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In situ degradation of biodegradable plastic mulch films in compost and agricultural soils

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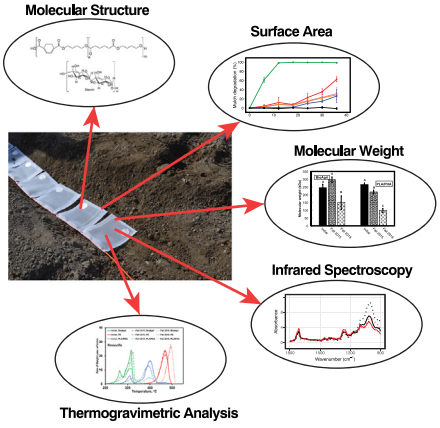
HIGHLIGHTS

- Biodegradable plastic mulches are a promising alternative to polyethylene mulches.
- We evaluated degradation of biodegradable plastic mulches in compost and soil.
- Degradation of biodegradable mulches in soil can take several years.
- Thermal time is a useful predictor for degradation in soils.
- Composting is a viable disposal method for biodegradable mulches.

GRAPHICAL ABSTRACT



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ABSTRACT

The global use of agricultural plastic films, which provide multiple benefits for food production, is expected to grow by 59% from 2018 to 2026. Disposal options for agricultural plastics are limited and a major global concern, as plastic fragments from all sources ultimately accumulate in the sea. Biodegradable plastic mulches could potentially alleviate the disposal problem, but little is known about how well they degrade under different environmental conditions. We quantified the degradation of biodegradable plastic mulches in compost and in soil at warm and cool climates (Tennessee and Washington). Mulch degradation was assessed by Fourier-transformed infrared (FTIR) spectroscopy, molecular weight analysis, thermogravimetric analysis (TGA), nuclear-magnetic resonance (NMR), and mulch surface-area quantification. Biodegradable plastic mulches degraded faster in compost than in soil: degradation, as assessed by surface-area reduction, in compost ranged from 85 to 99% after 18 weeks, and in soil from 61 to 83% in Knoxville and 26 to 63% in Mount Vernon after

Abbreviations: T_g, Glass transition temperature; T_m, Melting point temperature; ATR-FTIR, Attenuated total reflectance Fourier-transformed infrared; PBAT, Polybutylene co-adipate co-terephthalate; PLA, Polylactic acid; PHA, Poly(hydroxyalkanoate); EoD, Extent of Degradation.

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Soil incubation
Mulch degradation
Thermal time

36 months. FTIR analyses indicate that hydrolytic degradation of ester bonds occurred, and a significant reduction of molecular weight was observed. TGA and NMR confirmed degradation of biodegradable polymers. Our results indicate that biodegradable plastic mulches degrade in soil, but at different rates in different climates and that degradation occurs over several years. Faster degradation occurred in compost, making composting a viable disposal method, especially in cool climates, where mulch fragments in soil may persist for many years.

1. Introduction

The use of polyethylene as agricultural mulch is not environmentally sustainable. After deployment in agricultural fields, polyethylene mulches are contaminated with soil and agrochemicals, and therefore often not accepted by recycling facilities (Gonzalez-Sanchez et al., 2014; Steinmetz et al., 2016). Cost of removal and disposal of polyethylene mulch into landfills is high, and disposal facilities are not always readily available (Shogren and Hochmuth, 2004; Kasirajan and Ngouajio, 2012). Further, polyethylene mulch cannot always be completely removed from fields due to weathering that causes embrittlement and fragmentation of plastics (Steinmetz et al., 2016; Yan et al., 2014; Ramos et al., 2015; Zhang et al., 2016). This leads to terrestrial and aquatic pollution with plastic.

Alternative mulch materials, such as biodegradable plastics, could alleviate the environmental and disposal problems, but their sustainable application in agricultural systems will largely depend on their complete degradation and minimal impact on the environment. Biodegradable plastic mulches are intended to be tilled into soil, or removed and composted on-farm after usage; thus, it is important to evaluate their degradation in the environment they are intended to be used, to avoid plastic accumulation (Brodhagen et al., 2017; Sintim and Flury, 2017; Zumstein et al., 2019).

Biodegradation of plastics is usually assessed by measuring the conversion of organic carbon into CO_2 in sealed jars under controlled laboratory conditions (Sander, 2019). Standard tests and criteria have been developed to assure that a plastic is biodegradable in compost or soil. The European standard (EN 17033) for the use of biodegradable plastic mulch films in agri- and horticulture (EN 17033, 2018) requires that at least 90% of the organic carbon of the plastic is converted to CO_2 within two years when incubated in soil, either relative to a biodegradable reference substance (cellulose or poly (3-hydroxybutyrate)) or to the total amount of organic carbon in the plastic. The USDA National Organic Program (USDA-AMS, 2014) requires biodegradable biobased mulch films to (a) be biobased in accordance with ASTM D6866 (specifies 100% biobased carbon content, with 0.1–0.5% relative deviation as instrumental error), (b) degrade to at least 90% based on CO_2 loss in soil within two years or less, as evaluated with ASTM D5988 (ASTM International, 2012b), and (c) meet compostability specifications of ASTM D6400 (ASTM International, 2012a) or ASTM D6868 (ASTM International, 2017).

Under real soil and composting conditions, it is not possible to measure CO_2 release, and so proxy measurements, such as surface area remaining, FTIR spectroscopy, TGA, NMR, or molecular weight analysis, need to be used to assess biodegradation. Such proxy measurements, in combination with the standard laboratory tests, allow us to assess biodegradation in a real soil or compost. While many biodegradable plastics satisfy the standard and test criteria for biodegradation in compost and soil, reports of how well they degrade under real composting and field soil conditions have been inconsistent, partly due to differences in mulch properties and environmental conditions (Kijchavengkul et al., 2010; Koitabashi et al., 2012; Miles et al., 2012; Costa et al., 2014; Li et al., 2014; Dharmalingam et al., 2015; Selke et al., 2015; Moreno et al., 2017).

The main environmental factors that control degradation of biodegradable plastics in compost and soil are temperature, moisture, and microorganisms able to degrade the plastic (Brodhagen et al., 2015). These factors vary with climate, weather, soil type, and management practices. Thus, a biodegradable plastic mulch shown to undergo complete degradation in one environment may not degrade well in another. For example, Li et al. (2014) observed that after 24-month soil burial, mean loss in surface area of a BioAgri Ag-Film and BioTelo Agri, both biodegradable plastic mulches meeting the biodegradability criteria of laboratory tests (ASTM D6400), was 98% at Lubbock, TX, but 53% at Knoxville, TN, and only 6% at Mount Vernon, WA. It is thus important to evaluate degradation of biodegradable plastic films under a variety of environmental conditions.

The objectives of this study were (1) to quantify and assess the degradation of different biodegradable plastic mulches under both compost and soil conditions at two diverse geographic locations and environments, and (2) to determine how environmental conditions affect plastic mulch degradation.

2. Materials and methods

2.1. Study design

The overall design of this study involves the investigation of the in situ degradation of biodegradable plastic mulches in compost and soil. We used biodegradable plastic mulch films under standard agronomic practices and then buried the mulches in compost and soil. The experiment was carried out in two different climatic regions: a humid subtropical climate in Tennessee and a cool mediterranean climate in Washington. The experimental layout was a randomized block design with four replications. We sequentially removed buried mulch and analyzed the mulch with Fourier-transformed infrared spectroscopy, thermogravimetric analysis, molecular weight analysis, and macroscopic surface area. We further tested the mulches for biodegradation by CO_2 emission with a standard laboratory ASTM D5988 test.

2.2. Mulch materials used in experiments

Three commercial biodegradable plastic mulches (BioAgri, manufactured by BioBag Americas, Inc., Dunedin, FL; Naturecycle, manufactured by Custom Bioplastics, Burlington, WA; and Organix, manufactured by Organix Solutions, Maple Grove, MN) and one experimental biodegradable plastic mulch (PLA/PHA, manufactured by Metabolix Inc., Cambridge, MA) were used (Fig. 1). In addition, cellulosic-paper mulch (manufactured by Sunshine Paper Co., Aurora, CO) and a non-biodegradable polyethylene mulch (manufactured by Filmtech, Allentown, PA) were used as control treatments. The mulches were obtained in March–April 2015. BioAgri was produced with N-type Mater-Bi, a product made from polybutylene co-adipate co-terephthalate (PBAT) blended with starch. Naturecycle was produced with a blend of starch and polyesters, and Organix was produced with BASF ecovio grade M2351, which consists of PLA and PBAT. The PLA/PHA (polylactic acid/polyhydroxy alkanoate) experimental mulch consisted of 88.4% MD05-1501 (56% Ingeo PLA from Natureworks (Blair, NE), 24% Mirel™ amorphous PHA, 15% calcium carbonate and 5% plasticizer and processing additives), 10.0% of a masterbatch (20% carbon black in PLA 3052) prepared by Techmer PM (Clinton, TN), and 1.6% PLA. Biobased content of the mulches (BioAgri, 20–25%; Naturecycle, ~20%; Organix, 10%; PLA/PHA, 86%; paper, 100%; and

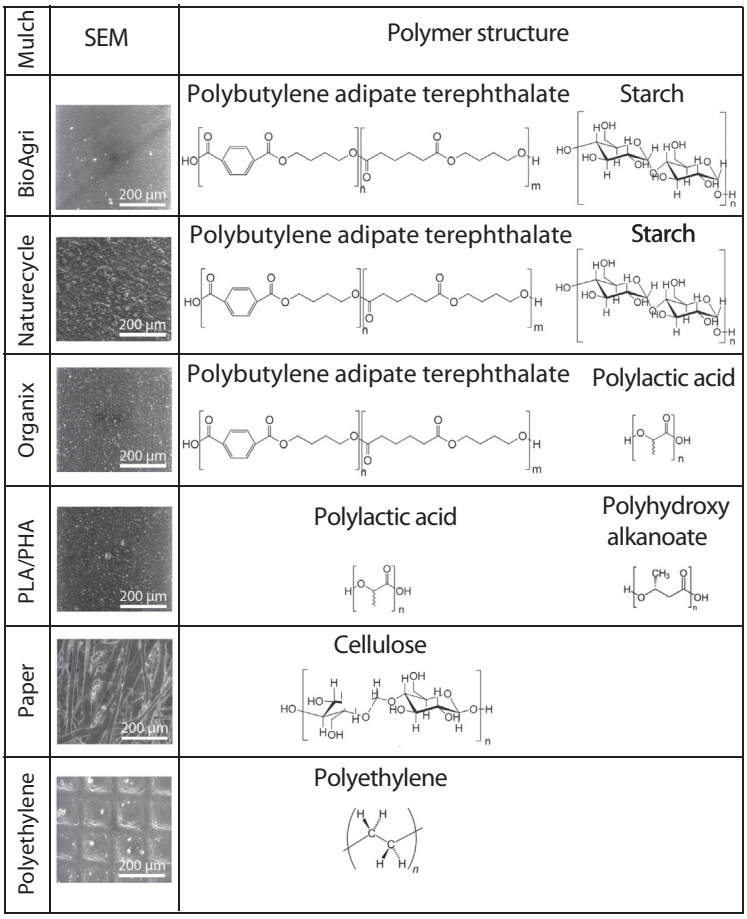

Fig. 1. Scanning electron micrographs of the studied mulches. Plots show the unused mulch surfaces and the chemical structures of their major constituents.

polyethylene, <1%) was provided by the manufacturers (Ghimire et al., 2018).

BioAgri, Organix, PLA/PHA, and the cellulosic paper satisfy the criteria of biodegradation in compost as specified in ASTM D6400 (Organix Solutions, 2017; Greene, 2018; BioBag, 2018; WeedGuardPlus, 2018), which prescribes that >90% of the organic carbon be converted into CO_2 within 180 days of simulated composting under controlled temperature conditions (ASTM International, 2012a). Naturecycle, which according to FTIR spectra (Hayes et al., 2017) contains similar polymers (i.e., PBAT: polybutylene co-adipate co-terephthalate) as BioAgri and Organix, is expected to satisfy ASTM D6400 criteria for composting. The ASTM D5988 test (ASTM International, 2012b) also showed biodegradability of cellulosic paper, BioAgri, and PLA/PHA in soil (SI Appendix "ASTM D5988 Biodegradation Test", SI Appendix Fig. S1). Thus, all our mulches, except polyethylene, are biodegradable in compost and soil based on CO_2 release tests.

2.3. Field deployment and characterization of mulches

The mulches, as received from the manufacturers, were used in field trials with pie pumpkin (*Cucurbita pepo*), green pepper *(Capsicum annuum L.)*, and sweet corn *(Zea mays convar.)* at the University of Tennessee's East Tennessee Research and Education Center in Knoxville, TN and the Washington State University's Northwestern Washington Research & Extension Center in Mount Vernon, WA. Pie pumpkin was grown during the 2015 and 2016 growing seasons. In 2017 and 2018, green pepper was grown in Knoxville and sweet corn in Mount Vernon. Each year after the growing season, the two field sites were planted with a winter wheat cover crop. More details on the field experiments are given elsewhere (Ghimire et al., 2018; Sintim et al., 2019a).

Knoxville has a sandy loam soil (59.9% sand, 23.5% silt, and 16.6% clay), classified as fine kaolinitic thermic Typic Paleudults, whereas Mount Vernon has a silt loam soil (14.2% sand, 69.8% silt, and 16.0% clay), classified as fine-silty, mesic Fluvaquentic Endoaquepts. The mulches were installed mechanically on raised beds arranged in a randomized complete block design with four replications. A no mulch treatment was also included to check for soil changes induced by mulches. Each raised bed was 0.2-m high, 0.8-m wide, and 9-m long, and there were five raised beds per plot.

The mulches used for the degradation study were installed in the field plots in May 2015. Mulch samples were removed from the soil surface in September 2015 after pumpkin harvest, and physicochemical properties of these field-weathered mulches were determined (SI Appendix "Physicochemical Characterization of Mulches", Table S1). Separate pieces of mulch (10 cm × 12 cm) were placed into white nylon meshbags (250-µm mesh opening, Industrial Netting, Inc., Minneapolis, MN). We chose a mesh with 250-µm opening so that we could optimize the capture of mulch fragments that have not been degraded while minimizing loss of fragments falling through the meshbags. We determined from a separate study (SI Appendix "Effect of Meshbags on Mulch Degradation") that the 250-µm opening was large enough to allow access of bacteria and fungi to degrade the mulches (SI Appendix Fig. S2). These meshbags were then installed into compost and soil as described below.

2.4. Composting of mulches

An aerated static pile of compost was built at the Washington State University Research & Extension Center, Puyallup, WA. The compost was prepared using broiler litter (28% vol.), dairy manure solids (28%), fish carcasses (2%), bedding (14%), and yard wastes (28%). The compost

was the same that was used in a previous study where we investigated the release of micro- and nanoparticles from biodegradable plastic mulch films (Sintim et al., 2019b). The feedstock was mixed with water to obtain a gravimetric water content of 55–65% (wt.) and C: N (g/g) ratio of 25–30:1. The compost pile was under cover to protect it from rain, and it was ≈2-m wide × 4-m long × 2-m high. Meshbags containing the mulch pieces were attached along a 4-mm thick nylon string, with each meshbag placed 2 cm apart. Each nylon string consisted of 24 meshbags (six mulch types with four replications that were randomly assigned), and represented one sampling date. Temperature was monitored continuously at different locations at 60-cm depth in the compost pile with TMC50-HD temperature sensors and U12-008 data loggers (Onset Computer Corp., Bourne, MA).

The meshbags were retrieved every two weeks for the first seven sampling times and then after 18 weeks of composting, making a total of eight sampling times. The compost study was carried out in October 2015 to February 2016 and replicated in October 2016 to February 2017, with field-weathered mulch samples from Mount Vernon, WA, only, taken after the field seasons of 2015 and 2016, respectively.

2.5. Soil burial of mulches

To test degradation in soil, the meshbags containing the field-weathered mulches from the 2015 growing season were buried at Knoxville, TN, and Mount Vernon, WA, in October 2015. The meshbags were attached to a 4-mm thick nylon string and aligned, with each meshbag placed 2 cm apart, with six meshbags per plot so that we could sample them destructively six times. The meshbags were placed at about 10-cm depth in the respective plots from where they were sampled. Thus, the meshbags were in soil directly underneath laid mulches during the subsequent growing season. Paper mulch could not be retrieved from the Knoxville field in October 2015 because it had disintegrated during the growing season. To test the degradation of paper mulch in Knoxville, we buried weathered paper mulch from Mount Vernon in Knoxville in May 2018.

The meshbags were sampled for analysis at 6-month intervals for 3 years. During major field operations each year, such as tillage, the meshbags not yet sampled were temporarily removed from the soil, placed in plastic bags, stored in a refrigerator at 4 °C, and re-buried within two weeks. We do not expect that removal of meshbags from soil causes an artifact because tillage also will loosen soil and detach plastic mulch from soil aggregates. Soil water content, temperature, and selected soil properties were measured as outlined in the SI Appendix "Measurement of Soil Properties".

2.6. Thermal time calculation

Thermal time (τ) accumulated during composting and mulch incubation in soil was calculated as (Campbell and Norman, 1998):

$$\tau = \sum_{i=1}^{n} \left(\frac{T_{\max,i} + T_{\min,i}}{2} - T_{\text{base}} \right) \Delta t \quad (1)$$

where $T_{\max,\,i}$ and $T_{\min,\,i}$ are daily maximum and minimum compost or soil temperatures at a given day i, n is the total number of days, Δt is the time increment of 1 day, and T_{base} is the base temperature, which was set at 0 °C. A 0 °C base temperature was chosen because microbial activity is suppressed considerably at subzero temperatures. The compost and soil temperatures are chosen as the ones measured at the location of the meshbags in the compost and in the soil at 10-cm depth. Thermal time was set to 0 °C-day if the average temperature for a given day was below the base temperature.

2.7. Measurement and quantification of mulch degradation

After removal from soil, the surface area of the mulch was measured by image analysis (SI Appendix "Estimation of Mulch Degradation in Soil"). The percentage of visual mulch degradation was then plotted as a function of time. In addition, we calculated the extent of degradation (EoD) as:

$$\text{EoD} := \frac{1}{t_{\text{tot}}} \int_0^{t_{\text{tot}}} f(t)\,\mathrm{d}t \quad (2)$$

where t is time, t_{tot} is total time the mulches were exposed to degradation, and $f(t)$ is the fraction of visual mulch degradation as a function of time. We use this function to better capture the dynamics of the degradation, rather than the cumulative loss of film surface area at time t_{tot}, where mulches may approach a similar level of degradation. The EoD ranges from 0 (no degradation) to 1 (immediate complete degradation).

Mulch degradation was further assessed by attenuated total reflectance FTIR spectroscopy, NMR, TGA, and molecular weight analysis. FTIR spectra (4000–600 cm^{-1}) were obtained with a IRAffinity-1 spectrometer (Shimadzu Co., Tokyo, Japan) equipped with a single reflection ATR system (MIRacle ATR, PIKE Technologies, Madison, WI). A resolution of 2 cm^{-1} and 16 scans per spectrum were used. Peak assignment was done according to Hayes et al. (2017). TGA was done with a Discovery TGA (TA Instruments, New Castle, DE) at a heating rate of 10 °C min^{-1} from room temperature (25 °C) to 600 °C in an unsealed platinum sample pan and an N_2 atmosphere. Weight-averaged molecular weight was measured by Gel permeation chromatography as described in Hayes et al. (2017). We measured the unused mulches, the field-weathered mulches, and the mulches retrieved from the fields in Fall 2018 and after 36-month of burial. Mulches were cleaned prior to measurements to remove soil impurities (Hayes et al., 2017).

2.8. Statistical analyses

Analysis of variance was performed for the calculated EoD and molecular weight data. Significance and mean comparisons (performed with the adjusted Turkey multiple comparison) were determined. To test effects of mulch treatments on enrichment of bacteria and fungi, we used a paired t-test on initial and final 16S and ITS gene copy numbers from Fall 2015 and Fall 2018. All gene copy numbers were log-transformed prior to analyses. A paired t-test was also used to compare the bacterial and fungal abundances between Tennessee and Washington for Fall 2015 season. Significance of all analyses were assessed at $P = 0.05$.

3. Results

3.1. Mulch degradation in compost

In compost, all biodegradable plastic mulches degraded at least 95% in 2015 and 85% in 2016 based on surface area measurements (Fig. 2A, C). PLA/PHA degraded rapidly within the first two weeks. The paper mulch did not degrade within the first 12 weeks in 2015 or within the first six weeks in 2016; but it degraded rapidly thereafter, reaching >85% degradation after 18 weeks both years. The temperature in the compost increased rapidly within a few days to about 80 °C, which likely impeded the activity of fungi, the major decomposers of cellulose. Indeed, degradation of cellulose began when the compost temperature decreased below about 55 °C (Fig. 2A,C, SI Appendix Fig. S3). Mulch degradation showed a strong correlation with thermal time, with a considerable lag period for the paper mulch, reflecting the time when temperatures were too high for cellulose degradation (Fig. 2E).

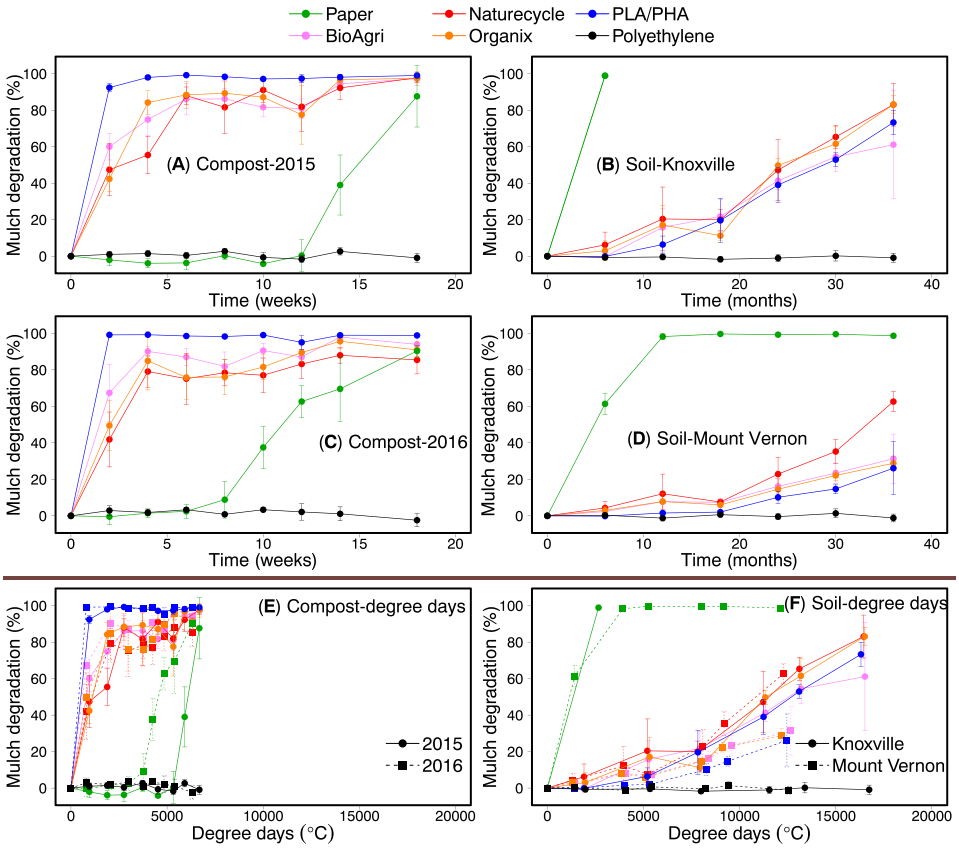

Fig. 2. Visual mulch degradation in compost and soil. A,C: in compost in 2015 and 2016; B,D: in soil in Knoxville, TN and Mount Vernon, WA. Points are slightly offset the *x*-coordinate to facilitate visibility of the standard deviations. The time axis for the soil degradation starts in October 2015, except for paper mulch in Knoxville that was first buried in May 2018; each 6-month period represents an alternating cold and warm season. Plots E and F show visual mulch degradation as a function of thermal time. Error bars are standard deviations of the mean (n = 4).

3.2. Mulch degradation in soil

In soil, the rate of degradation of the biodegradable plastic mulches was low initially and increased after about 1.5 years (Fig. 2B,D, Table 1). In contrast to the paper mulch, which degraded about 100% within 1 year, the biodegradable plastics showed degradation of only 20% in Knoxville and 15% in Mount Vernon within 1 year. Over the 3 years of the study, the biodegradable plastic mulches degraded continuously, with a pronounced seasonal pattern of increased degradation during summer.

Among the biodegradable plastic mulches, PLA/PHA degraded the slowest during the initial stages (Fig. 2B,D). However, it degraded more rapidly thereafter, becoming equivalent to the other biodegradable plastics (Fig. 2B,D).

The calculated extent of degradation (Eq. (2)) of the mulches in soil was similar among the biodegradable plastic mulches in Knoxville, but significant differences were found in Mount Vernon: Naturecycle > BioAgri = Organix > PLA/PHA (Table 1).

The paper mulch underwent rapid degradation in Knoxville and Mount Vernon, reaching ~100% degradation after six months of soil incubation in Knoxville and 12 months of soil incubation in Mount Vernon (Fig. 2B,D). This is consistent with known reports that cellulose undergoes relatively higher degradation in soil than polyesters, such as PBAT and PLA (Brodhagen et al., 2015; Miles et al., 2017). The comparative rate of biodegradation of pure polymers in soils has been reported as high (starch), to moderately high (cellulose), to moderate (PHA), to low moderate (PBAT), to low (PLA), and extremely low (polyethylene) (Brodhagen et al., 2015; Miles et al., 2017), which is consistent with our observed mulch degradation.

Bacterial and fungal abundances did not change in Knoxville during the experimental period; but in Mount Vernon, both bacterial and fungal abundances increased from Fall 2015 to Fall 2018 (SI Appendix

Table 1
Calculated extent of degradation (EoD, Eq. (2)) of the mulches after burying in compost for 18 weeks and in soil for 3 years. Note that only mulches from Mount Vernon were composted.

Mulch	Compost (18 weeks)		Soil (24 months)	
	2015	2016	Knoxville	Mount Vernon
BioAgri®	0.787 ± 0.031b	0.839 ± 0.032b	0.265 ± 0.056a	0.121 ± 0.016c
Naturecycle	0.757 ± 0.044b	0.735 ± 0.022c	0.327 ± 0.087a	0.189 ± 0.027b
Organix	0.790 ± 0.033b	0.781 ± 0.057bc	0.301 ± 0.039a	0.113 ± 0.020c
PLA/PHA	0.921 ± 0.007a	0.941 ± 0.005a	0.247 ± 0.009a	0.069 ± 0.012d
Paper	0.146 ± 0.038c	0.348 ± 0.031d	na	0.850 ± 0.006a
Polyethylene	0.007 ± 0.012d	0.016 ± 0.009e	−0.007 ± 0.008b	0.000 ± 0.003e

Values represent the mean ± standard deviation (n = 4). Within each year of composting and site (columns), means followed by same letter(s) are not significantly different. na: Paper mulch samples were not available to be buried in Knoxville because they underwent complete disintegration after deployment in the field.

Table S2). However, these changes cannot be attributed to tilled-in biodegradable mulches, because the same changes were also observed for the treatment where no mulch was applied.

All mulches underwent changes in FTIR spectra due to soil burial (Fig. 3). For PLA/PHA, the –OH bending and stretching regions (1082–1052 cm^{-1}, 1076–1000 cm^{-1}) increased after soil burial, particularly at Mount Vernon, reflecting hydrolysis of ester bonds. In addition, the COO stretching region (1800–1700 cm^{-1}) became narrow, with a maximum occurring at 1760 cm^{-1} and the portion of the band between 1700 and 1750 cm^{-1} decreasing. These results likely represent the preferred utilization of PHA as a carbon source, leading to a relative increase of PLA's carbonyl band (~1760 cm^{-1}) and decrease of PHA's carbonyl band (~1720 cm^{-1}) (Rudnik and Briassoulis, 2011; Hablot et al., 2014). This is consistent with observed increase of PLA's mass fraction and decrease of PHAs fraction observed via NMR analysis (Fig. 4A). The three commercially-available PBAT-based mulches underwent more substantial spectral changes due to incubation in the soil: decrease of peak intensities at 1750–1650 cm^{-1} (COO stretching) and 1450–1300 cm^{-1} (C-H_2 bend) and increase of intensities between 1127 and 800 cm^{-1} (C—O stretching), suggesting hydrolysis of these mulches (Hayes et al., 2017). For the polyethylene mulch, the spectral band occurring at 1127–800 cm^{-1} is attributable to photochemical reactions that occurred during the 2015 field season. After soil burial, these peaks disappeared, but we do not know the reason for this.

Thermogravimetric analyses indicate that soil burial led to a shift to higher temperatures of main heating stages of PLA/PHA and polyethylene mulch (Fig. 5). This is likely caused by minor components present in soil or water or those leached out from the mulches (Hayes et al., 2017). Peaks for the two main heating stages occur at 270 °C and 320 °C, which represent PHA and PLA, respectively. An increase in temperature for various heating stages of a material can also reflect an increase of a component's thermostability due to the formation of cross-links (Hayes et al., 2017). Peak of PBAT heating stage (390 °C), one of the main polymeric components of BioAgri, decreased and shifted to lower temperature after soil burial. This trend likely reflects a loss of molecular weight. However, for starch's heating stage (310 °C), the peak shifted to higher temperature and eventually started to even out after longer duration of soil burial. This reflects the utilization of lower molecular weight and lower crystalline morphological regions of the plastic mulch as a carbon source by microorganisms throughout the soil burial of 36 months.

Soil burial of mulches increased the weight (%) remaining at 600 °C as determined by TGA (Fig. 5). Any residual material remaining at 600 °C is likely due to inorganic components of the mulch or soil particulates adhered to the mulch, and is expected to increase in relative percentage if biodegradation of polymers occurs. After soil incubation, the weight % remaining at 600 °C was highest after 36 months of burial, for both BioAgri (63% and 41%) and PLA/PHA (35% and 28%) in Knoxville and Mount Vernon, respectively. Polyethylene did not show a weight change at 600 °C after soil burial.

The molecular weights of the polymers in BioAgri and PLA/PHA decreased substantially after soil burial in both Knoxville and Mount Vernon (Fig. 4B), suggesting degradation of the plastic polymers in the mulches.

4. Discussion

4.1. Environmental effects on degradation

The biodegradable plastic mulches degraded to a greater extent in soil in Knoxville than in Mount Vernon, which can partly be attributed to the greater weathering of biodegradable plastic mulches in Knoxville before incubation in soil (Hayes et al., 2017). Degradation was higher during the summer than in winter because the warmer temperatures promoted microbial activities. Irrigation during the summer provided sufficient moisture to keep water content, and correspondingly water potential, high each year. Thus, microbial activity was not limited by water during the summer (SI Appendix Figs. S4 and S5).

Degradation over time and across the two locations showed significant positive correlation with thermal time (Fig. 2F). After

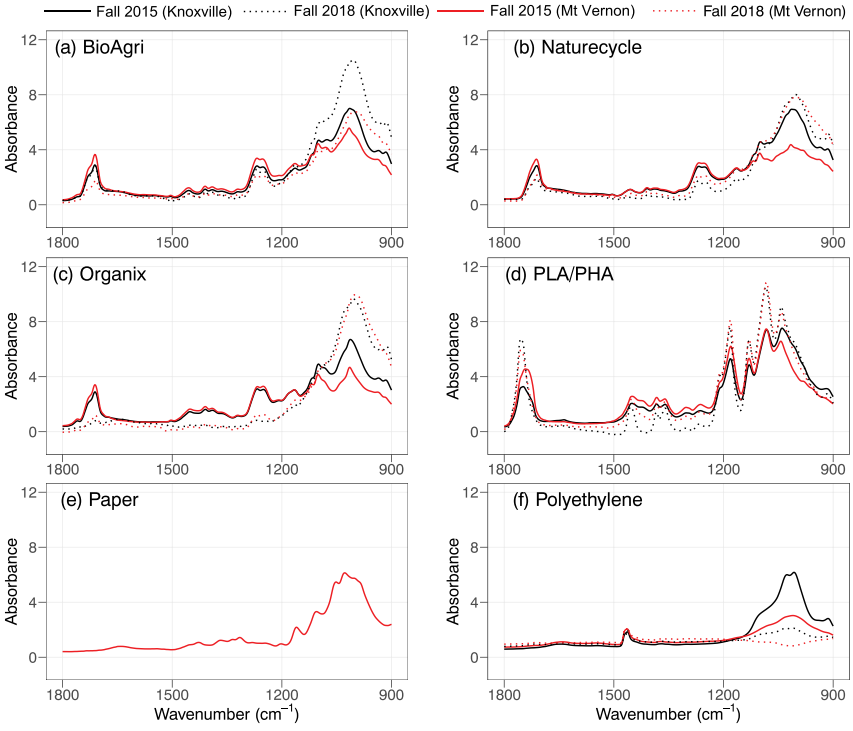

Fig. 3. Fourier-transformed infrared absorbance spectra. Spectra show the different mulches (initial, after 6-month field-weathering, and after 36-month soil burial) at Knoxville, TN and Mount Vernon, WA. Paper mulch was only available for analysis at Mount Vernon in Fall 2015, as it had deteriorated in Knoxville during the 2015 growing season and after soil burial at Mount Vernon. Data for Organix represent Fall 2016 rather than Fall 2018, because sufficient material could not be collected for analysis in Fall 2018.

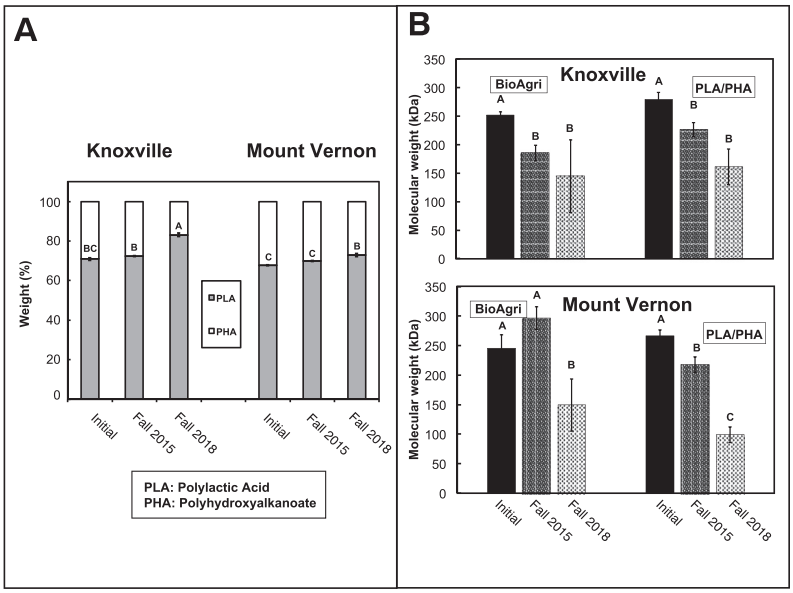

Fig. 4. NMR and molecular weight analysis. A: Relative mass percentages of PLA and PHA in PLA/PHA mulch determined by NMR analysis, showing the change of the distribution of PLA and PHA in the mulch at different sampling dates. B: Molecular weight of mulches (initial, after 6-month field-weathering, and after 36-month soil burial). Molecular weight refers to weight-averaged molecular weight. Only BioAgri and PLA/PHA were analyzed for molecular weights. Error bars are standard deviations of the mean, capital letters indicate significant differences among time for each mulch treatment at each location.

2 years, the degradation rate increased for biodegradable plastic mulches even during the winter period, especially in Knoxville. This is likely due to significant depolymerization and fragmentation of the mulches after the initial 2-year period, which increased their specific surface area.

Thermal time in Knoxville was 33% higher than in Mount Vernon, and mulch degradation in terms of surface area was two times higher in Knoxville than in Mount Vernon. Correlation of mulch degradation with thermal time calculated using air temperature did not differ much from thermal time calculated using soil temperature, and thermal time in soil was similar among the mulches; therefore, only the correlations with soil temperatures are shown in Fig. 2F. The variations in mulch degradation between Knoxville and Mount Vernon are much reduced when plotted as a function of thermal time rather than calendar time, indicating that temperature explained a substantial portion of the mulch degradation in soil.

Temperature has a major effect on the activity of microorganisms, which are ultimately responsible for the mulch degradation in soil. Initial soil conditions showed that the enzyme activity was less at Knoxville compared to Mount Vernon (SI Appendix Table S3), but microbial abundances were similar at both sites (SI Appendix Table S4), and there was no significant increase in microbial abundance in Knoxville that might explain an increased capacity for biodegradation (SI Appendix Table S2).

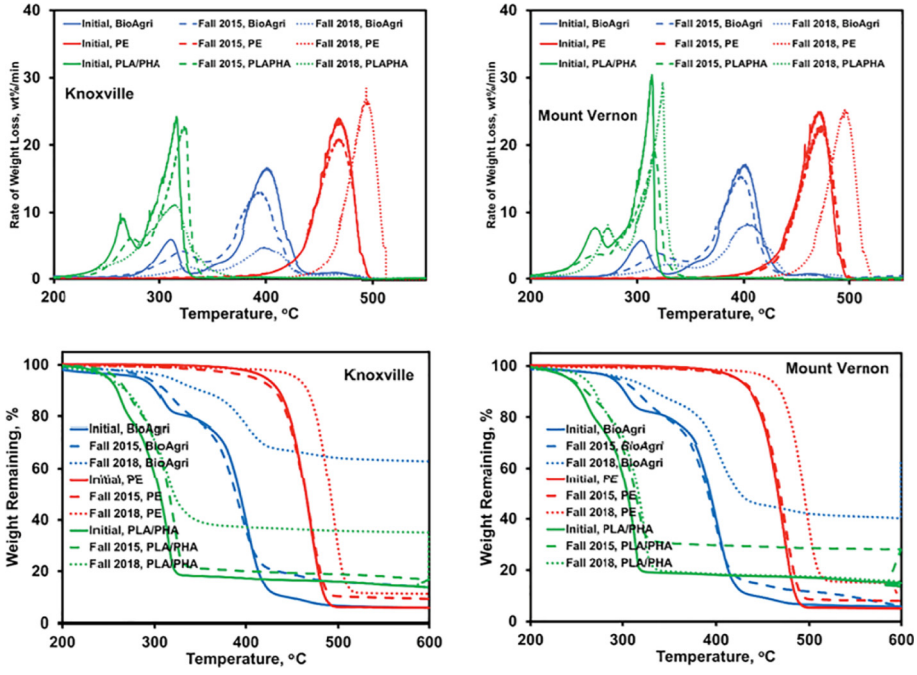

Fig. 5. Thermogravimetric analysis. Thermograms (top) and differential thermograms (bottom) of polyethylene, BioAgri, and PLA/PHA mulches.

The greater mulch degradation in Knoxville was therefore most likely due to the higher temperatures. However, since we observed different bacterial community structures between the two sites, it is possible that some of the difference in degradation rates may be attributed to having different soil bacterial taxa present at the two locations (SI Appendix Fig. S6).

4.2. Interpretation of mulch degradation in compost and soil

Degradation of the biodegradable plastic mulches is affected by mulch physicochemical properties, abiotic, and biological processes. For instance, PLA/PHA degraded more rapidly than BioAgri, Naturecycle, and Organix in compost, but degraded more slowly in soil. Degradation of PLA polymers is known to be limited at ambient environmental temperatures (Lyu et al., 2007; Tsuji et al., 2001; Farrar, 2008). PLA degradation occurs by hydrolysis of C—O ester linkages and enzymatic biodegradation (Kale et al., 2007). However, the high glass-transition temperature of PLA/PHA (T_g=49.2°C (Hayes et al., 2017)) inhibits the mobility of polymer chains at ambient temperatures, making them less accessible for biodegradation (Lyu and Untereker, 2009). Indeed, in soil the temperatures were well below T_g, whereas in compost they were above T_g during the active phase of composting; thus the PLA/PHA mulch more readily degraded in compost.

Soil moisture was not a limiting factor for mulch degradation during summer, which is the most active period for degradation, because the fields were irrigated. During winter, high soil moisture was likely limiting microbial activity, particularly in Mount Vernon, where soils became anoxic. Nonetheless, the biodegradable plastic mulches kept degrading during the winter season, likely during periods where soil temperatures were higher than 0 °C and soils were unsaturated.

The thermal time plots (Fig. 2E,F) suggest that, while temperature can explain a large portion of the variability in mulch degradation between Knoxville and Mount Vernon, other factors are important as well. One possible contributing factor is the difference in weathering when the mulches were exposed to environmental conditions during the growing season. Greater degree of photodegradative, hydrolytic, and oxidative degradation occurring at Knoxville during the growing season likely rendered the mulches more susceptible to microbial degradation after the mulches were buried in the soil.

The concave shape of the mulch degradation curves for soil (Fig. 2) further suggests enhanced degradation of the biodegradable plastics with time, likely because of increased depolymerization and fragmentation, which results in an increase in specific surface area. We fitted a second-order polynomial function to the experimental data (SI Appendix "Estimation of Mulch Degradation in Soil"). Overall, the dynamics of degradation of the biodegradable plastic mulches was well depicted by the function (SI Appendix Fig. S7 and Table S5). If we extrapolate mulch degradation with the function, we estimate that the biodegradable plastic mulches would attain 100% degradation after 38–46 months (or 15,700–19,800 °C-day) in Knoxville, and 48–74 months (or 14,100–23,100 °C-day) in Mount Vernon (Table 2). The similar thermal time requirement for complete mulch degradation at the two sites suggests that thermal time is a better predictor of mulch degradation than calendar time.

Table 2
Time for degradation. Estimated thermal time and calendar time to 100% degradation of the biodegradable plastic mulches in soil at Knoxville and Mount Vernon.

Mulch	Thermal time (°C-day)		Calendar time (months)	
	Knoxville	Mount Vernon	Knoxville	Mount Vernon
BioAgri	19,826	21,956	46.2	62.9
Naturecycle	16,026	14,142	38.5	47.5
Organix	15,725	23,139	38.1	72.4
PLA/PHA	16,805	21,989	40.4	74.0

5. Limitations and implications

Meshbags were temporarily removed from the soil during tillage operations, and this prevented physical disturbances to the mulches that occur during tillage; however, the mulch samples buried were small and well embedded into the soil after tillage, so that the lack of tillage in the presence of mulch would not have affected mulch degradation. Further, activities of meso- and macroorganisms that could have facilitated degradation of the mulches (Zhang et al., 2018) were inhibited because the meshbags did not allow access for such organisms. The meshbags themselves protected the mulches to some extent from degradation by reducing the surface area available for degradation. However, the rapid degradation of paper mulch in meshbags within 12 months in soil, consistent with previous studies (Miles et al., 2012; Li et al., 2014), suggests that the meshbags did not significantly impede degradation.

The measurement of degradation in this study (reduction in surface area by visual assessment, FTIR, TGA, NMR, and molecular weight analyses) is not equivalent to actual biodegradation, but a good proxy. The standard for measuring biodegradation would be to quantify the amount of organic carbon from the mulches converted to CO_2; however, that is not possible under in situ composting and soil conditions. While it is known that the biodegradable plastics used in our study indeed undergo biodegradation in laboratory tests (e.g., ASTM D5338, D5988), their incomplete macroscopic disintegration in field soil after 36 months is indicative of incomplete biodegradation.

Laboratory tests for biodegradation in compost and soil often use plastic polymers in powder form (ASTM International, 2015; ASTM International, 2012b; EN 17033, 2018), which increases the degradation rate as compared to when entire plastic film pieces are tested (Tosin et al., 2019). Slower degradation is thus expected in agricultural fields where plastic is present in the form of films.

Macroscopic degradation of the biodegradable plastic mulches after 36 months in soil ranged from 61 to 83% in Tennessee and from 26 to 63% in Washington. This low level of degradation, particularly in cooler climates like in Washington, raises questions about whether the application of biodegradable plastic mulches will be sustainable in the long-term when the mulches are repeatedly tilled into the soil. Plastic mulch may persist in the environment for longer periods when mulch fragments are washed into water bodies by soil erosion, or when fragments leach from the actively degrading topsoil into less degrading subsoil. Nonetheless, extrapolation of our data suggests that, given sufficient time, the biodegradable plastic mulches will likely degrade completely in soil.

Paper mulch degraded well in soil: ~100% macroscopic degradation occurred in both the warmer and cooler site in less than 12 months. While the biodegradable plastics did not degrade as well as paper in soil, they did degrade well in compost, making composting a viable disposal method, particularly in locations where soil degradation is slow.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

H.S., A.B., C.M., M.F. conceived and designed research; H.S., M.F. led overall study; H.S., M.F. wrote manuscript and analyzed data; H.S., A.B., M.F., M.E., S.B., S.S., J.D. conducted composting and soil experiments and analyses; D.H., L.W., M.A. contributed FTIR, molecular weight, NMR, TGA, ASTM 5988; all co-authors contributed to data interpretation and editing.

Appendix A. Supplementary data

Supplementary information includes details on ASTM D5988 test, mulch and soil characterization, meshbag study. Supplementary data to this article can be found online at doi: https://doi.org/10.1016/j.scitotenv.2020.138668.

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