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SOIL MICROPLASTICS SPECTRUM BASED ON VISIBLE NEAR-INFRARED SPECTROSCOPY

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Abstract

As the largest "repository" of microplastics, soil is affected by soil structure, microplastics category and particle size. In this study, the method of combining indoor simulation modeling and field verification is proposed. The reflectance of soil microplastic samples was collected by ASD FieldSpec4 Hi-Res spectrometer, NOR, MSC, SNV were used for spectral pretreatment, and differential transformations of different orders are used to enhance the spectral signal-to-noise ratio. The results showed that the spectral reflectance of microplastics decreased with the increase of microplastics content in soil. After FD and SD transform, the spectral features are enhanced obviously. The regression model based on NOR transformation of reflectivity combined with first deviation is the best, Rc^2, Rv^2, RMSEC and RMSEPare 0.75, 0.77, 0.16, 0.12,respectively.This study can provide a scientific basis for quantitative research on microplastics in farmland soil in northern Shaanxi, China.

Introduction

As one of the new persistent pollutants, microplastics (MPs) have received much international attention due to their potential threats to the marine environment, surface water systems (lakes, rivers, etc.), terrestrialsystems, and human health (Rochman 2018, Zhu *et al.* 2019, Zhang and Han. 2020). In 2015, microplastic pollution was listed as the second most important scientific problem in the field of environmental and ecological sciences, in addition to major global environmental issues such as global climate change, ozone depletion and ocean acidification (Wang *et al.* 2021). MPs are characterized by small particle size, large specific surface area, strong adsorption capacity, stable chemical properties and easy migration (Rochman 2018). They gather with a variety of organic pollutants in the ocean, soil and atmosphere, and accumulate continuously in aquatic ecosystems and terrestrial ecosystems, it poses a major threat to the global ecological environment (Bergmann *et al.* 2019, Wang *et al.* 2021). According to statistics, world has produced nearly 8.3 billion tons of plastics, 9% of which are effectively recycled, 12% of which are burned, the residual 79% are left in the landfill or ecological environment (Geyer*et al*. 2017). Statistics show that there are countless MPs in the ocean (Rochman 2018), land and even the atmospheric system (Tian*et al.* 2022). The treatment of MPs pollution has become one of the topics that contemporary people must face for harmonious coexistence with nature and sustainable development.

The results show that the visible near infrared spectroscopy (VNIRS) coupled machine learning technology for qualitative and quantitative study of soil MPs research scheme is feasible. In the 350-2500nm region, different MPs show significant differences in spectral characteristics (Corradini *et al.* 2019). Shan *et al.* (2018) used the hyperspectral imaging technology to collect

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images of soil samples from different materials in the 400-1000nm spectral range, and compared and analyzed the detection capabilities of Support Vector Machine (SVM), MPs with Markov distance maximum of 0.5-5mm. The accuracy of support vector machine algorithm for PE microplastic particles in the range of 1-5 mm and 0.5-1 mm is 84% and 77%, respectively. Corradini *et al*. (2019) used VNIRS and bayesian multiple regression to predict the content of PVC, PET, and LDPE at different concentrations (1 - 100 g/kg). The error of the prediction model was 10 g/kg, and the limit of detection of the model was about 15 g/kg. Paul *et al*. (2019) established support vector and partial least squares discrimination models based on VNIRS full spectrum band, and realized the detection and classification of 0.5-1.0% PE, PET, PP and PS. Ng *et al*. (2020) researched the classification of different gradients of PET and LDPE (≥ 3%, ≥ 1% and < 3%, < 1%) in soil based on VNIRS and convolutional neural networks (CNN), and the classification accuracy reached 64%. Qiu *et al.* (2020) and Zhao *et al.* (2021) used near-infrared hyperspectral imaging technology and based on migration learning to build a model for the pollution degree of transportable MPs among soils in different regions, and proposed an efficient migration strategy between different NIR spectral instruments.

Thus, this study was based on machine learning, the soil MPs prediction model of feature optimization variables is established. The research results will be widely used in the traceability, migration mode and risk assessment of MPs, providing scientific basis and theoretical basis for further establishing and improving large-scale soil MPs analysis methods, and providing a technical support system for the prevention, control and governance of soil MPs pollution risks.

Materials and Methods

In order to establish a prediction model more suitable for the abundance of MPs in the field environment, the project plans to collect plastics used in the field environment for indoor simulation sample preparation. The response mechanism and driving factors of soil texture, different micro plastic properties (species, particle size, color, abundance) and other multivariable factors to the spectral mechanism should be fully considered. In November 2021, the research group went to the farming pastoral ecotone in northern Shaanxi to conduct a preliminary investigation on the use of plastics. Yuyang District, Jingbian County, Dingbian County and Ordos City in Yulin City, Shaanxi Province have a long service life and a variety of plastics. The types of plastics are mainly drip irrigation belts, plastic mulch, greenhouses and woven bags (Table 1). On the basis of the previous investigation, taking into account the farmland cultivation method, crop planting mode and plastic use type, color, composition, etc., four kinds of plastic samples (drip irrigation water belt, plastic film, greenhouse film and woven bag) are collected after the crops are received (Fig. 1).

After plastic samples are collected, they are cleaned with ultrapure water. After drying, large pieces of plastic are sheared and crushed with scissors and pulverizers to obtain coarse particles. Ding *et al*. (2020) studied the magnitude and granulometric distribution of farmland soil MPs in northern Shaanxi Province, and found that the size range of MPs is 0-0.49, 0.5-0.99, 1-1.99 and 2-5 mm in northern Shaanxi, China, respectively.

Spectral data of microplastics and soil samples were conducted in the darkroom. The ASD Field Spec 4 spectroradiometer Hi Res NG is used to measure the reflectivity. The spectral wavelength measurement range is 350~2500 nm, the spectrum sampling bandwidths are 1.4 nm and 1.1 nm, respectively at 350~1000 nm and 1000~2500 nm. The resampling interval is 1 nm, and the number of channels is 2151. The detector consists of three parts: VNIR detector, SWIR1 detector and SWIR2 detector. To reduce the influence of environmental factors such as temperature and light intensity, this research uses Hi-Brite contactable high-precision probe with built-in halogen bulb to collect spectral data.

Table 1. Summary of investigation areas and plastic types.

Locations	Crop	Colour	Components
Yulin	Corn	White	PE, PP
	/	White, black	PE, PVC
Yulin city	Corn	White	PE, PVC
	Pepper	Black	PE, PVC
Yulin city	Cabbage	White, black, blue	PVC, LDPE
Ordos city	Pepper	White, black	PVC, LDPE
Yulin city	Pepper	White	PVC, LDPE
	Corn	White	PVC
Yulin city	Cabbage	White, blue	PVC, PE
	/	White	PVC
	Pepper	Blue, black	PVC, PE

LDPE (Low Density Polyethylene); PE (polyethylene); PP (Polypropylene); PVC (Polyvinyl Chloride).

Fig.1. Selection of typical areas of plastic pollution.

According to the experimental settings, add MPs to the terrarium (6 cm in diameter and 1.5cm in depth), so that it mixes well with the soil, scrape the surface of the sample with a ruler, and measure the soil spectroscopy. In the process of establishing the quantitative analysis model of MPs concentration in samples by collecting certain amount of sample spectral data. Considering the uneven spatial and concentration distribution of MPs in the soil, five different positions of the terrarium were randomly selected for soil spectrum acquisition, and 10 spectral curves were collected at each position. During the determination, the white board shall be used for correction.

Using View Spec to eliminate spectral curves, the average value is taken as the actual value of soil microplastics. In order to eliminate the effect of scattering between soil samples, this study conducted multiple scatter correlation (MSC), normalization (NOR), and standard normal variable (SNV) processing on the averaged reflection spectra. Different deviation transformation of the original reflection spectrum can effectively obtain the maximum and minimum wavelength positions, and can remove the noise generated by different backgrounds, and Savitzky-Golay convolution smoothing (fitting number: 2, window width: 11) is used to smooth and remove the dryness of the reflection spectrum.

Partial least squares regression (PLSR) is a new multivariate statistical data analysis method, which has been widely used in quantitative forecasting, it can effectively solve the problem of small sample size, and reduce the high linear correlation between the respective variables. PLSR takes into account the role of the target variable matrix while reducing the spectral dimension, and effectively combines with regression. In this study, the Markov distance method was used to eliminate abnormal samples, and sample set partitioning based on joint x-y distance (SPXY) was used to select 70% of the samples for modeling and the remaining 30% for validation. R^2, RMSE were used to verify the accuracy and stability of the model.

$$R^2 = \frac{\sum_{i=1}^{n}(\hat{y}_i - \overline{y}_i)^2}{\sum_{i=1}^{n}(y_i - \overline{y}_i)^2} \tag{1}$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{2}$$

Where, λ_i is the wave band of the wavelength i nm, y_i and $\hat{y}_i$ are the observed and predicted values of the test samples respectively; $\overline{y}_i$ is the average of the sample observations; m and n is the number of samples of calibration and validation.

Results and Discussion

Figure 2 shows the spectrum curve after mixing microplastics, PLS beta correlation coefficient, Principal component spectrum, and the trend of each spectrum curve is roughly the same. By comparing the curve morphology, the higher the content of microplastics in soil, the lower the reflectance of the corresponding spectral curve, showing a negative correlation. At 350 ~ 568 nm, With the increase of band, the reflectance curve tends to steepen. At 535~781 nm, the spectral curve growth trend becomes slightly slower. In the range of 780~1350nm and 1490~1797 nm, the reflectivity increases gradually. The spectral identification technique detects the number of particles by counting or estimating the number of microplastics in a standard volume of samples (Crawford and Quinn, 2017a). In addition, spectroscopic techniques cannot define microplastics by compounds (Hidalgo-Ruz *et al.* 2012).

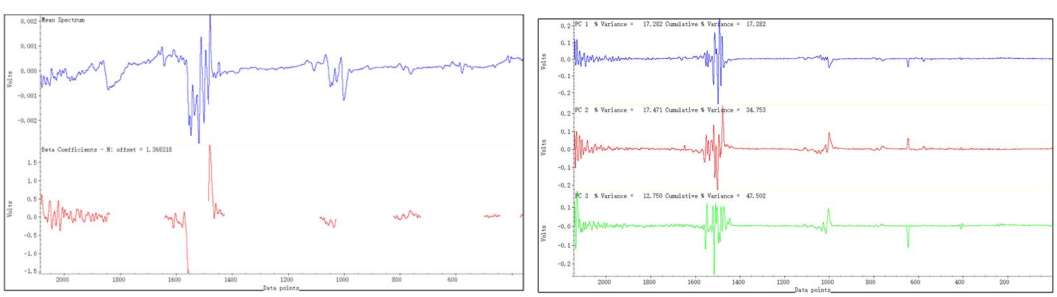

Fig. 2. PLS beta correlation coefficient and principal component spectrum.

In this study, the correlation between soil microplastics content and spectral reflectance was discussed, first order differential, second order differential and reciprocal logarithm of reflectance is shown in Fig. 3. By comparing the original reflectance, different order differential transformation can effectively increase the spectral characteristics. At 350~2500 nm, the content of soil microplastics was negatively correlated with the original spectral reflectance, reaching a maximum of - 0.23 at 2010 nm. Correlation coefficients of the first deviation of soil microplastics and reflectance at 1428 nm, 1982 nm, 1963 nm, 2204 nm and 2307 nm all reached above 0.5, showing a positive correlation. The maximum correlation coefficient is 0.55 at 1980 nm. Correlation coefficients of soil MPs with the second deviation of reflectance at 1100, 1460, 1960, 2367 and 2401nm are all above 0.5, which is a significant positive correlation. Through reciprocal logarithm transformation of reflectance, correlation analysis of microplastic content(Liu *et al*. 2014, Yin *et al*. 2021), the results show that the effect is not significant, and there are three water absorption peaks have a large correlation coefficient (Babin *et al*. 1993, Samtleben *et al*. 2008).

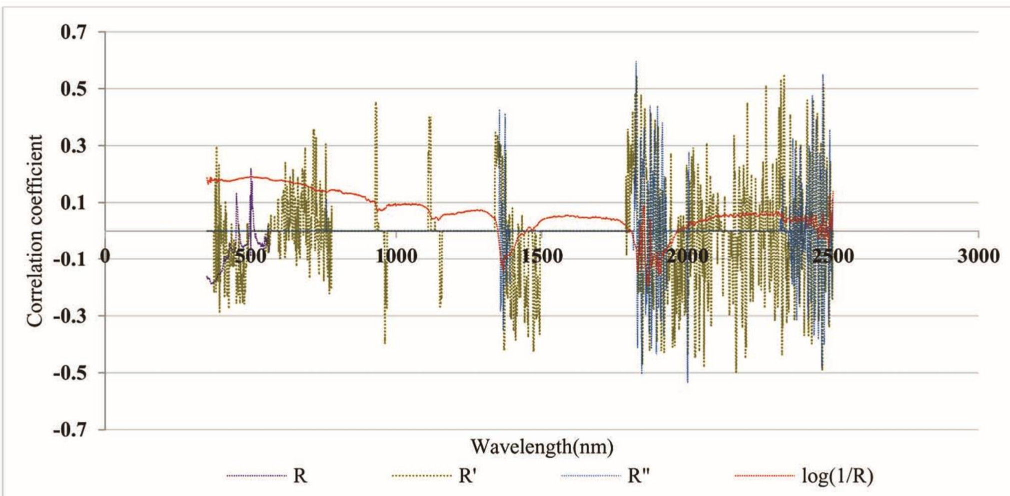

Fig. 3. Correlation of coefficient diagram of different reflection spectra and microplastics content.

In Table 2, the PLSR model is established with the bands with large logarithmic correlation coefficients of original reflectance, first deviation, second deviation and reciprocal reflectance as independent variables and microplastic content as dependent variables (Table 2). The comparison found that, the model established by MSC transformation of reflectivity combined with first deviation has the best effect, $Rc^2 = 0.75$, RMSEC = 0.15. In validation, the best preprocessing method is to combine NOR transformation of reflectivity with first-order differential to get the best prediction effect, $Rv^2 = 0.77$, RMSEP = 0.12. After summary, it is found that no matter what kind of pretreatment, The model with good modeling effect may not have the best prediction effect. Therefore, the PLSR model established by combining the first deviation with NOR transformation of reflectivity is the best ($Rc^2 = 0.75$, RMSEC = 0.16, $Rv^2 = 0.77$, RMSEP = 0.12).

In this research, hyperspectral inversion of soil microplastics content was performed, and the soil microplastic reflectance was pretreated with MSC, NOR and SNV, respectively. The hyperspectral inversion model of soil microplastics was established by using the FD,SD, LOG of reflectivity and PLSR.

Table 2. Statistics of soil micro plastic prediction model based on PLSR.

Model	Pretreatment	Combination	Calibration			Validation	
			Rc^2	RMSEC	Pc	Rv^2	RMSEP
PLSR	NOR	SG+ FD	0.75	0.16	10	0.77	0.12
	MSC	SG+ SD	0.60	0.33	10	0.71	0.15
	SNV	SG+ LOG	0.58	0.36	10	0.51	0.43
		SG+ FD	0.75	0.15	10	0.73	0.15
		SG+ SD	0.59	0.34	10	0.72	0.14
		SG+ LOG	0.59	0.35	10	0.61	0.34
		SG+ FD	0.74	0.18	10	0.75	0.16
		SG+ SD	0.59	0.35	10	0.72	0.14
		SG+ LOG	0.58	0.37	10	0.61	0.33

1. Compared to the soil microplastic reflection spectrum, the correlation of the soil spectral is significantly improved after differential transformation. There is a significant correlation between soil microplastics and the FD of reflectivity, the largest of correlation coefficient at 1980 nm, which is 0.55.

2. The PLSR established by FD after NOR pretreatment of reflectivity is better. Among them, the $Rc^2$and Rv^2 are 0.75 and 0.77,respectively. The modeling RMSEC and RMSEP are 0.16 and 0.12 respectively. The established soil microplastic prediction model has good stability and high prediction accuracy, which can realize the rapid determination of soil microplastic content.

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