



# Predicting soil microplastic concentration using vis-NIR spectroscopy

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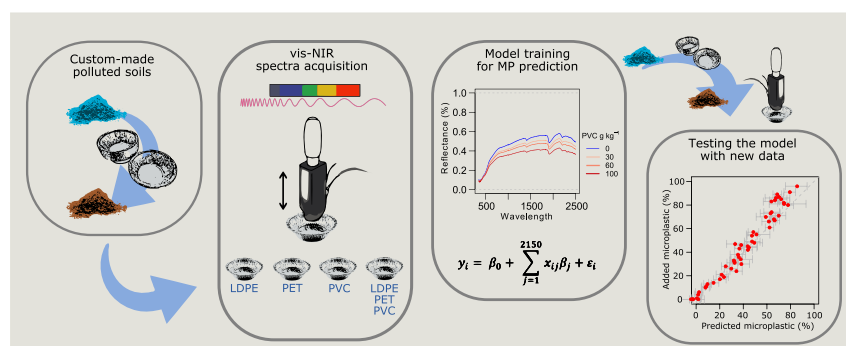
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## HIGHLIGHTS

- Methods to quantify and qualify microplastics in soils are slow and non-standardized.
- The spectra of a soil with microplastics were characterized with a spectrometer.
- The spectra was used to train a model for microplastic analysis in soils.
- The method was useful to quantify and qualify LDPE, PET, and PVC in soil samples.
- Fast methods to analyse microplastics could be developed using the same technique.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Microplastic accumulation in soil may have a detrimental impact on soil biota. The lack of standardized methods to identify and quantify microplastics in soils is an obstacle to research. Existing techniques are time-consuming and field data are seldom collected. To tackle the problem, we explored the possibilities of using a portable spectroradiometer working in the near infrared range (350–2500 nm) to rapidly assess microplastic concentrations in soils without extraction. Four sets of artificially polluted soil samples were prepared. Three sets had only one polymer polluting the soil (low-density polyethylene (LDPE), polyethylene terephthalate (PET), or polyvinyl chloride (PVC)). The fourth set contained random amounts of the three polymers (Mix). The concentrations of microplastics were regressed on the reflectance observed for each of the 2150 wavelengths registered by the instrument, using a Bayesian approach. For a measurement range between 1 and 100 g kg<sup>-1</sup>, results showed a root-mean-squared-deviation (RMSD) of 8, 18, and 10 g kg<sup>-1</sup> for LDPE, PET, and PVC. The Mix treatment presented an RMSD of 8, 10, and 5 g kg<sup>-1</sup> for LDPE, PET, and PVC. The repeatability of the proposed method was 0.2–8.4, 0.1–5.1, and 0.1–9.0 g kg<sup>-1</sup> for LDPE, PET, and PVC, respectively. Overall, our results suggest that vis-NIR techniques are suitable to identify and quantify LDPE, PET, and PVC microplastics in soil samples, with a 10 g kg<sup>-1</sup> accuracy and a detection limit ≈ 15 g kg<sup>-1</sup>. The method proposed is different than other approaches since it is faster because it avoids extraction steps and can directly quantify the amount of plastic in a sample. Nevertheless, it seems to be useful only for pollution hotspots.

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## 1. Introduction

While in marine environments plastic debris and microplastics (particles <5 mm) have long been considered pollutants and thus have been studied broadly since the early 1970s (Carpenter and Smith, 1972), less information has been collected about soil as a microplastic sink (Bläsing and Amelung, 2018). Yet, these particles have proven to be ubiquitous in terrestrial ecosystems (Souza Machado et al., 2018). Research on the topic has only begun over the last few years and is mainly focused on the impacts of microplastics on soil biota (Huerta Lwanga et al., 2016, 2017a; Maaß et al., 2017; Rillig et al., 2017). Researchers have struggled to identify and quantify microplastics in soil samples due to the lack of standardized methods (Souza Machado et al., 2018) since Rillig put forth the idea in 2012 (Rillig, 2012).

Although there are some methodologies available to detect and qualify microplastic concentrations in sediments and water, such as Raman and Fourier-transform infrared spectroscopy (FT-IR) (Crawford and Quinn, 2017b), these methods have not been standardized for complex matrices such as soils and require appropriate sample preparation (Crawford and Quinn, 2017a). Other alternatives are visual sorting, which is a simpler and cheaper option (Lots et al., 2017), and pyrolysis–gas chromatography–mass spectrometry (Pyr-GC–MS). While the former is subject to bias from human-errors and precision limitations (Ziajahromi et al., 2017), Pyr-GC–MS presents some drawbacks since it needs adequate concentration or separation steps, which could limit the analysis of large quantities of microplastics (Crawford and Quinn, 2017b; Löder and Gerdt, 2015). To tackle the problem, new chromatographic approaches that allow for bigger sample loads have been proposed, such as thermal desorption GC–MS (TED-GC–MS) (Dümichen et al., 2015; Dümichen et al., 2017).

All of the proposed methods require sample preparation steps with the density separation approach being the most broadly used to isolate microplastics from bulk samples. Flotation methods similar to the one proposed by Zubris and Richards (2005) and later by Zhang et al. (2018) are commonly used. These methods use density to differentiate between plastic particles and the particles naturally found in soil. This could include analytical steps needed to accelerate particle separation such as the use of saturated salt solutions and/or centrifugation (Duis and Coors, 2016; Pita and Castilho, 2017; Zhang et al., 2018).

Nevertheless, studies regarding the microplastic pollution of soil have been performed under laboratory conditions and have focused on the effects of microplastics on soil biota. These studies have seldom reported recovery rates or quality control procedures. Moreover, researchers commonly used only two or three plastic polymers with densities low enough to assure particle flotation since the quantification of soil microplastic content was not the core of their research (e.g. Huerta Lwanga et al., 2017a; Maaß et al., 2017; Ramos et al., 2015). In this regard, Ziajahromi et al. (2017) pointed out that standard sampling and processing methods for microplastics in organic-rich samples are still insufficient, highlighting the importance of thorough characterization of microplastics to avoid false detection and study biases. Pressurised fluid extraction (Fuller and Gautam, 2016) and elutriation (Claessens et al., 2013; Mahon et al., 2017) are the current alternatives but they are not free from interference.

Although straightforward methods for microplastic quantification take advantage of plastics' spectroscopic properties, such as FT-IR and Raman spectroscopy, the use of visible (vis), near-infrared (NIR), and shortwave infrared (SWIR) equipment to detect and characterize microplastics have received less attention. A vis-NIR spectrometer measures the amount of light that is reflected from a surface within the wavelength range of 350 to 2500 nm, giving a reflected percentage for each wavelength. This information can be correlated with the chemical composition of the sample and thus it allows for predicting the composition of new sample sets. As vis-NIR techniques have been useful to examine elemental composition directly on soil bulk samples (Conforti et al., 2018; Gandariasbeitia et al., 2017; Viscarra Rossel et al., 2016), it

could be possible to use these methods to avoid or reduce sample preparation steps, tackling one of the current problems in microplastic detection. Moreover, as the vis-NIR spectra is correlated with the chemical composition of the sample, this method could be useful in microplastic quantification.

There are public vis-NIR spectra datasets showing that different plastic polymers commonly found in the environment have different spectral signatures (reflectance along a wavelength range) (Garaba and Dierssen, 2017). Therefore, these plastic polymers might be identifiable by using vis-NIR spectrometric techniques. Nonetheless, to our knowledge, there have been no previous studies using these techniques to evaluate microplastics in soil samples. Our expectation for this work was to explore the possibility of using a vis-NIR analysis technique as a novel, fast, and scalable method to identify and quantify the amount of microplastics in soil. Consequently, the aim of this work was to predict the microplastic concentration (low-density polyethylene (LDPE), polyethylene terephthalate (PET), and polyvinyl chloride (PVC)) of soil samples using a portable spectroradiometer while avoiding extraction steps. We did so by making custom-made artificially polluted soil samples to evaluate the spectral characteristics of LDPE, PET, and PVC and their interaction with soil. Subsequently, we evaluated the quantification effectiveness of the device by training a multilinear model, regressing the quantity of the added plastic on the observed reflectance, to predict the microplastic content of a given sample. Lastly, the method we propose was used to predict the concentration of a specific plastic polymer in samples polluted with a mixture of LDPE, PET, and PVC, assessing the method's qualification capability.

## 2. Material and methods

### 2.1. Experimental design

To examine the concept of using vis-NIR techniques to quantify microplastics in soil, a spectroradiometer was used to record the reflectance spectra (Section 2.4) of laboratory-made polluted soil samples (Section 2.3). Four treatments were used to evaluate the performance of the technique, each including a different plastic polymer (Table 1). While the first three treatments included only one plastic polymer (LDPE, PET, and PVC), the fourth had concentrations of each of the three polymers used in the former treatments (Mix). Each treatment included a training and a testing dataset (Section 2.3) ranging in concentrations between 1 and 100 g kg<sup>-1</sup> (0.1 and 10% by weight) for LDPE, PET, and PVC, and 1 and 80 g kg<sup>-1</sup> (0.1 and 8.0%) for the Mix. The training set was used to train a linear model by regressing the known plastic concentration on the recorded reflectance (Section 2.5.2). The testing set was used to evaluate the accuracy of the model when predicting soil plastic concentrations for a new set (Sections 2.5.3 and 2.5.4). The testing data sets of the Mix treatment considered 3 measurement repetitions in order to evaluate the method repeatability (Section 2.5.4). An overview of the experimental design is shown in Fig. 1.

### 2.2. Soil and microplastic preparation

Loess top-soil (0–30 cm) collected in Limburg, The Netherlands was used (50% of sand, 50% of silt and clay, and 3% of organic matter). The soil was oven-dried at 40 °C and sieved at <2 mm. Low-density polyethylene (LDPE), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) particles were used as plastic pollutants. Polyethylene particles were obtained by freezing and milling low-density polyethylene pellets (SABIC® LDPE). The particles were classified by size after sieving the plastic powder. The fraction size that ranged from 1 to 0.5 mm was used. Polyethylene terephthalate particles were produced by chopping and grinding food and liquid PET containers with a modified paper crusher, passing the plastic residues through the machine several times. The particles were sieved to recover the 1 to 0.5 mm fraction. Polyvinyl chloride particles were made by filing and rasping a PVC

**Table 1**  
Treatments.

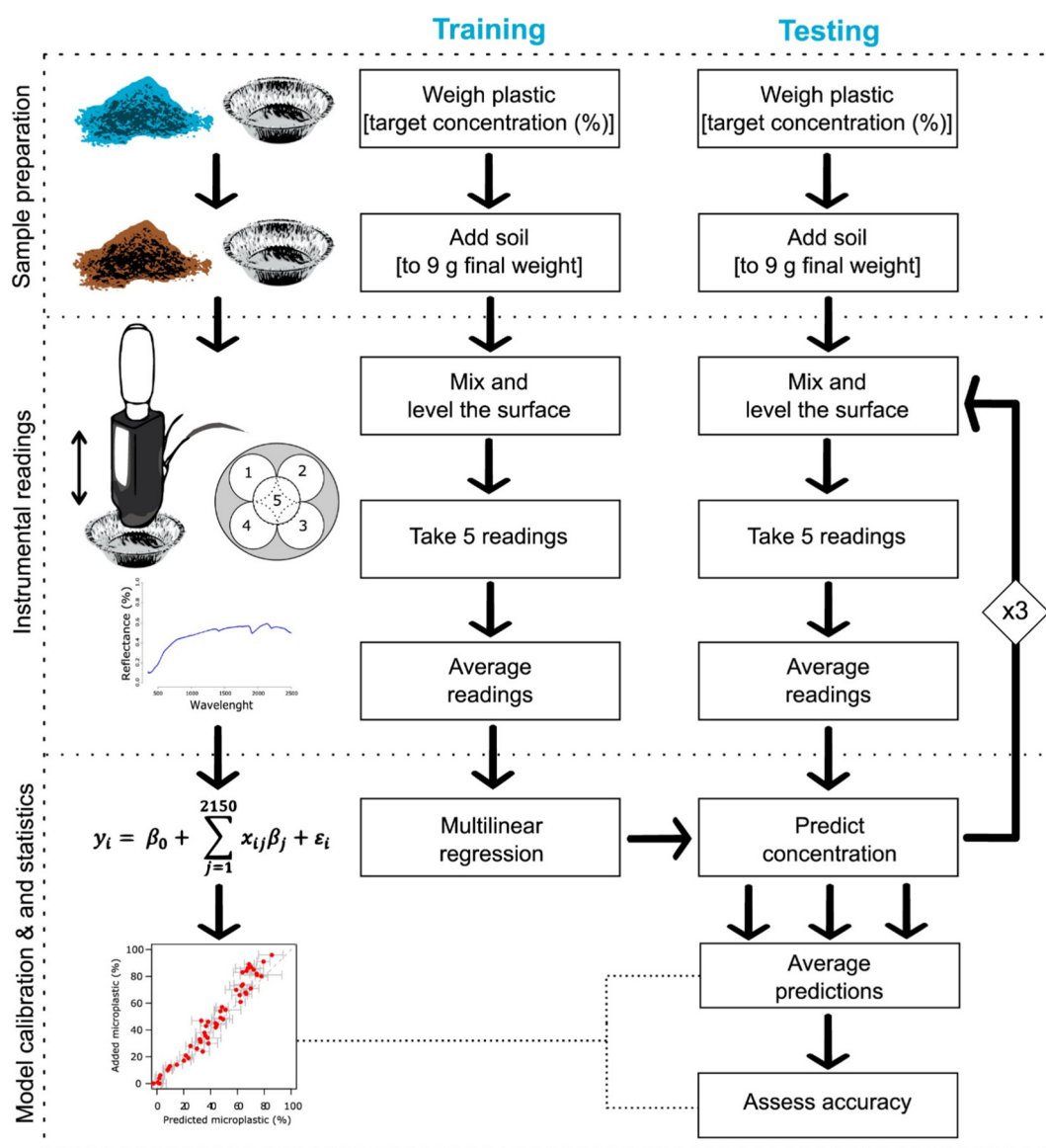
Treatment	LDPE	PET	PVC	Mix
Plastic polymer	Low-density polyethylene	Polyethylene terephthalate	Polyvinyl chloride	All three
Plastic colour	White	Various	Grey	Various
Source material	Pellets	Food packaging	Board	All three
Microplastics production method	Freezing; milling	Chopping; grinding	Filing; rasping	All three
Microplastics size range (mm)	1 to 0.5	1 to 0.5	1 to 0.5	1 to 0.5

board using a flat file and a rectangular sectioned rasp. The PVC chips were sieved and the 1 to 0.5 mm fraction stored. Once made, aluminium pots of 6 cm in diameter were used to hold the samples (Section 2.3).

### 2.3. Treatments and sample preparation

Four treatments of artificially polluted soil samples were made (Table 1). Each treatment comprised a training set to calibrate a predictive

model (Section 2.5.2) and a testing set to evaluate the model quantification and qualification effectiveness (Sections 2.5.3 and 2.5.4). The treatments LDPE, PET, and PVC comprised a set of 150 soil samples polluted with the corresponding plastic polymer plus ten pure soil controls ranging in concentrations between 0 and 100 g microplastics kg<sup>-1</sup> (0.0 and 10% by weight). The Mix treatment comprised twenty samples polluted with all three polymers used (PE, PET, and PVC) ranging in concentrations between 0 and 80 g microplastics kg<sup>-1</sup> (0.0 and 8.0% by weight).



**Fig. 1.** Analytical steps within a treatment. A defined microplastic weight was added to an aluminium pot according to the desired concentration and the total weight of the sample was set to 9 g by adding soil to the pot. The polluted sample was mixed and levelled to get an homogeneous surface and five readings were taken from different positions following a quincunx. The final measurement stood as the average of the five readings. The spectra recorded for the training data was used to calibrate a multilinear model by regressing the added amount of plastic on the observed reflectance. Later, the model was used to predict the concentration of microplastics of the testing set samples. Three predictions from three spectral replicates were made for each sample within the testing set to report the final result, which was used to assess the prediction accuracy.

### 2.3.1. Training sets

Treatments LDPE, PET, and PVC had each a training set of 100 samples plus five of the pure soil controls. For each treatment, the samples were made by adding cumulative plastic weights to the aluminium pots starting from 9 mg to 900 mg, increasing the amount of plastic added by 9 mg between each pot ( $\pm 0.001$  g model XL-410 Denver Instruments, NY). Later, soil was added to the pots for a total weight of 9 g. By this means, the obtained 100 samples presented a discrete microplastic concentration range from 1 to 100 g kg<sup>-1</sup> by 1 g kg<sup>-1</sup> steps (0.1 to 10% by weight). The training set of the Mix model comprised all samples made for treatments LDPE, PET, and PVC both from their training and testing sets.

### 2.3.2. Testing sets

The treatments for LDPE, PET, and PVC each had a testing set of 50 samples plus five of the pure soil controls. The amount of plastic and soil added to the pots, and thus the final concentration of microplastic of each sample, was defined by randomly selecting concentrations within the range of 1 to 100 g kg<sup>-1</sup> without replacement. The Mix treatment testing set had twenty samples plus five pure soil controls. Randomized amounts of the three plastic polymers (LDPE, PET, and PVC) were added to the aluminium pots for a total microplastic concentration in each sample of <80 g kg<sup>-1</sup> (8.0% by weight). Microplastic weights for this treatment were weighted with a  $\pm 0.01$  mg precision scale (model 210P Sartorius, Göttingen). The total weight of each sample was set to 9 g, adding the needed soil weight to the pots.

## 2.4. Vis-NIR spectral acquisition

General recommendations for soil analysis using vis-NIR Spectroscopy were followed (Wetterlind et al., 2013). Samples vis-NIR spectra were recorded using a portable spectroradiometer with a working range of 350 to 2500 nm (FieldSpec® 3 Analytical Spectral Devices, ASD Inc., CO). The spectroradiometer had a spectral resolution of 3 nm for the 350–1000 nm region and 10 nm for the 1000–2500 nm region, recording the spectrum with a 1 nm interval. A contact probe with a built-in halogen bulb was attached to the device. The probe allowed for direct measurements through a spot size of 10 mm. A Spectralon® white reference panel was used to calibrate the instrument every 10 min. Dark current measurements were made within the same time interval. For each sample, an average of 100 measurements was recorded as one independent reading.

Before recording the spectra, soil samples were homogeneously mixed with a stainless steel spoon and their surfaces were levelled. Five independent readings were recorded per sample and the probe placed in different points following a quincunx. The five recordings were averaged, obtaining a unique spectrum per sample. This procedure was performed three times for the samples in the testing sets of each treatment, producing three spectral replicates per sample within each testing set (Fig. 1). The complete reading procedure was performed three times for the training set of the Mix treatment in order to evaluate the method repeatability (Sections 2.5.3 and 2.5.4). The spectra of the pure plastic materials were recorded as reference. All spectra were recorded as vis-NIR reflectance (%). Before the statistical analysis, the spectra were centred and scaled by their variance. Additional pre-treatments such as differentiation or transformation to apparent absorption were not needed.

## 2.5. Data analysis

### 2.5.1. General spectra characterization

General spectral characteristics of the three polymers used were evaluated descriptively. The spectra acquired for the bare soil and the pure plastics were described visually and major trends individuated. The interaction between soil and the different amounts of added plastics was inspected to determine if the bare soil spectra presented changes

because of the increasing amounts of added plastics and, if so, to which extent. Evident changes in soil spectra with increasing amounts of added plastic were notated.

### 2.5.2. Predictive model

A Bayesian approach to a multiple linear regression was used to predict the plastic content of a soil sample using its spectral data. This approach has proved to be useful in studies where a large number of predictor variables outnumber the observations. The whole procedure and detailed description of software and available models can be found in Pérez and de los Campos (2014). Separate models were fitted to each treatment according to their plastic polymer. For the Mix treatment, three models were evaluated independently, one for each type of polymer, setting the added amount of the polymers not being evaluated to 0 (Mix [LDPE], Mix [PET], and Mix [PVC]). Using the spectra acquired for the training samples, the added amount of microplastic was regressed on the standardized spectra using the linear model

$$y_i = \beta_0 + \sum_{j=1}^{2150} x_{ij}\beta_j + \varepsilon_i$$

where  $y_i$  is the added amount of microplastic of a given sample  $i$ ,  $\beta_0$  is the intercept (the expected value of  $y$  when the wavelengths are set to their means),  $\{x_{ij}\}$  is the reflectance at each wavelength for a given sample  $i$ ,  $\beta_j$  is the effect of the wavelengths, and  $\varepsilon_i$  is the error term, assumed to be normally distributed with mean zero and variance  $\sigma_\varepsilon^2$ . Following this assumptions, the conditional distribution for the added microplastics to the samples is

$$P(y|\theta) = \prod_i^n N\left(y_i|\beta_0 + \sum_{j=1}^{2150} x_{ij}\beta_j, \sigma_\varepsilon^2\right)$$

where  $y = \{y_i\}$  represents the added amount of microplastics of all soil samples given  $\theta$ , which stands for the collection of all the model parameters ( $\beta_0$ ,  $\{\beta_j\}$ , and  $\sigma_\varepsilon^2$ ). The relation is given by a normal distribution with mean  $\beta_0 + \sum_{j=1}^{2150} x_{ij}\beta_j$ , and variance  $\sigma_\varepsilon^2$ .

The model parameters ( $\theta$ ) are estimated by a probability function, also known as prior density distribution or prior. The prior allows drawing samples from a posterior density distribution when is used jointly with the conditional distribution (or likelihood). The posterior density distribution corresponds to the estimated plastic contents for a given treatment. Here, the prior density for the model parameters ( $\theta$ ) was as follows

$$p(\theta) = N(\beta_0|0, 1e^{05}) + \chi^{-2}(\sigma_\varepsilon^2|df_\varepsilon, S_\varepsilon) + \prod_{j=1}^{2150} p(\beta_j),$$

where...

$$p(\beta_j) = t(\beta_j|5, S_\beta) Ga(S_\beta|rate, shape) \cdot Ber(\pi|p) beta(p|shape_1, shape_2)$$

In this prior, the intercept ( $\beta_0$ ) is estimated from a normal distribution ( $N$ ) of mean 0 and large variance ( $1e^{05}$ ), treating this intercept as a fixed effect. As the wavelengths were scaled and centred, the intercept represents the predicted value of  $y$  when the predictor values  $\{x_{ij}\}$  are set to their means. The variance ( $\sigma_\varepsilon^2$ ) is estimated from a scaled-inversed  $\chi^2$  with  $df_\varepsilon$  degrees of freedom and  $S_\varepsilon$  scale parameter. Finally,  $\{\beta_j\}$  are estimated from a joint probability of a scaled-t density and a point of mass at zero. By this means,  $\{\beta_j\}$  parameters are drawn from a scaled-t density distribution with 5 degrees of freedom, and a scale parameter  $S_\beta$  that is drawn from a gamma ( $Ga$ ) distribution with rate and shape as parameters. The draws are turned on/off ( $\pi = 1$  or 0) according to a Bernulli distribution ( $Ber$ ) with the  $p$  parameter drawn from a beta distribution that has itself  $shape_1$  and  $shape_2$  as parameters. The last step induced variable selection. The prior used here is usually



referenced as BayesB and has proven to work sufficiently in complex spectra problems (e.g. [Ferragina et al., 2015](#)).

The BayesB model is implemented in the R environment ([R Core Team, 2017](#)) package 'BGLR' (Bayesian Genomic Linear Regression) by [Pérez and de los Campos \(2014\)](#). The authors provided a comprehensive list of the algorithms implemented, and a list of working examples. The software provided a series of rules to estimate all the high-order hyperparameters of the model ( $df_e$ ,  $S_e$ ,  $S_\beta$ , rate, shape, shape<sub>1</sub>, shape<sub>2</sub>) that need to be specified. The rules were established to produce uninformative but proper priors (does integrate to one). The software drew estimates from the posterior distribution using a Gibbs sampler with scalar updating, meaning that all  $\{\beta_i\}$  estimates were drawn within one step. As the distribution of  $\{\beta_i\}$  estimates did not have a closed form, their samples were drawn using a Metropolis-Hastings algorithm. The full algorithm implemented by the BGLR package is described step by step in [Meuwissen et al. \(2001\)](#).

Inferences (estimates of  $\{y_i\}$ ) were based on  $1e^{06}$  samples collected from the posterior after discarding  $1e^{05}$  samples. The convergence of the posterior chains to a stationary state was evaluated following the Gelmans and Rubin's approach using three chains. The method is implemented and fully described in the R package 'CODA' (Output Analysis and Diagnostics for MCMC) ([Plummer et al., 2006](#)).

### 2.5.3. Statistical analysis

The samples comprised in the testing set of each treatment were measured three times to predict three probable added amounts of plastic per sample using the model ([Sections 2.4 and 2.5.2](#)). As a Bayesian regression was used, the expected values of  $\{y_i\}$  were not unique, but a normal distribution with mean  $\{\hat{y}_i\}$  and standard deviation  $\{\sigma_{y_i}\}$  ([Section 2.5.1](#)). A Monte Carlo approach was used to average the three inferences out from the three spectral repetitions, drawing 1000 scenarios out of each of the three expected values of  $\{y_i\}$ . The simulated predictions were averaged and the interquartile range (IQR) calculated to report a final result ([Fig. 1](#)). The testing set of the Mix treatment were counted with three final results per each sample, as the whole reading-predicting procedure was performed three times per sample.

### 2.5.4. Assessment of prediction accuracy

The accuracy in the prediction of each treatment was addressed using the testing sets. The linear relationship between the added plastic as concentration and those predicted by the model ( $\{\hat{y}_i\}$ ) was evaluated. Firstly, a linear regression was adjusted to the added and predicted concentrations, calculating the slope of the linear relationship ( $m$ ) and the coefficient of determination ( $R^2$ ). Secondly, the Pearson correlation between the added and predicted concentration was observed. Finally, the

root-mean-square deviation (RMSD) was calculated as  $RMSD = \sqrt{\sum (\hat{y}_i - y_i)^2 / N}$ , where  $y_i$  is the added plastic as concentration and  $\hat{y}_i$  the predicted by the model for a sample  $i$ , with  $N$  number of samples. The RMSD stands here as a descriptive measure of the differences between the model predicted values and the added concentrations of plastic. The RMSD approach is widely suggested for vis-NIR model assessments ([Wetterlind et al., 2013](#)). In addition to the linear relationship between the variables, the model residual variance ( $\sigma_e^2$ ) and the expected value of  $\{y_i\}$  standard deviation ( $E[\sigma_{y_i}]$ ) were used to compare between the models from the different treatments.

The method detection limit was defined as the concentration of plastic in  $g\ kg^{-1}$ , which gives a predicted concentration equal to three times the standard deviation of the predicted concentration of the bare soil samples (blanks) included in the testing set of treatments.

The testing set of the Mix treatment was used to evaluate the repeatability of the method, since three final results were obtained for each sample. The coefficient of variation (CV) was calculated (standard deviation/mean) for each final prediction of added microplastic, using the results from all of the 20 samples to estimate the descriptive statistics

of the CV (quantiles, mean, standard deviation). Furthermore, the coefficient of repeatability (CR) was assessed as the 95% confidence interval for expected differences in the final prediction of the same sample.

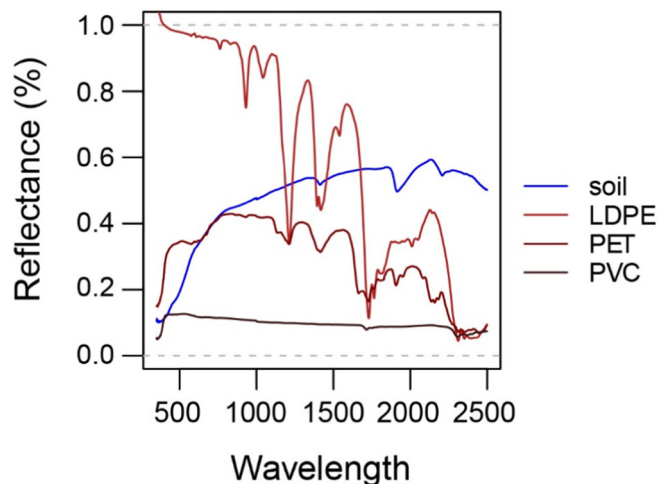
## 3. Results

### 3.1. Spectral characteristics of the different plastics polymers and their interaction with soil

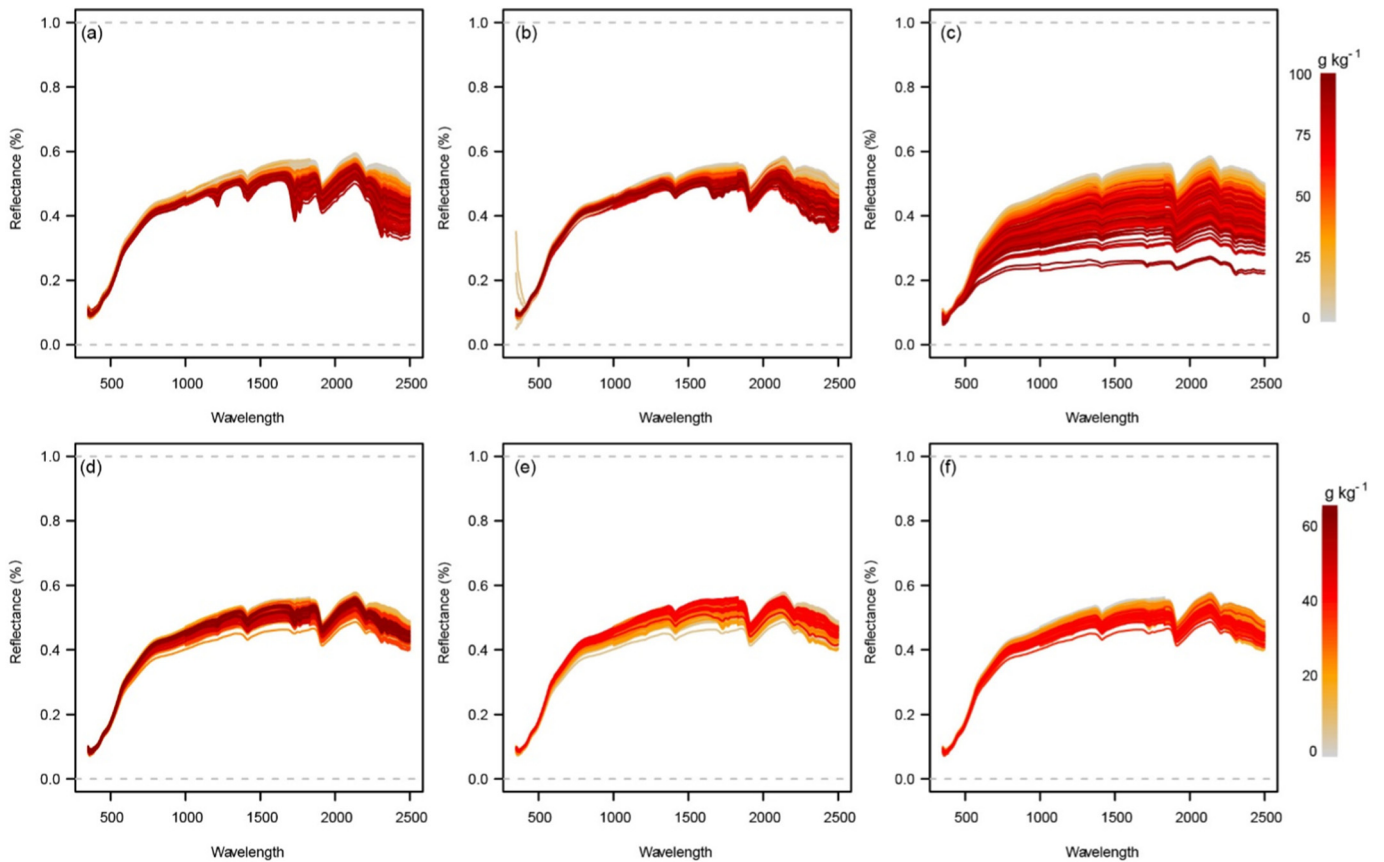
The spectra recorded as reference for the plastic polymers revealed that the three plastics presented different behaviours along the studied wavelength range ([Fig. 2](#)). Furthermore, the bare soil spectral signature stood out without overlapping with any of the plastics studied. The only exception was within the 650 to 800 nm range, in which the soil signal joined that of PET. While all three plastic polymers presented a lower reflectance than the soil at the shortwave infrared range (from 1700 nm onwards), the behaviour at the near infrared and visible range varied among polymers.

Low-density polyethylene presented a high reflectance within the visible range diminishing while the wavelength increased. It was the brighter of the three plastic polymers evaluated and was brighter than the soil within the visible and near infrared range. It presented three major and distinctive absorption peaks at 1210, 1420 and 1730 nm, and two minor peaks at 930 and 1040 nm. Polyvinyl chloride presented the higher absorption among all plastic polymers studied. Its reflectance was consistently lower than that of the soil, decreasing steadily through the wavelength range. Reflectance values for PVC were below 13% across the whole range studied, shrinking below 10% at wavelengths above 1000 nm. This plastic presented two subtle absorption peaks at 1720 and 2300 nm. Finally, PET fell between PE and PVC. Within the visible range, PET presented a higher reflectance than that of the soil, overlapping the soil signal between the 650 and 800 nm when it reached its higher reflectance (43%). At wavelengths >800 nm, PET reflectance started to decrease progressively until it merged with LDPE and PVC signals at 2300 nm (reflectance = 8%). Polyethylene terephthalate presented distinctive absorption peaks at 1210, 1420 and 1730 nm matching LDPE behaviour.

Soil samples with added microplastics presented changes respective to the bare soil spectral signature along all of the wavelengths recorded ([Fig. 3](#)). While there were virtually no distinctions within the visible range up to 800 nm, at higher wavelengths, the soil reflectance contracted proportionally to the amount of plastic added as pollutant. In this way, the soil reflected less light with increasing plastic concentrations at the near and shortwave infrared range. As the data shows, the proportion of the reduction in the reflectance due to the plastic addition



**Fig. 2.** Spectral characteristics of the soil and the different plastics polymers used. Reflectance of pure references (100%) of LDPE, PET, and PVC and soil.



**Fig. 3.** Changes in the vis-NIR spectrum of a soil when increasing amounts of (a) LDPE, (b) PET, or (c) PVC are added, and when a combined amount of the same polymers are spiked (d–e), tracing (d) LDPE; (e) PET; (f) PVC one at a time (Mix treatment).

depended on the wavelength at which the reflectance was measured and the plastic polymer added. On the one hand, since all plastics decreased their reflectance when the wavelength increased, the proportion of the reduction was higher when the measurements were taken at longer wavelengths. On the other hand, plastics determined soil reflectance in different degrees as they have distinctive optical properties. For example, at a given wavelength and similar plastic concentration, PVC decreased soil reflectance to a higher degree than LDPE, due to PVC's stronger absorption. Congruently, the stronger absorption peaks observed for LDPE were reflected by the spectral signature of a soil polluted with this polymer.

### 3.2. Predicting added microplastic concentrations in soil samples

The model performance presented the highest correlation coefficient and the best fit for the LDPE treatment (Table 2). This treatment also showed the lowest residual variance ( $\sigma_e^2$ ) and expected value of  $y_i$  standard deviation ( $E[\sigma_y]$ ) among the treatments that comprised one plastic polymer and had an equally-sized training set (LDPE, PET, and PVC). The slope of the linear relation ( $m$ ) between the added plastic and the predicted concentration suggested a slight underestimation of the soil plastic content. Fig. 4 indicates that the underestimation of LDPE increased as the amount of plastic added increased. The RMSD shows that predicted concentrations had a standard deviation from the added amount of  $8 \text{ g kg}^{-1}$ , which represents around the 8% of the concentration range studied ( $0\text{--}100 \text{ g kg}^{-1}$ ). A direct implication is that predictions of LDPE concentrations below  $10 \text{ g kg}^{-1}$  could lead to false positives. Nevertheless, the detection limit estimated for LDPE was  $3 \text{ g kg}^{-1}$ .

The model performance for PET showed the lowest fit across all treatments. Yet, the correlation was significant and close to 0.80 and although the  $\sigma_e^2$  was higher than for LDPE, it stayed close to that of PVC.

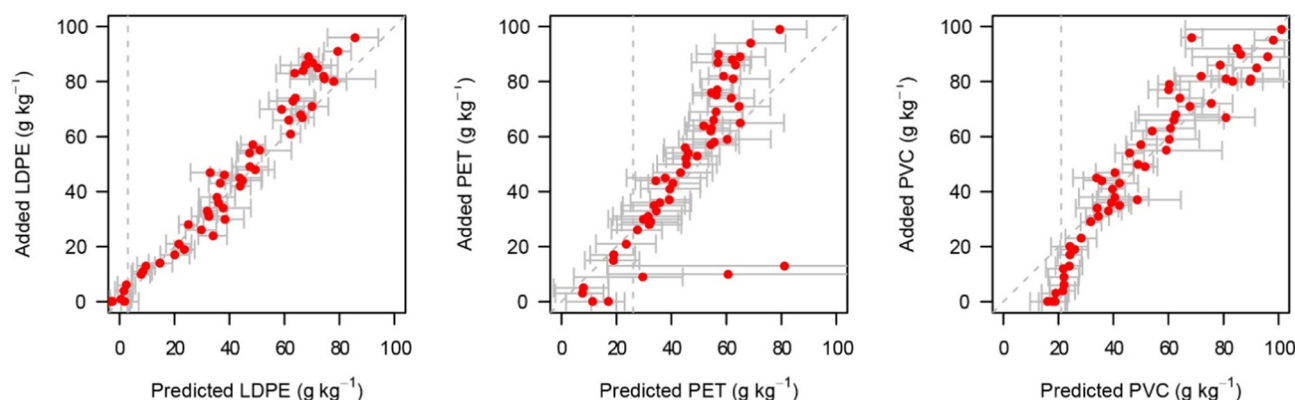
Contrariwise, the  $E[\sigma_y]$  was large, standing out with a figure that approached 10% of the concentration range studied. The observed  $E[\sigma_y]$  reflects back to a large RMSD, which is detached from all other treatments with a value twice as large. Fig. 4 suggests that the goodness of fit decreased at PET concentrations above  $60 \text{ g kg}^{-1}$  and that there were outliers within the samples. On one hand, as the samples were custom-made by adding a precise amount of plastic, the outliers were kept since they reflect PET properties and not laboratory mistakes. On the other, the model performance was assessed a second time pruning the predictions above  $60 \text{ g kg}^{-1}$ . Evaluating the predictions within the pruned concentration range increased the model fit ( $R^2 = 0.89$ ) and the correlation (Pearson's  $r = 0.95$ ), and decreased the RMSD ( $7 \text{ g kg}^{-1}$ ) considerably.

PVC treatment stood close to LDPE, showing a similar fit and correlation. Nonetheless, the  $\sigma_e^2$  was the highest of all treatments. The observed  $E[\sigma_y]$  was larger by about  $2 \text{ g kg}^{-1}$  compared to that of LDPE and  $4 \text{ g kg}^{-1}$  smaller than that of PET. The RMSD shows that predictions

**Table 2**

Indicators of prediction accuracy for each treatment. Coefficient of determination ( $R^2$ ), linear relation ( $m$ ), root-mean-square deviation (RMSD), Pearson's  $r$  (Correlation), model residual variance ( $\sigma_e^2$ ), expected value of  $y_i$  standard deviation ( $E[\sigma_y]$ ), and detection limit (DL).

Treatment	$R^2$	$m$	RMSD ( $\text{g kg}^{-1}$ )	Correlation	$\sigma_e^2$ ( $\text{g kg}^{-1}$ )	$E[\sigma_y]$ ( $\text{g kg}^{-1}$ )	DL ( $\text{g kg}^{-1}$ )
LDPE	0.96	1.13	8	0.98	0.064	5	3
PET	0.62	1.24	18	0.79	0.148	11	26
PVC	0.90	1.13	10	0.95	0.154	6	21
Mix [LDPE]	0.79	1.25	8	0.89	0.057	2	15
Mix [PET]	0.82	1.66	10	0.90	0.071	1	12
Mix [PVC]	0.89	1.28	5	0.94	0.057	2	14



**Fig. 4.** Predicted microplastic concentrations in samples against added microplastic weights for LDPE (left), PET (centre) and PVC (right) treatments. The red dots stand for the predicted mean, while the grey bars stand for the  $\pm$ IQR. The diagonal dashed grey line corresponds to the 1:1 linear relation, while the vertical corresponds to the detection limit.

had a standard deviation from the added PVC around  $2 \text{ g kg}^{-1}$  larger than that of LDPE. Once again, the RMSD suggests that predictions of PVC below  $10 \text{ g kg}^{-1}$  could lead to false positives. In the same direction, Fig. 4 indicates that predictions of added values below  $25 \text{ g kg}^{-1}$  adjust poorly to a 1:1 linear relation. Similarly to LDPE, PVC treatment did not show extreme outliers.

### 3.3. Predicting the concentration of a single microplastic polymer in soil samples with more than one polymer type

In general terms, the Mix treatment had a lower goodness of fit than LDPE, PVC, and the pruned PET (Table 2). Within this treatment, the correlation between the added amounts of microplastics and the predicted value fluctuated around 0.90, which was not far from the Pearson's  $r$  observed for LDPE and PVC. Moreover, the  $\sigma_e^2$  was on average three times smaller than that of PET and PVC due to the larger number of samples included in the Mix training dataset respect to the remaining treatments. This is equally applicable to the  $E[\sigma_y]$ , which was consistently smaller for all plastic polymers when they were predicted under the Mix scenario (more than one plastic polymer present in the sample) respect to the remaining treatments.

Low-density polyethylene presented the lowest fit when its concentration was predicted under the extra noise of the Mix treatment (Table 2, Mix [LDPE]). Nonetheless, the Mix [LDPE] predictions presented a significant correlation with the added plastic, which was similar but slightly lower than that of Mix [PET] and Mix [PVC]. The  $\sigma_e^2$  was the lowest of all treatments, matching that of Mix [PVC]. The  $E[\sigma_y]$  was considerably lower than that observed when low-density polyethylene was predicted in the LDPE treatment because of the larger training set. Its value was, however, the highest among the plastic types predicted within the Mix treatment. The observed RMSD was equal to that of LDPE, and was  $2 \text{ g kg}^{-1}$  smaller than that of Mix [PET]. Regarding the repeatability, Mix [LDPE] predictions had the lowest coefficient of variation (CV) of the Mix treatment, which presented a 3% interquartile range (IQR) with a median of 8% (Table 3). The coefficient of repeatability (CR) showed that predictions of low-density polyethylene

concentrations in soil samples polluted with more than one polymer were expected to vary up to  $8.4 \text{ g kg}^{-1}$  for the same sample. Fig. 5 shows that the Mix [LDPE] predictions did not deviate from the 1:1 ratio with the added low-density polyethylene, and that there were no outliers within the treatment.

Mix [PET] predictions showed a higher correlation with the added concentration of plastic and a better fit compared to the PET treatment (Table 2, Mix [PET]). The best goodness of fit echoed in a relatively lower RMSD for Mix [PET] than that of PET. The CV presented an interquartile range of 18% with a median of 20% (Table 3). This was the highest CV observed for all plastic polymers predicted for the Mix treatment. However, the CR for Mix [PET] was the lowest observed, indicating that the expected variation of repeated measurements will most probably be under  $5.1 \text{ g kg}^{-1}$ . Despite the higher accuracy in repeatability that Mix [PET] presented compared to Mix [LDPE] and Mix [PVC], its predictions continuously underestimated the amount of plastic added to the soil sample, as was revealed by the linear 1:1 relation (Fig. 5). In this regard, the observed value of  $m$  was the larger among treatments (Table 2).

Mix [PVC] predictions presented the best fit and the highest correlation with the added microplastic among all Mix treatment plastic assessments (Table 2, Mix [PVC]). The RMSD observed was the lowest among all treatments. However, the repeatability was weaker than that of Mix [LDPE] showing a CV with an interquartile range of 11% and a median of 15%. The CR was the broadest observed for Mix predictions, indicating that repeated measurements are expected to vary up to  $9.0 \text{ g kg}^{-1}$ . Fig. 5 shows a good adjustment between the predicted concentrations and the added amount plastic to the 1:1 linear relation, although the observed  $m$  value indicates a tendency to underestimate the added plastic content.

## 4. Discussion

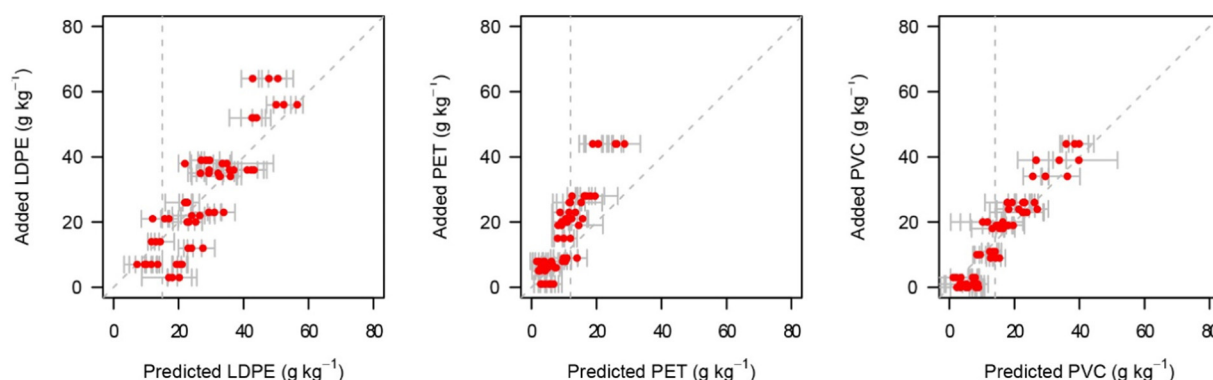
### 4.1. Vis-NIR qualitative and quantitative prediction capabilities

The vis-NIR method proposed was able to predict microplastic concentrations of LDPE, PET, and PVC in soil samples, presenting an

**Table 3**  
Repeatability indicators for Mix treatment. Minimum, maximum, quantiles, and mean for the observed coefficient of variation for the same sample. Coefficient of repeatability presented as the 95% confidence interval for differences in predictions for the same sample.

Treatment	Coefficient of variation (%)							Coefficient of repeatability ( $\text{g kg}^{-1}$ )	
	Min	1st Qu	Median	Mean	3rd Qu	Max.	SD	$p = 0.025$	$p = 0.975$
Mix [LDPE]	1	6	8	8	9	23	5	0.2	8.4
Mix [PET]	3	12	20	25	30	90	22	0.1	5.1
Mix [PVC]	3	9	15	15	20	33	8	0.1	9.0





**Fig. 5.** Predicted LDPE (left), PET (centre), and PVC (right) concentrations in samples against added weights for the Mix treatment. The red dots stand for the predicted mean, while the grey bars stand for the  $\pm 1QR$ . The diagonal dashed grey line corresponds to the 1:1 linear relation, while the vertical corresponds to the detection limit.

approximate accuracy of 8, 5, and 9  $\text{g kg}^{-1}$  (upper boundary of the repeatability coefficient) and a detection limit of 15, 12, 14  $\text{g kg}^{-1}$  for LDPE, PET, and PVC, respectively. The method was fast, taking about 3 min to complete each independent reading (five spectra acquisition). Moreover, it was able to predict the microplastic concentration in samples that had composite amounts of microplastics, showing qualitative and quantitative analytical capabilities. This was different than visual identification techniques and FT-IR and chromatographic techniques such as Pyr-GC-MS or the more recently proposed thermal desorption gas chromatography mass spectrometry (TED-GC-MS) (Dümichen et al., 2017).

On the one hand, visual identification techniques attempt to count or estimate the number of microplastics over a given area, resulting in a number of particles detected in a standard volume of sample (Crawford and Quinn, 2017b). This leads to possible biases due to the presence of misleading organic or clay particles that might be wrongly counted as plastics (Souza Machado et al., 2018; Ziajahromi et al., 2017). While this drawback has been partially overcome by semi-automated computer estimations, there is still a point at which a human operator needs to decide what on the image to be processed is plastic and what is not (Zhang et al., 2018). Moreover, visual techniques cannot qualify microplastics by compound and can only classify different particles by colour, size, and shape (Hidalgo-Ruz et al., 2012). Therefore, visual techniques usually rely on additional qualification steps performed by FT-IR (Mahon et al., 2017).

On the other hand, FT-IR deals with microplastics isolated from bulk samples. This method is useful to qualify the plastic type that is present within a sample. Nonetheless, FT-IR instruments were slow in acquiring the spectral images, even when equipped with a focal plane array that increases the sample area to be measured (Minténig et al., 2017). Moreover, samples containing multiple microplastics polymers are known to constitute a challenge for FT-IR spectroscopic analysis (Fuller and Gautam, 2016), but new automated approaches offer a solution to the problem of identification (Primpke et al., 2017). In this regard, efforts have been recently made to not only qualify but to quantify the microplastic content (Simon et al., 2018). The opportunity that vis-NIR spectroscopy offers, however, is that it allows the quantification and qualification of the microplastic content in soil samples using one analytical step.

However, the use of vis-NIR spectroscopy is not free from the challenge of polymer recognition. The predictions made by the spectroradiometer method worked better when homogeneously coloured plastics were added to the samples (LDPE, PVC). Prediction accuracy was diminished when multi-coloured plastic was used (PET). Similarly, interference due to dyeing molecules has been reported in other techniques of microplastic recognition (Lots et al., 2017). Besides the higher RMSD observed for PET, the drop in prediction accuracy was also revealed by the increase in the deviation of PET predictions ( $E[\sigma_y]$ ).

The decrease in accuracy is an obvious limitation because a bigger spectral library (training set) that can take different colours/dyes into account is needed to avoid colour-related-noise, as will be discussed in Section 4.3.

The use of NIR spectroscopy has recently been tested by Paul et al. (2018). In this work, the authors used a spectrometer to predict whether a soil sample held PE, PET, polypropylene, polystyrene, and/or PVC. Despite they have used a different statistical approach, a similar dependency on the training set was found. Thus, made-to-measure reference samples are needed to avoid false positives (see Section 4.3). Besides the similarities, the method described by Paul et al. (2018) was not able to predict plastic content, and was limited to classifying the samples as positive or negative for the presence of microplastics. Therefore, the quantitative prediction capabilities showed by the regression approach constitute a step forward for microplastic detection in soil samples.

#### 4.2. Avoidance of microplastic extraction in vis-NIR techniques

The use of the spectroradiometer proposed in this work circumvents the need for microplastic extraction. Moreover, while only minimal sample preparation (drying and sieving) was carried out during this study, spectroradiometers could be used to measure bulk soil samples thus avoiding extensive sample preparation (Xu et al., 2018). The avoidance of microplastic extraction steps gives rise to two major differences with respect to current techniques. Firstly, it reduces the total time devoted to sample analysis, making the overall analytical time shorter. Secondly, it removes the need for sample preparation and this reduction in manipulation diminishes biases caused by human handling (Ziajahromi et al., 2017).

The extra steps commonly required for sample preparation increase the analytical time. Flotation methods take between 12 and 24 h to complete not to mention the time needed to dry samples, filters, and sieves (Lots et al., 2017; Zhang et al., 2018). Pressurised fluid extraction remains a fast alternative (15 min), but this method is not perfect and can result in recovery rates  $>100\%$  (Fuller and Gautam, 2016). To date, elutriation has not been tested on soil samples, but the total processing time to isolate microplastics from sand particles takes up to 30 min (Claessens et al., 2013). Furthermore, when the elutriation extraction was tested on samples rich in organic matter (sludge), the overall processing time was longer (Mahon et al., 2017). The complexity of wet separation methods has pushed researchers to explore new techniques. The use of electrostatic separators is one of the most recent techniques (Felsing et al., 2018). Despite the fact that it has a promising future, the extraction itself takes 4 h to complete and it has not been tried in soil. Therefore, skipping the extraction steps and reducing sample preparation time are definitely advantages to using spectroradiometers.



However, current extraction techniques could lead to biases caused by sample manipulation. Flotation, fluid extraction, and elutriation involve many steps consisting of watering, sieving, and filtering as well as the intermediate steps of brushing particles from filters or sieves onto microscope slides, petri dishes, or centrifuge tubes (Fuller and Gautam, 2016; Mintenig et al., 2017; Zhang et al., 2018). Reported recovery rates indicate around 10% from interferences. Authors frequently claim that the sample preparation steps are not standardized which makes dealing with complex matrices such as soil challenging to researchers. Here again, the use of spectroradiometers to directly measure microplastic content in soil samples is an advantage.

#### 4.3. Method limitations

The need for a training set to predict the content and type of polymers within a soil sample constitutes a limitation for the proposed method. A comprehensive training data set is necessary in order to expand the technique further to encompass other polymers and concentration ranges. Moreover, as vis-NIR spectra varies for different soil types, increasing or decreasing the amount of reflected light, different soil types should also be considered when an analysis is performed (Viscarra Rossel et al., 2016). Therefore, a made-to-measure training library is needed to establish a calibration curve for each scenario to be predicted. The method success rates rely on the meticulous construction of this calibration curve. Thus, exploratory analyses are needed to understand which plastic polymers are to be expected and at which concentration ranges.

Despite the fact that generating a made-to-measure training dataset for a given scenario could be time consuming, the advantage is that once constructed, it could be used indefinitely. This is similar to the spectral libraries that use the FT-IR instruments to identify different polymers (Crawford and Quinn, 2017b). Furthermore, acquired sets could be enhanced by new additions since the results showed that larger the training data, the better the prediction.

Another limitation could be the crude predictions of microplastic concentrations ( $\text{RMSD} \approx 10 \text{ g kg}^{-1}$ ) and detection limits  $\approx 15 \text{ g kg}^{-1}$ . Worldwide, there is a lack of environmental monitoring campaigns reporting expected concentrations of microplastics in soils (Bläsing and Amelung, 2018), making it difficult to know if the assessment capability of the method proposed could be useful for general monitoring purposes. Table 4 presents some of the values reported so far.

According to the information reviewed, the proposed method would only be suitable for the study case used in the work of Fuller and Gautam (2016). However, theoretically, it would be also applicable under some of the critical scenarios projected by Ng et al. (2018). All of the cases

examined microplastic hotspots. While Fuller and Gautam (2016) evaluated soil samples located near an industrial area, Ng et al. (2018) estimated expected concentrations of plastics for soils with high rates of sludge application. Although the pathways by which microplastics reach the soil are yet unclear (Vollertsen and Hansen, 2017), there is an increasing assumption that sludge application could be one of the leading routes (Nizzetto et al., 2016). Therefore, the method could be used to rapidly quantify and qualify microplastic content in hotspots such as industrial and dump sites and arguably in agricultural soils with recurrent sludge applications. Consequently, the proposed vis-NIR technique could be coupled to monitoring campaigns where other more precise but time-consuming strategies are used.

Noticeably, the use of the proposed method in hotspots should be done with care. Vollertsen and Hansen (2017) studied microplastic occurrences in Danish soils either with or without sludge application and found only trace concentrations of microplastics in both management scenarios. Thus, it is not always true that sludge applications naturally imply the presence of a microplastic hotspot. Furthermore, in China's Loess plateau, where plastic mulch has been used for almost 20 years to cultivate crops, the concentration of microplastics in soil samples measured a maximum of 0.1% (Zhang et al., 2018).

While the avoidance of extraction procedures constitutes an advantage of vis-NIR spectroscopy, the detection limit could be lowered using concentration steps. While carrying out the separation steps increases the total analytical time, the inherent reading speed of the spectroradiometer results in faster analysis than performing particle image evaluations. New developments in dry extraction using electrostatic separators are promising (Felsing et al., 2018) and should be tested in soil. To this propose, new separator prototypes must be designed, taking into consideration both the sample volume and the processing time.

We propose that by coupling the presented methodology with a proper separation step, the method could be used not only in hotspots, but for general microplastic quantification and identification in soil samples. As an example, we conducted a short trial to test how far the quantification capabilities can go if the polymers are isolated from the matrix (soil, sludge, etc.) before measuring with the spectroradiometer. Using activated charcoal filter paper (Macherey-Nagel MN 728) as a background media, the reflectance of increasing amounts of each polymer was recorded. Following the same statistical approach, the method was able to predict in milligrams the amounts of microplastics particles deposited over the filter. The test showed a DL of 0.7, 1.2, and 1.0 mg for LDPE, PET, and PVC, with a RMSD of 0.7, 0.7, and 1.1 mg, respectively (Fig. 6). The accumulation of the plastic particles over the filter could be achieved by flotation and filtration steps at the end of which the particles remain trapped within the filter. Nevertheless, the coupling of the method with separation steps needs to be studied further, as the matter exceeds the expectations of the present work.

#### 5. Conclusion

Our results suggest that it is possible to use vis-NIR techniques to identify and quantify LDPE, PET, and PVC microplastics in soil samples. To this purpose, a spectroradiometer with a working range from 350 to 2500 nm can be used to predict microplastic concentrations with an accuracy of  $10 \text{ g kg}^{-1}$  and detection limit of  $\approx 15 \text{ g kg}^{-1}$ . The method proposed is different than other approaches, being faster, avoiding extraction steps, and directly quantifying the amount of microplastics in a sample.

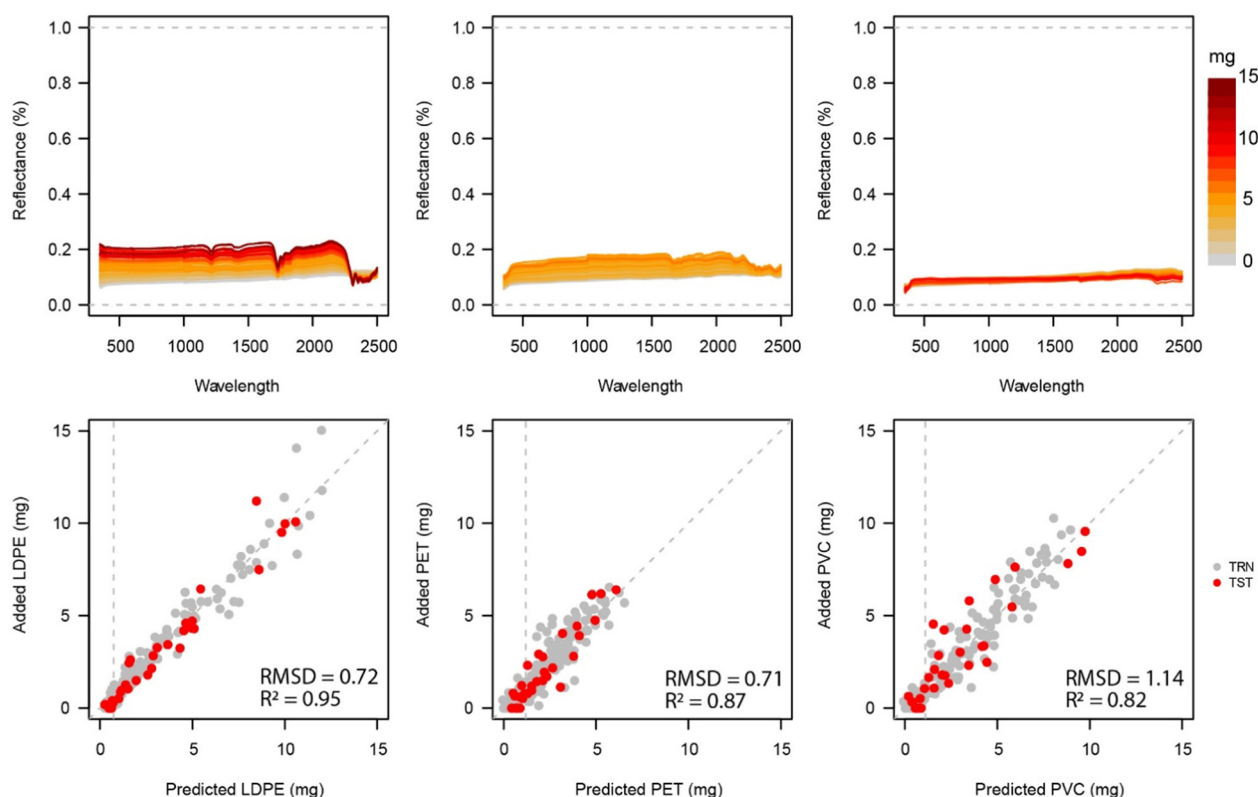
Our work constitutes a proof of concept in using vis-NIR techniques to qualify and quantify microplastics in soil samples. However, there is a lot to uncover in order to develop a useful technique that can be applied to multiple scenarios. The development of a general purpose spectral library will be one of the most challenging milestones in developing this method. On the bright side, a comprehensive spectral library could be built progressively and include smaller libraries compiled for more

**Table 4**  
Reported concentrations of microplastics in soil samples. Lower (L) and higher (H) concentrations reported in %. The methods used for extraction and quantification are included (extraction & quantification).

Author	L (%)	H (%)	Place	Extraction & quantification
Fuller and Gautam (2016)	0.03	6.75	Australia	Pressurised fluid extraction & FT-IR
Zhang et al. (2018)	<0.01	0.11	China	Flotation & semi-automated visual identification
Huerta Lwanga et al. (2017b) <sup>a</sup>	–	–	Mexico	Flotation & visual identification
Vollertsen and Hansen (2017)	<0.01	<0.01	Denmark	Flotation FT-IR
Ng et al. (2018) <sup>b</sup>	<0.01	<0.01	Denmark	Flotation FT-IR
	1.44	9.88	Australia	Theoretical estimation
	0.31	2.00	USA	Theoretical estimation
	0.03	0.39	Europe	Theoretical estimation

<sup>a</sup> These authors reported microplastic concentrations in number of particles per gram (0–2.77 particles  $\text{g}^{-1}$ ). Therefore, there is not a direct way to estimate the concentration.

<sup>b</sup> Ng et al. (2018) reported theoretical input values of microplastics to soils through sludge application. The maximum value reported corresponds to an extrapolation of the highest rate disposed after 15 years of sludge application.



**Fig. 6.** Above: change in the reflectance of activated charcoal filter paper when increasing amounts of LDPE (a), PET (b), and PVC (c) are added to the filter. Down: predicted weights of LDPE (d), PET (e), and PVC (f) added to the filter against the known weights. A hundred and fifty samples (i.e. filters + a known concentration of polymer) were registered per polymer, using 120 records as a training group (grey dots) and 30 records as a testing set (red dots). Validation was performed using the testing set. Dotted grey vertical lines indicate the DL for each polymer, while diagonal stands for the 1:1 linear relationship.

specific goals. Direct on-site measurements of microplastics in soil at hotspots ( $>15 \text{ g kg}^{-1}$ ) should be tested, exploring the possibility of the complete suppression of sample preparation. Finally, as a proof of concept, this work provides an opportunity for other applications or devices that use vis-NIR spectra acquisition –such as hyperspectral cameras– to be used in studies that deal with microplastics.

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