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A novel way to rapidly monitor microplastics in soil by hyperspectral imaging technology and chemometrics *



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ABSTRACT

Hyperspectral imaging technology has been investigated as a possible way to detect microplastics contamination in soil directly and efficiently in this study. Hyperspectral images with wavelength range between 400 and 1000 nm were obtained from soil samples containing different materials including microplastics, fresh leaves, wilted leaves, rocks and dry branches. Supervised classification algorithms such as support vector machine (SVM), mahalanobis distance (MD) and maximum likelihood (ML) algorithms were used to identify microplastics from the other materials in hyperspectral images. To investigate the effect of particle size and color, white polyethylene (PE) and black PE particles extracted from soil with two different particle size ranges (1-5 mm and 0.5-1 mm) were studied in this work. The results showed that SVM was the most applicable method for detecting white PE in soil, with the precision of 84% and 77% for PE particles in size ranges of 1–5 mm and 0.5–1 mm respectively. The precision of black PE detection achieved by SVM were 58% and 76% for particles of 1-5 mm and 0.5-1 mm respectively. Six kinds of household polymers including drink bottle, bottle cap, rubber, packing bag, clothes hanger and plastic clip were used to validate the developed method, and the classification precision of polymers were obtained from 79% to 100% and 86%-99% for microplastics particle 1-5 mm and 0.5-1 mm respectively. The results indicate that hyperspectral imaging technology is a potential technique to determine and visualize the microplastics with particle size from 0.5 to 5 mm on soil surface directly.

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1. Introduction

Recently discarded plastic products have been a rapidly increasing and significant global environmental issue. Around 260 million tons (MT) of plastic products were used annually (Thompson et al., 2009) and 8300 MT plastics had been produced globally (Geyer et al., 2017). In the United States, 12.8% plastic waste is discarded as municipal solid waste but only 9% plastic is recovered for recycling (US Environmental Protection Agency, EPA, 2015). The plastic debris in the environment are commonly polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET) and polyvinylchloride (PVC) (Rocha-Santos and Duarte, 2015), which comprise 72.9% of the plastic products globally. Substantial

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quantities of discarded plastics in the environment are gradually degraded into millions of small plastic particles under a series of physical and chemical reactions (Cole et al., 2011), and those with a size smaller than 5 mm are defined as microplastics (Wright et al., 2013). The abundance of global microplastics was estimated to be at least 4.85 trillion debris (Eriksen et al., 2014), weighing 93,000 tons (van Sebille et al., 2015). These plastic fragments accumulating in the environment are considered to be quite stable, high durable and potentially lasting for a long time in the natural environment (Andrady, 2011; Cozar et al., 2014). Microplastics pollution was first recognized in various aquatic ecosystems, including ocean (Waller et al., 2017), fresh water (Horton et al., 2017), sediments (Bergmann et al., 2017) and shorelines (Browne et al., 2011). However, few research groups studied microplastics in terrestrial ecology (Liu et al., 2017; Rillig, 2012). Estimate of 100,000-700,000 tons of microplastics enter soil in Europe and North America annually which exceeds the entire microplastics in the marine surface (Nizzetto et al., 2016). These microplastics occurred on the

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terrestrial ecosystems either as primary microplastics from small size of plastic materials or secondary microplastics from the degradation of larger plastic fragments (Liu et al., 2017). The sewage sludge, waste water and plastic films used in agriculture are major sources of microplastics in soil environment (Liu et al., 2017; Nizzetto et al., 2016).

Once microplastics have entered soil, they will threaten agroecosystems. Microplastics release toxic chemicals additives, which endanger the soil environment (Browne et al., 2013; Koelmans et al., 2014; Kwon et al., 2017). Besides, plastics is a sorbent of other toxic pollutants such as persistent organic pollutants (POPs) and metals pollutants (Bakir et al., 2016; Besseling et al., 2013; Brennecke et al., 2016; Shim and Thomposon, 2015). Especially, when plastics carrying pollutants are taken-up by biota, it may generate negative effect in the food chain (Jovanovic, 2017; Karlsson et al., 2017; Lwanga et al., 2016; Santana et al., 2016; Zhao et al., 2016). Therefore, microplastics in soil should be systematically monitored through quantification methods quickly and accurately.

Varieties of techniques have been developed for determining microplastics in environmental matrices. In general, microplastics analysis consists of two steps: separation of plastic or suspected plastic particles from environmental matrices (Quinn et al., 2017) followed by physical and chemical characterization for confirmation of plastics. Density separation has been commonly used for microplastics separation, which usually costs a few hours for separating the microplastics from sand or sediments which have higher density. After separation, microscopy is a widely used method to identify physical morphology of microplastics and spectroscopy (e.g., Fourier-transform infrared (FT-IR) and Raman spectroscopy) commonly works on the chemicals identification (Crichton et al., 2017; Lenz et al., 2015; Faure et al., 2015). These identification techniques require individual particle analysis, which means physical and chemical properties of plastics or suspected plastics are determined one by one. To reach a statistically reliable statement about the occurrence of microplastics, a large number of particles must be analyzed, which would be time consuming.

In view of this, there is considerable interest in developing a new technique to determine and map microplastics distribution in soil rapidly and accurately. Hyperspectral imaging contains tens of hundreds of narrow spectral bands from visible to infrared region and tens of thousands of spatial pixels. In consequence, it is possible to identify chemical compounds of each spatial pixel according to their spectral information. Hyperspectral imaging technology was used to determine plastics contamination in sea water filtrates. In this case, plastic and suspected plastic were identified visually and manually transferred to glass petri dishes for future images acquisition. 84% of pixel recognition on household polyethylene plastic was obtained (Karlsson et al., 2016). However, the microplastics were separated from seawater manually before hyperspectral images acquisition.

The aim of the present study was to identify and determine microplastics in soil directly without microplastics separation, and to visualize the distribution of microplastics by hyperspectral imaging technique. Microplastics used in this work were separated from the field samples and identified by Raman spectroscopy prior to hyperspectral imaging. Hyperspectral images were acquired from soil samples covered with fresh leaves, wilted leaves, rocks, branches and the extracted microplastics. Chemometrics and image preprocessing methods were used to identify microplastics with particle sizes between 0.5 and 1 mm from soil samples directly. The developed method was further assessed by using additional six kinds of household plastics including drink bottle, bottle cap, rubber, packing bag, clothes hanger and plastic clip with the same particle size on soil.

2. Materials and methods

2.1. Sample collection

Soil sampling was done at the coastal wetland region (40.685° N, 122.135° E) along Liaobin bay district, Panjin, China. Soil was collected from top 5 cm layer at the points covered with the visible plastics as shown in Fig. 1 and taken back to laboratory. The original soil sample weighed 3 kg, and was divided into two equal groups. One group was analyzed for microplastics extraction and identification in traditional way, and the other group was analyzed by hyperspectral imaging technology, combined with chemometrics.

2.2. Extraction and identification of microplastics

Density separation was commonly used to separate microplastics from sediments based on density differences (Nuelle et al., 2014). 30 g soil and 80 mL saturated sodium chloride (NaCl) solution were fully mixed in a 100 mL beaker. The mixture was stirred for 0.5 h and stranded 12 h until the upper suspension clear. Then the extracts floating on the surface of the saturated NaCl solution were picked out visually using a stainless steel needle (length 23 cm, diameter 3 mm), and placed at a petri dish containing deionized water. Repeat stirring and standing process for 3 or 4 times until no extracts floating on the surface of NaCl solution was observed. After extraction, microscopy and Renishaw inVia Micro-Raman Spectrometer were used to observe the morphology and identify the chemicals of the microplastics.

2.3. Sample preparation

Microplastics with size ranges from 0.5 mm to 5 mm were found occupying more than 90% of total microplastics from Oujiang, Jiaojiang and Minjiang Estuary (Zhao et al., 2015). To investigate the effect of particle size on the classification results by using hyperspectral imaging technology, microplastics were divided into two particle range: 1–5 mm and 0.5–1 mm. White and black microplastics found in soil samples were prepared to study the color effect on the final classification results. The white and black plastics extracted in section 2.2 were sheared into microplastics manually and filtered by stainless steel mesh sieves, with two kinds of size range: 1-5 mm and 0.5-1 mm. Fresh leaves, dry branches, wilted leaves and rocks were obtained in the field and used to simulate the field environment in laboratory. In order to prevent the influence of soil moisture, soil samples were dried in vacuum oven (Senxin, DZG-6050, China) at temperature of 80°Cfor eight hours before hyperspectral image acquisition. Two experiments were conducted based on microplastics particle size: (1) white microplastics (1–5 mm), black microplastics (1–5 mm), rocks, wilted leaves, fresh leaves, dry branches were mixed and covered on the surface of dried soil samples randomly. Ten pieces of each type material were used per sample; (2) white microplastics (0.5–1 mm), black microplastics (0.5-1 mm), rocks, wilted leaves, fresh leaves, and dry branches were mixed and covered on the surface of soil samples randomly. To get the similar cover area, one hundred pieces of each type microplastic (0.5–1 mm) and ten pieces of the other materials as above mentioned were prepared. In order to guarantee the stability of the detection models, five replicate tests were conducted for experiment (1) and (2) respectively. Soil samples were scanned by hyperspectral imaging system, obtaining image information and spectral information.

2.4. Hyperspectral imaging system

The hyperspectral system used a CCD camera (Headwall

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