

The Bioplastic Library of Polymers (BLoP): A Raman and μ ATR-FTIR Spectroscopy Library for Detection of Bioplastics

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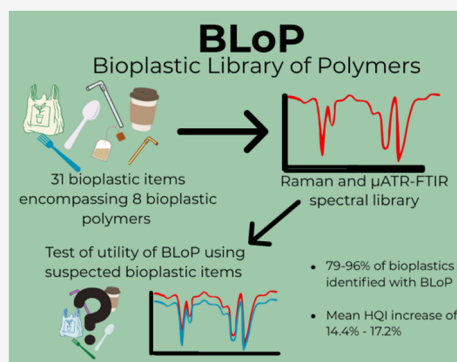
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ABSTRACT: Bioplastics, biobased or biodegradable polymers, have begun to be adopted as an alternative to petroleum-based plastics. Despite their growing use, research on the occurrence of these materials in the environment as pollution is nascent. Here, we provide a library of bioplastic spectra known as the Bioplastic Library of Polymers (BLoP), intended to improve the detection of bioplastic materials in environmental samples by using Raman spectroscopy and attenuated total reflectance Fourier transform infrared spectroscopy (μ ATR-FTIR). BLoP contains spectra collected from 31 items across 8 different bioplastic polymers acquired from a variety of consumer goods currently on the market. We used samples of suspected bioplastics to validate the ability of BLoP to identify bioplastics. Using our library, we were able to confirm the material type as bioplastic for 79% of samples with Raman and 96% of samples with μ ATR-FTIR. When testing these suspected bioplastic samples with BLoP and other standard commercial libraries, 75 and 73% of the top five library matches were entries from BLoP for Raman and μ ATR-FTIR, respectively. This library is intended to be used in conjunction with other commercial and open-access libraries to improve the detection of bioplastic materials in the environment.

KEYWORDS: bioplastics, polymers, spectroscopy, microparticles, microplastics, materials



1. INTRODUCTION

With the immense global issue of plastic pollution,¹ demands for more sustainable alternatives to replace petroleum-based plastics have grown.² Emerging alternatives to traditional plastic polymers are bioplastics. The term “bioplastics” encompasses a variety of different materials, either defined by the material being biodegradable and/or being composed of biological materials.³ From this definition, bioplastics can be classified into three main groups: (1) nonbiodegradable bioplastics that are biobased or partly biobased; (2) biodegradable biobased bioplastics; or (3) biodegradable fossil fuel-based bioplastics.³ This broad definition allows for a variety of different materials to be considered bioplastics, with novel polymers continuously being developed.

Though they only represent about 0.5% of plastics being produced annually, global production capacity for bioplastics is growing across different sectors.⁴ Estimates suggest that global production capacity is expected to more than double from 2.47 million tonnes as of 2024 to 5.73 million tonnes by 2025.⁴ Common types of bioplastics include polylactic acid (PLA), polyhydroxyalkanoates (PHAs), polybutylene succinate (PBS), thermoplastic starches (TPS), poly(butylene adipate-co-terephthalate) (PBAT), and others made from corn and soy proteins. PLA currently dominates the global market for bioplastics, with 37.1% of bioplastic global production, but other bioplastics are also growing in use.⁴ Bioplastics are being

adopted into various markets globally, used for many products including flexible and rigid packaging materials, fibers, and consumer goods like three-dimensional (3D) printing filaments.^{4,5}

While bioplastics have been proposed to be a sustainable alternative to traditional fossil fuel-based plastics, the sustainability of bioplastics has been challenged due to the variability of how these materials break down at the end of their use.^{6,7} Many bioplastics require specific environmental conditions to break down (e.g., certain pH, temperature, and aerobic conditions) and often only degrade in an industrial composting environment.⁸ Not all regions have the industrial composting infrastructure required to break down these materials, and outside of these conditions, bioplastics may not degrade as intended by the manufacturer. If these materials are not disposed of correctly, such as entering landfills or the environment, their degradation may vary in speed and completeness depending on the environment, item thickness, additives, and polymers.^{7,9} In some cases, during degradation,

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bioplastics may produce microparticles, like the microplastics generated from plastic items.^{10–13}

Though bioplastic materials are known to shed microsized particles when the conditions for full degradation to their original monomers are not present (e.g., industrial composting), few studies of environmental matrices have documented the presence of microbioplastics.¹⁴ This is in part due to inadequate analytical methods to detect microbioplastics.^{9,14} In addition, few studies have assessed the impacts these microsized bioplastic particles may have on organisms.¹⁵ Of the few studies using microbioplastics, some suggest that they may cause harm to organisms.^{16–18} For example, a review of studies investigating the impacts of microbioplastics in marine systems concluded that they have similar effects to microplastics.¹⁹ However, these studies are limited in testing a few taxa and predominantly use PLA and PBAT. These gaps indicate that more research is required to assess the fate and ecotoxicological impacts of bioplastic particles in the environment.

Spectral reference libraries allow for improved detection of materials and polymers of anthropogenic particles in environmental samples. In addition, reference libraries allow for verification of materials used in toxicity tests, allowing researchers to meet QA/QC requirements.²⁰ The use of these libraries has been demonstrated to improve success in identifying microparticle materials.^{21–23} For instance, when tested in comparison to standard commercial libraries available for Raman spectroscopy, the use of SLoPP/SLoPP-E accounted for 63% of the top five matches of particles.²³ Currently, few samples of bioplastics are included in open-access libraries. No bioplastic spectra are in SLoPP/SLoPP-E, eight PLA entries are included in FLoPP/FLoPP-E, and two PLA entries and one polyhydroxy butyric acid (PHB) entry are in the Primpke database.^{22–24} Okoffo et al. developed a comparable resource to assess five bioplastic polymers using pyrolysis–gas chromatography–mass spectrometry, but the same kind of resources have not been produced to analyze bioplastics with Raman spectroscopy or Fourier transform infrared (FTIR) spectroscopy.²⁵

Here, we present an open-access spectral library for the detection of bioplastic polymers: Bioplastic Library of Polymers (BLoP). We created two versions of this library: one for use with FTIR and the other for Raman spectroscopy. Items used to make this library were obtained from a variety of sources, including product packaging, single-use foodware, and other consumer goods. Library items were collected to represent some of the diversity of bioplastics currently available on the market (different bioplastic polymers, colors, sources, uses, etc.) as best we could. The efficacy of BLoP was validated using materials that were both suspected to be and not suspected to be bioplastics (e.g., samples from other projects or items on the market). We created this library to provide reference spectra that will improve researchers' ability to accurately identify bioplastics in samples of macro- and microplastics.

2. METHODS

2.1. Particle Preparation

Bioplastic materials for BLoP were collected opportunistically from three different sources in Toronto, Ontario, Canada, between April and August 2025 (Supporting file: [BLoP Itemized Table](#)). In total, 31 items were used to create BLoP. To provide a library that is robust to what might be encountered in environmental samples, we attempted

to collect a diverse range of bioplastics representing different colors, morphologies, and polymers currently on the market. Some bioplastic samples were single-use straws collected from Toronto food service businesses ($n = 5$). Straws were only used in the library if they were labeled with the bioplastic compound they were made from. Other samples were consumer products purchased from online vendors ($n = 17$). Finally, some bioplastic samples were reused from the creation of the FTIR library of plastic particles (FLoPP) ($n = 8$).²² For researchers working with FLoPP already, we created an FTIR version of BLoP without these eight entries to avoid duplication (in addition to a version of the library with them included for researchers not using FLoPP). Each item was documented with relevant metadata: source (i.e., where purchased from, reused from FLoPP, or what food service business collected from), brand name, color, and collection date.

To prepare library items to be analyzed, we cut a small piece (<5 mm) from each item and mounted the piece on double-sided sticky tape on a sheet of clear acetate stored in a Petri dish. Each piece was circled and labeled with its own unique sample ID.

2.2. Raman Spectroscopy Analysis

To create the Raman spectral library, we used a HORIBA XploRA PLUS Confocal Raman Microscope. The instrument is equipped with 785 and 532 nm excitation lasers and a Charged Couple Device (CCD) detector (−60 C, 1024 × 256 pixels). Following recommendations provided in Munno et al., only the 532 nm laser was used to acquire spectra for the library to improve the signal-to-noise ratio and allow for inclusion of the C–H stretching region, which can be used to identify polymers without being confounded by dye signatures.²³ All spectra were collected with the 100× Long Working Distance (LWD) objective. The maximum laser power of the instrument was 14.7 mW for the 532 laser with 100× LWD. Each day prior to use, the instrument was calibrated using a silicon sample. From each bioplastic sample, three spectra were collected from randomly chosen spots on the sample, and the best quality spectra were used for the library (based on the size of peaks relative to the baseline). Matches for each library item were generated using ParticleID software with standard libraries and SLoPP and SLoPP-E installed (Table S1).²³

For each sample, starting setting recommendations from Munno et al. were followed (i.e., 532 nm laser, 1500 nm grating, 25–50% filter, 4 s acquisition time, 4 s accumulation, 100 μm slit, 300 μm hole size, 0 s delay time).²³ All library sample spectra were collected using the 532 nm laser with a 1500 nm grating, but some deviations to the other parameters were made on a case-by-case basis. We collected spectra from the 200–3500 cm^{−1} range. Minimal baseline corrections were applied, if necessary. For each library entry, the parameters used to acquire the spectra were recorded, and LabSpec6 (.l6s) and text (.txt) files were saved.

2.3. μATR-FTIR Spectroscopy Analysis

To create the μATR-FTIR version of the spectral library, we collected spectra using a Nicolet iN10 infrared microscope (Thermo Fisher Scientific) using a cooled detector in attenuated total reflectance (ATR) mode (15× objective, 0.7 numerical aperture) with a germanium ATR tip. A background spectrum was automatically collected every 300 min and was also taken between each sample. Between samples, the germanium tip was wiped with 70% ethanol on a KimWipe or lens cleaning cloth to remove any residues from the previous sample. Settings used to acquire spectra were 8 cm^{−1} resolution, 32 scans, and a 4000–675 cm^{−1} range. From each sample, at least two spectra were collected from randomly chosen spots. The best spectra (minimal noise and clear peaks) out of those taken for each sample was used in the library. Matches for each sample were determined using OMNIC Picta software (Thermo Fisher Scientific) with standard libraries provided by Thermo Fisher Scientific as well as the Primpke Polymer Library and FLoPP/FLoPP-E (Table S1).^{22,24}

2.4. Library Creation

For both versions of the library, library entries were generated for each sample to include an identifier that it is a bioplastic material, the base material or polymer abbreviation, sample number, color, item,

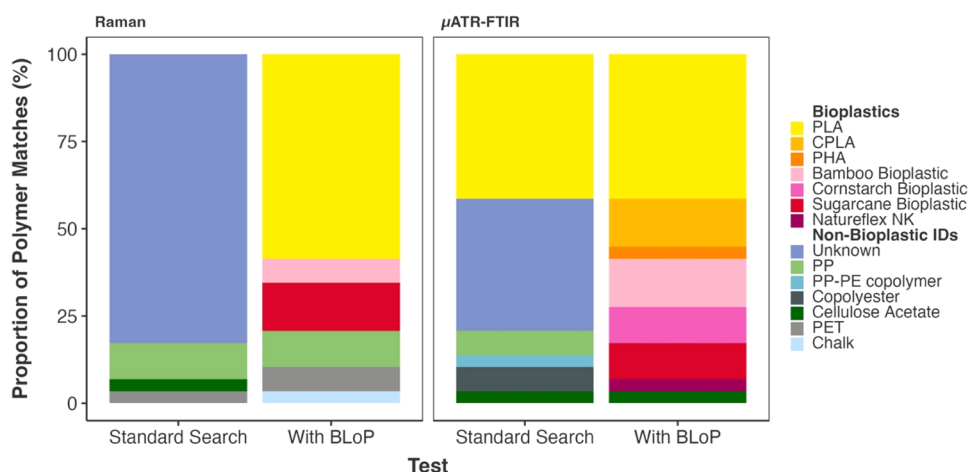


Figure 1. Proportion (%) of polymer matches for the samples used for validation of BLoP analyzed with Raman (left panel) and μ ATR-FTIR (right panel) with just standard libraries and with BLoP in addition to the standard libraries. Bioplastic matches are shown in warm colors, nonbioplastics are shown in cool colors, and samples with no conclusive match (unknown) are shown in purple.

and morphology (e.g., “PHA Bioplastic 1. Blue Straw Fragment” or “Sugarcane Bioplastic 1. Brown Cutlery Fragment”). Note that numbering restarts for each bioplastic material type (e.g., PLA samples 1–18, sugarcane bioplastic samples 1–3). The material of the items in the library was based on labeling by the manufacturer. We tried to validate that materials used in the library were labeled accurately by analyzing each item via μ ATR-FTIR and Raman with standard libraries loaded. This validation test of library materials was unsuccessful due to a lack of pre-existing matches to use (i.e., there were no bioplastics in the Raman libraries that we could validate with prior to the creation of the library).

In some cases, bioplastic items we collected to be used in the library were indistinguishable from traditional fossil fuel-based polymers ($n = 5$) (Figures S1 and S2). For instance, some straws that were labeled as being composed of agave matched library entries as polypropylene (Figures S1 and S2). To avoid conflating bioplastics and nonbioplastics for library users, we chose to exclude these five items from BLoP.

2.5. Testing the Application of the Library

To test the utility of the library to improve spectral matching, we used samples of suspected bioplastics ($N = 29$) separate from those used to create the library. Some of these suspected bioplastics ($n = 13$) were straws collected from businesses in Toronto that were initially tested using a Raman spectrometer with no conclusive match and were suspected to be a bioplastic material based on visual examination (i.e., plastic-like appearance but unable to achieve a spectroscopy match to a plastic polymer). Other samples were opportunistically collected foodware items and packaging from various businesses that had labeling to suggest they were bioplastics but had no mention of material type (i.e., “biodegradable,” “compostable,” etc.; $n = 16$) (Supporting file: BLoP Itemized Table). As with the library materials, samples were prepared by cutting a small piece and then mounting it on double-sided sticky tape on a sheet of acetate in a Petri dish. These samples were first tested using each instrument (Raman and μ ATR-FTIR spectrometers) with only the standard databases loaded (Table S1). For both instruments, these samples were rerun with BLoP loaded in addition to the standard spectral databases. During each test, the top five polymer matches, the corresponding library for each match, and the Hit Quality Index (HQI) were recorded for each sample.

For both versions of the library, we tested if BLoP led to false-positive matches when used in conjunction with other libraries (i.e., testing if particles composed of nonplastic or plastic were falsely identified as a bioplastic). For each instrument, we used 40 randomly chosen spectra for microparticles that had previously been identified to be plastic ($n = 32$) or natural materials ($n = 8$; e.g., cotton). For the

assessment of the Raman version of BLoP, we used spectra from the creation of the SLoPP library ($n = 17$), spectra that had been used to validate the functionality of SLoPP ($n = 10$), and spectra from particles present in fish tissue samples caught from Lake Ontario ($n = 13$).^{23,26} To assess the μ ATR-FTIR version, we used spectra used to create the FLoPP library ($n = 17$) and spectra from particles collected from the Humber River watershed ($n = 23$).²²

3. RESULTS AND DISCUSSION

3.1. Bioplastic Library of Polymers (BLoP)

To create BLoP, we used 31 bioplastic spectra, covering a variety of polymers not included in other libraries. For the μ ATR-FTIR version, we only used 23 of these spectra as we excluded 8 PLA entries that were previously included in FLoPP.²² BLoP includes eight different bioplastic polymers: polylactic acid (PLA), crystallized polylactic acid (CPLA), polyhydroxyalkanoate (PHA), a sugarcane-based polymer, a cornstarch-based polymer, a bamboo-based polymer, and three proprietary polymers: Flaxstic, Mater-Bi, and NatureFlex. Polymer acronyms used in the library are listed in Table S2. Most library materials were PLA (58% of entries; $n = 18$), aligning with 2024 data showing that PLA is the dominant bioplastic produced globally.⁴ Due to the availability in sourcing these materials, most of the items used in the library were single-use straws (33%, $n = 10$) and 3D printing materials (20%, $n = 6$) (Table S3). Materials used for the library include eight colors (white, brown, clear, blue, black, orange, silver, and green), with the majority being white (30%, $n = 9$), followed by clear (26%, $n = 8$) (Table S4). The materials added were predominantly in the form of fragments (80%, $n = 25$) with some film morphologies (17%, $n = 5$) and one fiber morphology (3%, $n = 1$) (Table S5). In creating a library with a diverse collection of items encompassing various sources, uses, morphologies, and colors, we aimed to improve the rate of successful matches, as has been demonstrated by the creation of other spectral libraries.^{22,23} The library files for BLoP are provided as the Supporting Information: see Supporting Information “BLoP SI Library Spectra Files”, to see a detailed inventory and to access the library files for Raman or μ ATR-FTIR spectroscopy.

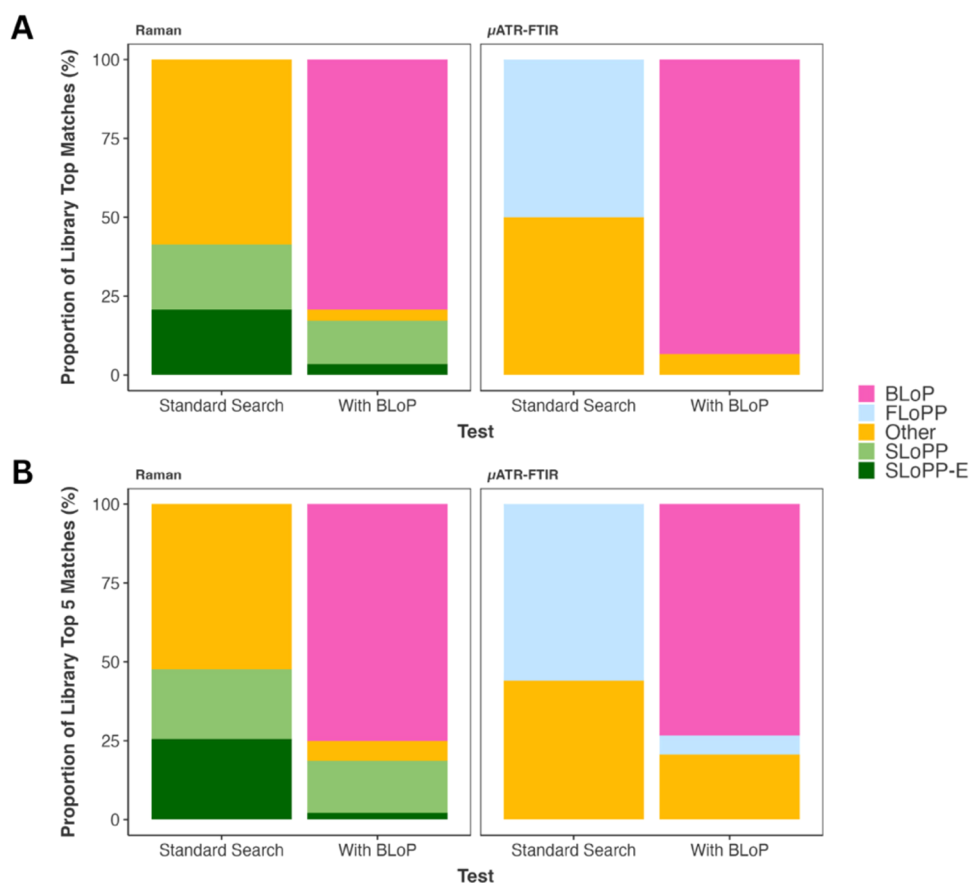


Figure 2. Proportion (%) of the library top matches for previously unknown samples with just standard libraries loaded and with BLoP loaded as well as the standard libraries for Raman (left panels) and for μ ATR-FTIR (right panels). Panel (A) shows only the library for the top match (29 samples, 29 library matches per instrument), and panel (B) shows libraries for the top five matches for previously unknown samples (29 samples, 145 library matches per instrument). BLoP matches are shown with pink.

3.2. Analytical Improvements Using BLoP

Our test using suspected bioplastic materials demonstrated the utility of BLoP to identify bioplastic polymers using both Raman and μ ATR-FTIR spectroscopy. These suspected bioplastics ($N = 29$) were either determined to have no conclusive match with standard libraries (i.e., “unknown”) or had labeling to suggest they were bioplastics (i.e., “compostable,” “biodegradable,” etc.) (Table S6). In this utility test using Raman spectroscopy, 79% of these suspected bioplastics were identified as bioplastics with matches from BLoP when it was included with the other libraries in the search (23/29 samples) (Figures 1 and 2A). Prior to including BLoP for spectral matching, 83% of these samples were unidentifiable using Raman spectroscopy (24/29 samples; Figures 1 and 2A). Similarly, for μ ATR-FTIR, 96% of suspected bioplastics were identified using BLoP when compared against standard libraries (28/29 samples; Figures 1 and 2A). Prior to using BLoP, 38% of these suspected bioplastics were unidentifiable, 41% were identified as PLA using FLoPP, and the remaining 17% were matched to other materials. For both instruments, BLoP improved the identification of bioplastic materials compared to standard libraries.

Besides improving the top match, our test of suspected bioplastics using Raman spectroscopy showed that matches to BLoP composed 75% of the top five spectral database matches based on HQI ($N_{\text{matches}} = 145$, top five matches per sample; Figure 2B). Likewise, for the μ ATR-FTIR test, 73% of the top

five matches were entries from BLoP ($N_{\text{matches}} = 145$, top five matches per sample; Figure 2B). This was lower than for Raman because the FLoPP library was included in the matching process and already includes eight PLA reference materials, which reduced the overall matching rate of BLoP.²² The high frequency of BLoP in the top five matches based on HQI suggests that there is greater confidence in the match and makes it easier for researchers to more reliably identify these materials.

Besides successfully identifying bioplastics, BLoP also improved the quality of the matches achieved for these materials with both Raman and μ ATR-FTIR spectroscopy as measured by HQI, a matching algorithm applied by the instrument’s software. In testing BLoP with Raman spectroscopy, the mean HQI for the validation samples increased by an average of $14.4 \pm 13.4\%$ (range increase of HQI: 0–45.6%) with standard library searches (Table S7). Similarly, for μ ATR-FTIR, the top match HQI increased by a mean of $17.2 \pm 15.3\%$ (range of increase of HQI: 1.8–65.5%) (Table S8). This demonstrates the ability of BLoP to improve confidence in matching bioplastic materials.

Both instruments were relatively consistent in their ability to identify bioplastics, but there was some variability. 76% of particles were identified as bioplastics by both instruments (22/29 suspected bioplastics; Table S9). Not all samples that were identified as bioplastics by both instruments matched to the same specific polymer. Only 55% of suspected bioplastics were matched to the same bioplastic polymer using both

instruments (16/29 suspected bioplastics; Table S9). There were some suspected bioplastics that were identified by one instrument but were unable to be matched confidently and considered to be inconclusive with the other instrument (7/29 suspected bioplastics). Of the samples that were identified by only one of the two instruments, we observed that μ ATR-FTIR performed better at identifying bioplastics compared to Raman: 20% of particles were identified with μ ATR-FTIR but not Raman (six suspected bioplastics), while just 3% were identified with only Raman (one suspected bioplastic) (Table S9).

In our tests for false-positive matches (analyzing known plastic and natural particles to see if they are misidentified as bioplastics with BLoP), we found that no particles were misidentified as a bioplastic (0/40 for each instrument; Tables S10 and S11). For both instruments, BLoP entries were not in the top five matches for any of the particles run for the false-positive test. This suggests that the rate of false positives from using BLoP in addition to standard microplastic libraries is negligible.

3.3. Applications of BLoP

By using BLoP in addition to other open-source spectral libraries, researchers can improve their ability to confidently identify bioplastics. Using BLoP has applications for environmental monitoring of anthropogenic microparticles and macrodebris, improvement of waste sorting in recycling processes, and source apportionment. For instance, multiple bioplastic polymers have been shown to break down into nano- and microparticles similarly to microplastics in the environment, suggesting these particles should be better monitored in future studies.⁶ We intend this library to be used as a companion with open-access microplastic libraries, which have been valuable tools for researchers studying microplastics (e.g., it could be added to Open Specy).²¹

3.4. Limitations

BLoP was successful in enabling the detection of some bioplastic materials; however, there are still challenges in identifying bioplastics. We were able to include only eight kinds of bioplastics in the library, but many other kinds exist, and new polymers are continually being synthesized, creating a diversity of materials akin to plastics. BLoP also only includes nondegraded bioplastics, which may limit the ability of the library to aid in the identification of environmentally weathered microbioplastics. Other spectral libraries include materials sourced from the environment, which improve polymer detection when analyzing environmental samples.^{22,23} We recommend that in the future, researchers add environmentally sourced particles identified as bioplastics to improve this spectral library.

Many items that we considered adding to the library did not clearly specify what bioplastic material they were composed of, so we did not add them due to this lack of confidence in their composition. In addition, some bioplastics are difficult to distinguish from traditional plastic polymers (“drop-in” polymers, chemically equivalent polymers that are replacements for fossil fuel-based versions).² For example, we experienced challenges differentiating some allegedly biobased polymers from traditional fossil fuel-based polymers and were unable to include these indistinguishable polymers in our library as a result (Figures S1 and S2). We believe the difficulty in distinguishing drop-in bioplastics is a limitation associated with the methodology (i.e., spectroscopy), and further analyses

would be required to determine the material more confidently (e.g., pyrolysis–gas chromatography–mass spectrometry). However, it is also possible that these materials were incorrectly labeled as bioplastics and instead were traditional plastic polymers. Not only do these bioplastics pose issues for detection in environmental samples where they may be confused with traditional plastic polymers, but they may also pose issues in waste streams.²⁷ In recycling of polyethylene (PE) products, even just 1% of contamination of PLA can significantly impact the quality of the recycled PE product, demonstrating the issues associated with indistinguishable drop-in bioplastics mistakenly entering recycling facilities and contaminating recycled products.²⁷ As such, methods for the detection and identification of these drop-in bioplastics should be further studied.

Though BLoP was effective in differentiating bioplastic materials from traditional plastic polymers, we observed some inconsistencies with the matching between instruments (Table S9). This could be related to differences in how spectra are collected between machines: μ ATR-FTIR collects spectra through light absorption, while Raman acquires spectra vibrationally using a laser.²⁸ Also, this could be due to the low sample size for bioplastic polymers in the library; other than PLA, only 13/29 entries were non-PLA. Notably, we encountered difficulties distinguishing some PLA samples from poly(ethylene terephthalate) (PET)/polyester using Raman spectroscopy. For instance, using μ ATR-FTIR, one suspected that the bioplastic was initially identified as copolyester; when using BLoP, it was identified as PLA; and on Raman, it was identified as PET/polyester, even with BLoP included as a library.

We also collected only spectra using one collection method for μ ATR-FTIR, but future work to expand BLoP to work with other collection methods would be useful for laboratories working with other particle analysis workflows (e.g., reflectance mode).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.5c18940>.

BLoP SI Library Spectra Files: All files needed to use BLoP are provided here, including a read-me document, a spreadsheet inventory of the library, and library files in formats compatible with Raman and μ ATR-FTIR (ZIP)
BLoP SI Tables and Figures: Tables providing further information about the materials used to create and test the library, as well as figures showing the spectra discussed in the manuscript (PDF)

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Notes

The authors declare no competing financial interest.

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