM) was performed to observe and quantify microbial cells on BDM surfaces before and after product application (compost tea, humic and acetic acids). Plastic mulch samples (BASF 0.6 and Novamont 0.6) were collected in autumn 2019.

Split-Split Plot Analysis of Variance (ANOVA)	<i>p-</i> Value <sup>z</sup>
Significance	
mulch treatment x	0.10
degradation product <sup>y</sup>	0.24
collection timing w	0.76
mulch treatment:degradation product	0.89
collection timing:mulch treatment	0.02
collection timing:degradation product	0.008
collection timing:mulch treatment:degradation product	0.46

 $<sup>\</sup>overline{z}$  *p*-value with significance at  $\alpha = 0.05$ .  $\times$  Mulch samples (BASF 0.6 and Novamont 0.6) were collected in the 2019/2020 study.  $^y$  Split-split plots were treated with degradation products (compost tea, humic and acetic acids).  $^w$  Mulch samples were collected before treatment application, as well as 48 h, and 1 and 2 weeks after product application.

### 3.3. Mulch Surface Deterioration

The PSE measurements were used to monitor changes in BDM physical and mechanical strength and were observed through rips, tears, and holes on the mulch that exposed the soil surface. The application of potentially degrading products to the surface of BDMs had some effect on mulch surface deterioration (p = 0.03 and 0.03; Table 6), but product efficacy varied among mulch treatments and between years. Degradation products were applied during the autumn and spring times. Split-split plots treated in autumn were sprayed again in the spring for a combined (spring and autumn) application; however, timing of product application did not affect mulch surface deterioration (p = 0.45 and 0.11). The effect of surface applied products on surface deterioration differed by BDM product. Novamont 0.6 deterioration was not affected by the degradation products, whereas humic and acetic acids application to BASF 0.6 affected mulch surface deterioration in both field studies. Deterioration of Novamont 0.7 was the lowest among all BDMs, and humic acid was the only degradation product that increased its deterioration over time.

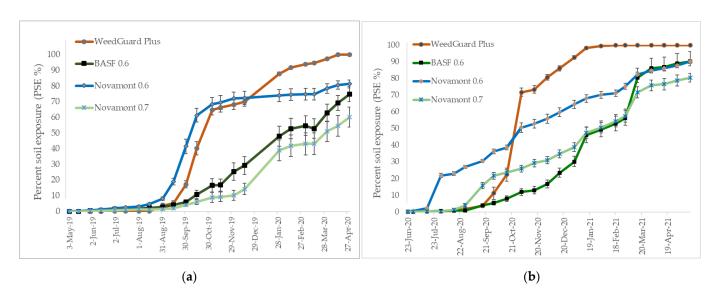
The PSE during the 2019 growing season was minimal after mulch application and began to increase by 15 September 2019 (Figure 3). Changes in environmental conditions from September and thereafter, such as increased rainfall, strong winds and mechanical damage by wildlife, contributed to PSE progression. Furthermore, the mulch was fully exposed as there was no crop to cover its surface or hold it in place (wind can enter the planting holes and lift the mulch causing it to tear). Mulch surface deterioration for WeedGuard Plus and Novamont 0.6 increased rapidly compared to the other mulch treatments. By 4 November 2019, PSE for WeedGuard Plus and Novamont 0.6 exceeded 50%. At the same time, PSE for BASF 0.6 was approximately 17% and for Novamont 0.7 it was 9%. Thereafter, PSE continued to increase but the rate of deterioration slowed. PSE exceeded 50% for BASF 0.6 by 14 February 2020 and by 1 April 2020 for Novamont 0.7. By the last month of PSE assessments (30 April 2020), PSE across all mulch treatments varied. WeedGuard Plus achieved 100% PSE followed by Novamont 0.6 (81%), BASF 0.6 (75%) and Novamont 0.7 (60%) (Figure 3).

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**Table 6.** Surface deterioration measured as percent soil exposure (PSE) of soil-biodegradable mulch (BDM) following application of degradation products, using split-plot analysis of variance (ANOVA). Field experiments were established in Spring 2019 and Spring 2020 testing three plastic BDMs (BASF 0.6, Novamont 0.6, and Novamont 0.7) and one cellulose paper mulch (WeedGuard Plus). Potentially degrading products (compost tea, dairy-based compost, acetic and humic acids) were surface applied in autumn and spring.

Mulch Treatment	Degradation Product <sup>z</sup>	Percent Soil 2019–2020	Exposure (PSE %) 2020–2021
	Control	67.5 abcd <sup>y</sup>	85.6 abcd
DACE O.	Humic acid	78.1 abc	91.9 ab
BASF 0.6	Acetic acid	85.0 abc	88.8 ab
	Compost tea/compost	68.8 abcd	71.3 cd
	Control	88.8 ab	90.6 ab
Novamont 0.6	Humic acid	79.4 abc	86.3 abcd
Novamont 0.6	Acetic acid	85.0 abc	86.9 abcd
	Compost tea/compost	78.8 abc	88.8 ab
	Control	60.9 bcd	70.6 d
Novamont 0.7	Humic acid	90.0 ab	88.1 abc
Novamont 0.7	Acetic acid	37.3 d	78.8 bcd
	Compost tea/compost	52.5 cd	80.0 bcd
	Control	100.0 a	100.0 a
WeedGuard	Humic acid	100.0 a	100.0 a
	Acetic acid	100.0 a	100.0 a
Plus	Compost tea/compost	100.0 a	100.0 a
	<i>p</i> -value	0.03	0.03

 $<sup>^{\</sup>rm Z}$  Soil-biodegradable plastic mulches (BDMs) were treated with degradation products in September 2019 and April 2020 in the first-year study. In the second-year study products were applied in September 2020 and May 2021.  $^{\rm Y}$  Means followed by the same letter within a column are not significantly different at p < 0.05 using a means comparison with a Tukey's honestly significant difference test for all dates.



**Figure 3.** Percent soil exposure (PSE) of soil-biodegradable mulches (BDMs) (BASF 0.6, Novamont 0.6, Novamont 0.7 and WeedGuard Plus, where  $0.6 = 15.2 \mu m$  thickness and  $0.7 = 17.8 \mu m$  thickness) from (a) May to April 2019/2020 (L); and (b) June to April 2020/2021 (R).

In the second-year study, PSE was low from the date of application (23 June 2020) to 17 September 2020 for all mulch treatments except Novamont 0.6 (Figure 3). Damage to the mulch during installation by the drip tape caused small rips and tears that were later amplified in the Novamont 0.6-treated plots with changes in weather. Mulch products used in the second year were from the same rolls as were used in the first-year study. Rolls of BDMs were stored in cool conditions (25 °C) and were protected from potential environmental weathering factors. However, it is possible that Novamont 0.6 may have undergone some deterioration during storage that could have compromised its quality and accelerated deterioration [31]. Environmental conditions, such as moisture, humidity,

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and heat, as well as BDM storage conditions, can contribute to agricultural weathering; therefore, mulch manufacturers recommend that BDMs are only stored for no more than 1.5 years [6].

By 17 September 2020, PSE increased for all BDMs and continued to increase at an accelerated but varied rate for each BDM (Figure 3). The PSE reached over 50% for WeedGuard Plus by 1 November 2020, by 16 November 2020 for Novamont 0.6, and by 16 February 2021 for BASF 0.6 and Novamont 0.7. Complete mulch deterioration for WeedGuard Plus was observed on 16 February 2021. By 15 May 2021 (the last date for PSE assessment), Novamont 0.6 reached 90% PSE followed by BASF 0.6 (85%), and Novamont 0.7 (80%). Overall, PSE was considerable both years, but it did not represent BDM degradation or loss of mulch mass.

# 3.4. Mulch In-Soil Degradation

WeedGuard Plus achieved 100% in-soil degradation during both growing seasons as predicted and demonstrated in studies by Miles et al. [8,31]. Due to environmental weathering and its rapid degradation rate, samples of WeedGuard Plus could not be collected for decomposition bag samples. Decomposition bag samples for both Novamont treatments and BASF 0.6 were retrieved 6 months post burial. Mulch surface area loss ranged from 4.9 to 24.1% on average. Degradation products did not increase mulch surface area loss (p = 0.89), but it differed between mulch treatments, with Novamont 0.6 demonstrating greater mulch surface area loss (19.9% on average; p = 0.0097). However, there was not an interaction among degradation product and mulch treatment (p = 0.66, Table 7). Mulch surface area loss of samples in decomposition bags retrieved after 12 months of burial was greater than the 6-month retrieval timepoint (p = 0.34) and varied from 4.3 to 36.8%. There were minimal differences in mulch surface area loss among mulch treatments: Novamont 0.6 (26.2%) > Novamont 0.7 (17.8%) > BASF 0.6 (11.8%) (p = 0.093) and the degradation treatment applied (p = 0.12).

**Table 7.** Mulch surface area loss of soil-biodegradable plastic mulch treatments (BASF 0.6, Novamont 0.6 and Novamont 0.7, where  $0.6 = 15.2 \,\mu m$  thickness and  $0.7 = 17.8 \,\mu m$  thickness) 6 and 12 months after burial in nylon decomposition bags. Burial took place in June 2020 in the corresponding split-split plots at a depth of 10 cm. A faba bean (*Vicia faba* L.) cover crop was seeded over the decomposition bags at a planting density of  $168 \, kg/ha$  after burial.

Mulch Treatment	Degradation Product	Mulch Area Loss 6 Months	Post-Burial (%) 12 Months
	Control	10.5	15.0
DACE O.	Humic acid	4.9	16.6
BASF 0.6	Acetic acid	5.7	11.1
	Compost tea	7.1	4.3
	Control	21.2	25.5
NI	Humic acid	14.3	18.0
Novamont 0.6	Acetic acid	24.1	36.8
	Compost tea	19.9	24.3
	Control	11.4	16.3
	Humic acid	17.4	22.4
Novamont 0.7	Acetic acid	7.6	23.4
	Compost tea	5.4	9.1
	<i>p</i> -value	0.66	0.34

# 4. Discussion

Mulch surface deterioration of all BDMs was high and although in-soil degradation was low, most BDMs in this study underwent more extensive in-soil degradation than reported in prior studies conducted under similar environmental and climatic conditions [5,15,21]. BDMs are susceptible to deterioration due to the nature of their feedstocks that generally have lower mechanical strength properties than PE, including breaking force

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and elongation [32]. The thickness of BDMs also contributes to the degradation rate, with thinner BDMs expected to deteriorate and undergo faster environmental weathering [8,15].

Weather-induced damage is a primary factor of deterioration causing BDMs to weaken and fragment with increased exposure [8,20]. BDMs were susceptible to weathering elements in both field trials. Precipitation and strong winds from September to April/May likely contributed to reduced BDM elongation and breaking forces, which may have exacerbated existing holes, rips and tears. As expected, the thinner mulch treatments (Novamont 0.6 and BASF 0.6) deteriorated faster; however, Novamont 0.7 deterioration followed closely. An important factor to consider from this study is that mulch surface deterioration may differ if crops are planted with BDMs, with plant canopy either increasing protection from weathering or heightening the extent of deterioration. In the case of Zhang et al. [15], raspberry was planted with Novamont and BASF mulch treatments and raspberry prickles damaged the mulch surfaces as the canopy matured. Understanding the factors that drive BDM deterioration are critical, as growers will have to consider multiple factors when choosing a BDM, including its thickness and expected length of environmental exposure. This will help ensure that a BDM's operational lifetime aligns with a crop's growing cycle. It is also important to note that visual assessments of deterioration are not indicative of degradation [33]. BASF 0.6 deterioration was significant, but the extent of in-soil degradation observed was relatively low.

BDM degradation is often faster in compost than in soil [5], yet in this study the application of compost tea and compost had the lowest efficacy on increasing mulch surface deterioration among all products. These results are consistent with the findings of Samuelson et al. [34] who found neither product (compost tea and compost), nor application frequency influenced BDM degradation, which they attributed to environmental differences in field site location and mulch type (PLA and starch-polyester mulch). Industrial composting conditions can be more favorable for BDM degradation than soil as higher temperatures help drive soil microorganism activity and weaken the polymer molecular structure of BDMs. Although these surface-applied products have the potential to alter the biological or chemical properties of soil, the products do not replicate the exact composting conditions that help drive degradation processes [34]. Similarly, when the products are applied to BDM surfaces, the potential to support microbial colonization may be limited. Furthermore, the economic implications of using these degrading products with BDMs will need to be evaluated if a farmer considers using them. Even though the initial purchase cost of BDM is approximately double the cost of PE mulch [35], the estimated total net change in profit due to BDM adoption compared to PE mulch is USD 189 hectare<sup>-1</sup> [35]. This increase in profit is due to mulch removal and disposal savings associated with BDM use. However, cost savings may be reduced or lost depending on the price of these degrading products.

Temperature affects the polymeric structure of polylactic acid (PLA) and polybutylene adipate-co-terephthalate (PBAT), which influences the mechanical behavior of the BDM. Soil temperatures during both growing seasons were well below the glass transition temperature (Tg) of PLA (Tg =  $63.0\,^{\circ}$ C) and above for PBAT (Tg =  $-34.0\,^{\circ}$ C) [36], and this likely contributed to the varying levels of in-soil degradation. The glass transition temperature represents the stages between the polymer's glassy state to a ductile state. When the ambient soil temperature is below the glass transition temperature of a plastic polymer, the molecular structure is in its glassy state and is therefore stiff and rigid [37]. As a result, the polymer chain mobility and the hydrolysis of C—O ester linkages is limited, thereby restricting access to water and biodegradation [5,20]. Under field conditions, BDMs composed of PLA feedstock are expected to biodegrade at slower rates [38,39], due to its high glass transition temperature, which is not often attained at ambient soil temperatures [5].

BASF and Novamont mulch treatments are both composed of different ratios of PBAT; however, BASF also contains PLA, while Novamont mulch treatments are also composed of starch polymeric feedstocks. Soil temperatures during both years were too low to influence the PLA-based BDM (BASF 0.6) to transition to a ductile state. However, the soil

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temperatures were above the glass transition temperatures of PBAT, thereby influencing its transition to a ductile state that allowed PBAT-based BDMs (Novamont 0.6 and 0.7) to be more flexible and susceptible to in-soil degradation. Adding PBAT to PLA can help lower the barrier to water and oxygen [36], and BDMs containing a higher ratio of starch will have a higher estimated comparative rate of degradation in soil [40]. Aside from the polymeric components and their relative amounts, the type and quantity of additives and minor components incorporated during film extrusion are important factors to consider. The complete composition of BDMs is not disclosed by mulch manufacturers and often varies by mulch product. How well BDMs degrade can be further influenced by this, either directly due to the degradability of each component, as well as indirectly through their impact on the mulch film during the extrusion process, or due to changes to its physiochemical properties by diverse weathering conditions [18]. Findings from this field study are consistent with prior research that did not include products to enhance BDM deterioration and degradation, where Novamont mulch treatments degraded more rapidly than BASF mulch treatments [15,41,42].

In-field volumetric water content was not a limiting factor for BDM degradation; however, low soil temperatures and increased soil moisture during the nongrowing seasons potentially reduced degradation, as the soil became saturated and anoxic [5]. Nonetheless, the extent of degradation observed after 12 months of burial indicates that the degradation process was still occurring year-round. This is similar to work by Griffin-LaHue et al. [43], where BDM fragments retrieved after 4 years of continuous use and 2 years after final soil incorporation was 4-16% of the total mulch mass that was incorporated into the soil, demonstrating that although degradation was slower than laboratory-based assays (≥90% degradation within 2 years), degradation was occurring at a steady and relatively rapid rate. In addition, the findings from the aforementioned study suggest that thermal time rather than calendar days is more representative of BDM degradation under field and laboratory conditions. The BDMs incorporated in soil under a Mediterranean climate are predicted to achieve 90% in-soil degradation between 21 and 58 months, depending on the BDM utilized. While the degradation treatments did not directly influence in-soil degradation, some samples achieved approximately 30% degradation in soil. Based on these results, it is anticipated that the BDMs will achieve complete in-soil degradation within 4 years. In contrast, it can take up to 300 years for PE mulch to degrade [44], thus BDMs can be a more sustainable mulching option, despite degradation occurring over longer timespans in some environments relative to the laboratory-based standards.

It is known that on-farm management practices directly influence the extent of BDM degradation in soils. BDMs applied in this study were similar to the BDMs evaluated by Zhang et al. [15]; however, an additional and different factor that could have contributed to in-soil degradation in the current study was the use of a faba bean cover crop in the field that the decomposition bags were buried in. Many retrieved decomposition bags were observed to have roots intertwined through them that contributed to further BDM fragmentation. Smaller and weathered fragments are more susceptible to biodegradation; therefore, it is likely that faba bean roots increased BDM in-soil degradation. In addition, plants such as faba bean can produce root exudates such as organic acids, sugars, amino acids, phenolics and secondary metabolites that attract and provide nutrients for beneficial soil microorganisms [45]. Thus, root exudates can be important to support and enhance microbial activity and have the potential to accelerate BDM in-soil degradation. Furthermore, faba bean is well known for its ability to enhance nitrogen supply in soil via biological nitrogen fixation after crop decomposition [46], which can further support microbial activity. While the use of mustard (Brassica juncea), cereal rye (Secale cereale) and hairy vetch (Vicia villosa) cover crops did not enhance BDM in-soil degradation, as noted in the findings by Samuelson et al. [34], knowledge on how various cover crops influence degradation of BDMs is still limited. It would be valuable to investigate how the incorporation of a diversity of cover crops and their root architectures and exudates impact BDM degradation.

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A limitation to consider in the current study is the size of BDM samples used in the decomposition bags to assess in-soil degradation. Even though we followed established protocols for assessing the in-soil degradation of visible fragments [5,15,34], it is worth considering that these fragments may not be representative of the actual fragment size that remains after tillage and, hence, may be too large to accurately assess anticipated in-soil degradation. A more realistic evaluation would be made if fragments were collected post-tillage, measured for initial area, placed into decomposition bags and into the soil, and collected annually until the visible surface area was completely degraded. It would also be beneficial to explore how different tillage practices affect degradation as degradation rates can be influenced by fragment size. A smaller fragment size would increase the surface area available to soil microorganisms, thereby facilitating the degradation process. Using alternative tillage practices that are more effective in breaking down BDMs into smaller fragments would therefore be worthwhile to investigate.

#### 5. Conclusions

The application of potentially degrading products on the surface of BDMs could be an effective management practice to enhance mulch surface deterioration, but product efficacy needs to be assessed for each BDM. Degradation treatments used in this study did not increase mulch surface deterioration of Novamont 0.6, but the application of humic and acetic acids to BASF 0.6 did increase mulch surface deterioration. However, for Novamont 0.7, increases in deterioration were only observed with the application of humic acid. Visual in-soil degradation differed between BDMs and was not increased by the application of degradation products. Still, more extensive degradation was observed in all BDMs after 12 months of soil burial than reported in studies conducted in regions with similar climatic and soil conditions.

In this study, faba bean was established as a cover crop directly after BDM till-down. Faba bean roots penetrated through multiple BDM samples within the decomposition bags and increased breakdown into smaller mulch fragments that could have made BDMs more susceptible to microbial degradation. The effect of faba bean root exudates on soil microorganisms found near the roots of the BDM samples may have positively influenced microbial activity and degradation. Future field studies should investigate the degradability of additional commercially available BDMs, particularly in environments where biodegradation rates are intrinsically low. This would provide more reliable assessments of in-soil degradation and support the development of regional predictive models. Gaining a deeper understanding of BDM degradability across diverse growing regions may provide growers with relevant information to determine if BDMs are suitable for their production systems.

**Author Contributions:** L.W.D. conceived the research idea. L.W.D., H.Z. and C.A.M. planned the research methodology. L.W.D., H.Z., B.M., M.K. and D.G.-L. collaborated on the scanning electron microscopy and microbe quantification protocols. M.K. supported B.M. and H.Z with SEM instruction and data collection. H.Z. and B.M. conducted the field studies and gathered data. B.M. and L.W.D. analyzed and interpreted the data. B.M., L.W.D. and C.A.M. wrote and edited initial drafts. All authors have read and agreed to the published version of the manuscript.

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