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Condition of composted microplastics after they have been buried for 30 years: vertical distribution in the soil and degree of degradation

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Abstract:

Microplastics in soils are a growing concern. Composting household wastes can introduce microplastics to agroecosystems, because when unsorted compost is used as a fertilizer, the plastic debris it contains degrades to microplastics. This paper examines the distribution and degradation of microplastics in agricultural soil samples to investigate their potential mobility. The source of microplastics was a household waste compost added to the soil more than 30 years before the study. The microplastics were sorted from a plot-composite soil and characterised by Attenuated Total Reflectance combined with Fourier transform infrared spectroscopy (ATR-FTIR). The microplastics are present in the cultivated depth but have not been transferred deeper (2.9 g kg⁻¹ in the 0–5 cm soil depth against 0.9 g kg⁻¹ in the 30–35 cm soil depth). Polyethylene (PE), polypropylene (PP), polystyrene (PS) and Polyvinylchloride (PVC) were identified in the forms of heterogeneous fragments, films, and fibres and accounted for 90% of the total microplastics. Advanced degradation observed was mainly assumed to be due to composting, though the plastic may have degraded further in the soil matrix. Highly degraded plastics are a greater danger for further leaching of contaminants into soil and our food supply.

Keywords: Microplastics, Household wastes, Compost, Soil, ATR-FTIR, Plastic degradation

1. Introduction

Global plastic production reached nearly 370 Mt in 2019 [1], and plastic waste has increased apace. Around 79% of plastic waste is estimated to end up in landfills or in the environment [2], leading to plastic accumulation in all environmental compartments [3–6]. Additives in polymer formulations make plastics durable. Accordingly, they become complex persistent contaminants once they reach the environment [7]; the polymer itself is only a part of the cause of negative effects on organisms and ecosystems; contaminants also play a role [8–12]. Although plastic debris is ubiquitous, its investigation in terrestrial environments, especially in soils, is recent. Plastic sources and inputs to soils are numerous, including agricultural practices such as plastic mulching [13,14], greenhouse use [15], irrigation [16], sewage sludge spreading [17–19], and organic fertiliser applications [20]

Compost is an increasingly common component of organic fertilisers. Composting reduces the overall waste that is incinerated or landfilled [21], especially for household waste. Soil fertilisation with household compost has many recognised benefits, such as stabilising soil structure, improving water retention, and increasing organic matter and essential nutrient content; this reduces the need for synthetic chemical fertiliser applications [21–24]. However, when this practice became popular in the 1990s, household waste was composted without prior sorting, and contained plastics, glass and metals [25]. Recent developments in policies and regulations emphasised thus the sorting of wastes before composting and the control of the compost quality. As an example, in France, films, expanded polystyrene, and other plastics with particles larger than 5 mm should not exceed 0.3% and 0.8% of dry matter, respectively (*NF U* 44-051). But no regulation exists for plastics that have particles smaller than 5 mm.

Nonetheless, research into the plastic content of household compost is recent [20,26–29]. Plastic debris abundance is variable. Gui et al. [27] determined an average 0.05–5 mm dry matter concentration of 2400 ± 358 particles kg⁻¹. By contrast, Edo et al. [29] found a concentration of $5x10^3$ to $20x10^3$ particles kg⁻¹. for 0.05–5 mm plastics. That plastic debris is mainly microplastics (< 5 mm), dominated by fibres, fragments, and films, of which 85 to 90% are < 2 mm [26,29]. This is in agreement with studies that found that the composting process enhanced plastic degradation to make more, smaller particles [27,30,31].

However, the fate of microplastics in soils amended with household compost was only reported in two studies [26,32]. Watteau et al. [26] highlighted the presence of microplastics in fractions > 50 μ m in soil amended with household compost for 10 years. In an experimental study of microplastic spatial distribution in agricultueral soils amended with a compost made of municipal solid wastes, business and commercial wastes, Cattle et al. [32] observed the

Journal Pre-proot

presence of fragments and films within the cultivation depth. However, no information was provided on the identity of those polymers, their state, or their abundance. Long-term microplastic condition in soils has only been measured over a 32-year span, by Otake et al. [33]. More detailed studies are needed to fully characterise and understand the extent of the contamination in soil, especially in the long term.

Composts are generally mixed into the soil via agricultural practices, principally tillage. The conditions of the compost and contaminants it contains are then drastically modified in terms of the surrounding matrix, pH, and physicochemical and biological reactions. Several questions then arise about the future of this plastic debris buried in the soil. Will the plastic particles be mobile? Few elements exist in the literature to answer this question. Recent studies suggested that microplastic mobility could be enhanced by bioturbation from earthworms [34,35], collembolans [36], and plant roots [37]. Soil pore size restricts the mobility of large microplastics, though smaller microplastics can flow with water [38]. This study only looked at the top 15 cm of soil, and no information exists for the deeper layers. The number of wet-dry cycles is also a controlling parameter for microplastic vertical migration [39]. These results were acquired from soil column experiments and no data yet exist under environmental conditions. Mobility depends on particle size and degradation state. Plastics are indeed degraded on particles which size decrease with the polymer degradation degree [40,41]. However, no information exists on the depth to which microplastics can be found in agricultural soil, and what parameters control this distribution: their state of degradation? only physical factors such as plowing? biological factors?

The present study examined how microplastics in soils moved vertically and degraded over time. For this purpose, a soil that had ben amended with household compost 30 years ago was studied. As the initial waste had been composted without sorting first, it contained abundant plastic debris, and other anthropic particles and contaminants (i.e., glass, metals). The large proportion of degraded plastic debris thus expected made this soil perfect for our study. Microplastics were extracted from the 2–5 mm soil depth. Infrared measurements were performed to identify and characterise microplastics at different depths and discuss their potential migration. Finally, the extent of degradation was assessed from the analysis of the carbonyl functions from the Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra. This study demonstrates the impact of physical factors such as agricultural practices on the distribution of the plastic debris in agricultural soil in environmentally relevant conditions. We also studied the impact of the plastic debris sources and life cycle on their degradation.

2. Materials and Methods

2.1. Site description and soil sampling

The sampling site is located in Cléry-Saint-André, in central France. In the 1990s, to manage the growing amount of urban waste, the local authorities allowed a waste management company to begin composting it. Before composting, household waste was crushed but not sorted; it still contained fragments of plastic and glass. Several agricultural parcels were fertilised with this compost and then tilled, leading to the spread and burial of plastic debris. This study was carried out on a parcel of land that had received the household compost in the spring of 1990. The soil is a well-drained cambisol (WRB), enriched in pebbles and developed from alluvial deposits. Each year, the soil was ploughed and then sown with a drill coupled to a rotary harrow. The average depth of tillage was approximately 35 cm and 15 cm for the rotary harrow. The land was planted for 15 years in rotation with sunflower and rye, with annual ploughing. Since 2005, the parcel has been used as a meadow.

2.2. Soil sampling

The parcel was divided into three 20 m x 5 m plots to get a suitable representation of the entire field. A composite soil profile was performed on each plot from 8 sub-profiles from 0–60 cm. Sampling was carried out every 5 cm of depth (i.e., 0-5 cm, 5 to 10 cm). Hence, three composite soil profiles were sampled. The same protocol was used to sample the soil of a neighbouring parcel of land, free of compost, to use as the soil reference. Soil samples were dried at ambient air and sieved at 5 and 2 mm. Geochemical and granulometric analyses were performed by the Service des Roches et Minéraux (SARM, France) and the Laboratoire d'Analyses des Sols (LAS, France). The two soils present the same sandy to sandy-silty texture and the same geochemistry at 40 cm deep. However, the amended soil is enriched in major and trace elements on the first 35 cm of the soil profile (Details in **S1**).

2.3. Microplastic extraction and sorting

Microplastics were manually extracted with tweezers using a binocular loupe from the 2 to 5 mm soil fraction in all the layers of the 3 soil profiles (Fig. 1). They were washed with ultrapure water in an ultrasonic bath for 30 min. Organic matter was removed with 1 M NaOH for 24 h at room temperature. Then, microplastics were two times washed with ultrapure water followed by a 30 min ultrasonic bath. Although the Fenton reagent is recognised as the most suitable for removing organic soil matter from microplastics [42], we did not use this type of oxidation

Journal Pre-proof

because the addition of Fe²⁺ could disturb further analysis (i.e., Fe speciation and its impact on metals). Microplastics were only rinsed with ultrapure water and dried at 50°C for 24 h, and sorted a second time. They were finally weighed to determine their distribution in g kg⁻¹ soil. Finally, microplastic from each layer were mixed to obtain a composite per layer. The distribution of fragments, films and fibres was determined in the sieved soil fraction. The recovered microplastic shape is highly dependent on the sorting protocol. Zhang and Liu [15] showed that 72% of plastic particles are associated with soil aggregates. A preliminary disaggregation of soil (i.e., wet sieving, density separation) should release more particles and especially fibres [15,27,43]. However, in the present study, as performed by Weithmann et al. [20]), microplastic sorting was carried out on the sieved soil fractions.



Fig. 1. Microplastic extraction and sorting protocol. P1, P2, and P3 correspond to the composite soil profiles.

The characterisation by Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) was performed on the 0–5, 15–20 and 30–35 cm depths where microplastics were the most concentrated. For each layer, plastic debris were sorted a third time based on their colour, gloss, film, fibres, hard or soft particles. If this sorting was fine enough to validate that each fraction corresponded to the same polymer, they were weighed to determine the polymer distribution (g kg⁻¹ soil)[.] The quality of the sorting was further validated by ATR-FTIR analysis (see below). Accordingly, the microplastic distribution was also estimated as particle number kg⁻¹ soil for the most encountered polymers, i.e. PE, PP, PS, and PVC, considering only fragments and films (**S2** and Figure **S1**).

Acidic digestion was used to determine the trace element loading on the microplastics collected from the contaminated soils. Methodology and results were detailed in S1, Table S3. This methodology combined with the ATR-FTIR analysis ensured then the representativeness

of the results because 1) each soil sample was a composite sample of the plot, 2) the sampling

and sorting was carried out twice manually, and 3) the sorting was finally validated by the ATR-FTIR analysis of each sorted particles, (more than 300 spectra produced).

2.4. Microplastic characterisation

2.4.1.Scanning electron microscopy and element analysis (SEM-EDX)

The surfaces of the extracted and washed microplastics were imaged by scanning electron microscopy (SEM - JEOL-JSM 7100 F) at a working voltage of 10 kV. SEM is equipped with an Energy Dispersive X-Ray Spectroscopy (EDX- Oxford Instruments AZtecEnergy) for the semi-quantitative analysis of the elements. The microplastics studied were films or fragments of different colours (black, white, blue) from the soil surface layer (0–5 cm). Samples were glued on a carbon tape and a thin layer of Au-Pd was deposited on the sample by cathode pulverisation.

2.4.2. Infrared spectroscopy (ATR-FTIR) for polymer identification

More than 300 ATR-FTIR spectra of microplastics were registered. The microplastic identification was performed by comparing the spectra with an in-house database (references to known plastic packaging and plastic standards from Sigma-Aldrich). The main polymer of each plastic debris was identified based on matching a set of specific and unambiguous bands of each standard with the bands in the sample spectra (**S4**).

2.4.2.1. Spectra acquisition

ATR-FTIR spectra were acquired with a Jasco spectrophotometer (FT/IR-4100) using the Spectra Manager software. The ATR accessory (Miracle, Pike) is composed of a ZnSe crystal of 2 mm size with a fixed incident angle of 45° allowing a single reflection. Each spectrum between 3700 and 600 cm⁻¹ was the average of 128 scans with a 2 cm⁻¹ resolution. The background was recorded in the air.

The major degradation pathway of polymers such as PE, PP, PS, and PVC is a radicalbased oxidation that can be induced by UV, and leads to the formation of free unstable radicals and finally to chain scissions [44]. Different species are generated during this process (Figure S2) leading to different degradation pathways, which coexist. Whatever the step, the degradation species have chemical functions with carbonyl bonds (C=O) that can be generally found on the ATR-FTIR spectra in the 1600–1850 cm⁻¹ wavenumber range [45]. However, the C=O bond vibration wavenumber depends on the chemical groups as reported in Gulmine et al. [46]. They depicted a deconvolution of the C=O band, with several species of the degradation

Journal Pre-proot

pathway (Figure S2), and other groups such as carboxylic acid and ester. For a single polymer, the ATR-FTIR spectrum of an unaltered plastic will be different from the virgin polymer, due to additives.

For instance, phtalates (note that phthalate plasticisers are esters and present a C-O band in the 1000–1100 cm⁻¹ range), carbonate (fillers), cobalt diacetate (pigments), fatty acid amide (slip agents) etc. as reported by Hahladakis et al. [47] have also C=O bond [47]. As an example, pure PE and a pristine black PE film (Figure S1) have both a supplementary band close to 1750 cm⁻¹. Discriminating C=O due to polymer degradation from residual additives is thus challenging.

A second difficulty lies in the plastic residence time in the soil. Microorganisms biofilm can develop on microplastic surface. Exposure to the environmental conditions may sensitive some plastic to microbial colonization (i.e. [48,49]). Chen et al. observed that the amount of biofilm increase with time exposure and the microplastic concentration in a greenhouse soil. The most abundant genus were Methylophaga, Saccharimonadales, and Sphingomonas, known to decompose organic materials and biodegrade organic contaminants [49]. ATR-FTIR can detect exopolysaccharide from the C-O large bonds in the 1000–1100 cm⁻¹ range. Proteins have two typical bands associated with the amide function: amide I (C=O) close to 1650 cm⁻¹ and amide II (CN + NH) close to 1550 cm⁻¹. Natural biofilms are not easy to remove from the surface of microplastics. Several authors showed that an alkaline cleaning at pH \approx 11 at 50°C is not enough efficient [50–54] However, the washing procedure used here, namely 1M NaOH (pH = 13) for 24 h and 2x30 min ultrasound bath (section 2.2.) was expected to allow the biofilm removal. Few SEM pictures randomly acquired did not revealed any remaining micro-organisms or residual biofilm (Fig. 4). Note that the C-O mass of bands due to polysaccharides has classically a much higher intensity than the protein amide I & II bands. The protein amide I and II bands have equivalent intensity [55]. Without a large C-O band, the presence of biofilm cannot be proved.

The ATR-FTIR normalised spectra of PVC-microplastics (S4, Figure S4) suggests that no biofilm was present after cleaning, or that no biofilm had developed before cleaning. For PE, PP, and PS, a large band was present in the 1000–1100 cm⁻¹ range (S4, Figure S4). However, if some bands were in the C=O region including amide I vibration, the band of the amide II vibration at 1550 cm⁻¹ was not present. The absence of the amide II bands shows that if a biofilm was present, it was removed by the cleaning procedure. Therefore, except for the additives with C=O bonds, every change in the C=O region on the ATR-FTIR spectra could be attributed to

polymer degradation. Note, however, that the intensity of C-O mass of bands compared to that of C=O band could suggest an efficient but incomplete biofilm removal.

2.4.2.2. Carbonyl index

With respect to the above comments, carbonyl functions C=O can be used to estimate the degree of oxidation of plastic surfaces (S3, Figure S3). Several authors calculated the degree of oxidation by determining the carbonyl index (CI) of pure polymers from ATR-FTIR spectra. The CI is the ratio of the intensity of the C=O bands to a reference band specific to the polymer [31,56–59]. In the absence of a calibration curve, variations of CI only allow semi-quantitative analysis. In the literature, CI was calculated with different approaches: i) the single-band method, a single C=O function is targeted (acid or ester or aldehyde, etc.) by choosing a specific associated wavenumber [31,56,57]. This approach provides information related to a particular degradation reaction, ii) In the multiple-band method, a range of C=O wavenumbers is selected which covers different chemical functions (acid + ester + aldehyde, etc.) [58,59]. This method provides an overview of the global degradation.

Thus, any CI increase proves the degradation increase. Moreover, any change in the shape of the large C=O band (shoulder appearance, etc.) reveals modifications of the oxidation states that have been reached. For example, Almond et al. [59] made their CI calculation using the range 1650–1800 cm⁻¹ for pure PE and PP voluntary degraded.

As already mentioned, in the present study, microplastics are supposed to be different from pure polymers, however the plastics we analysed were mainly single-base polymers, not composite, as shown by ATR-FTIR analysis. Thus, the method from Almond et al. [59] was adapted to avoid misinterpretations due to possible confusion in the discrimination of bands between plastic additive and polymer degradation. Regardless of their origin, bands related to carbonyl functions are localised between 1600 and 1800 cm⁻¹. The spectra of formulated PE, PP, PVC and PS-based commercial plastics used as complementary references all had of a band between 1700 and 1750 cm⁻¹. Those formulated plastics are either coloured or flexible while the standards are colourless and rigid and don't show any band in the 1600–1800 cm⁻¹ range. Accordingly, the carbonyl function range was limited to 1600–1700 cm⁻¹ for the CI calculations, except for PS for which the 1610–1700 cm⁻¹ range was selected because there is a PS reference band at 1600 cm⁻¹[60].

It is important to note that the intensity of the C=O band on a raw ATR-FTIR spectra is related to several parameters other than the quantity of oxidised groups. The penetration depth of the IR beam in the sample must also be considered justifying the use of CI instead of only the C=O

band intensity. Finally, for a semi-quantitative approach, an internal standard has to be selected as said above. The most commonly used is the band between 1400–1500 cm⁻¹, related to C-H or CH_2 = bonds, depending on the considered polymer [60]. Those bonds are not significantly affected by the oxidation of the polymer.

In this study, the CI was thus calculated following the multiple-band method for PE, PP, PVC, and PS based microplastics according to equations (1) to (4):

$$CI_{PE} = \frac{Abs (1600 - 1700 \ cm^{-1})}{Abs (1450 - 1475 \ cm^{-1})} \quad (1)$$

$$CI_{PP} = \frac{Abs (1600 - 1700 \ cm^{-1})}{Abs (1425 - 1477 \ cm^{-1})} \quad (2)$$

$$CI_{PVC} = \frac{Abs (1600 - 1700 \ cm^{-1})}{Abs (1400 - 1450 \ cm^{-1})} \quad (3)$$

$$CI_{PS} = \frac{Abs (1610 - 1700 \ cm^{-1})}{Abs (1425 - 1460 \ cm^{-1})} \quad (4)$$

With:

CIx: the carbonyl index of the X polymer

Abs(x-y): the absorbance of the large band in the x-y wavenumber range calculated with respect to a baseline taken from $1800-1900 \text{ cm}^{-1}$. The CI calculated with a different protocol cannot be directly compared to present CI except if no band existed between 1700 and 1800 cm⁻¹ on the literature spectra (pure virgin polymer).

2.4.2.3. Statistical Analysis of CI

The differences in the average of the CI calculated for the three soil layers were assessed using one-way ANOVA (Welch's tests). The Tukey or the Games-Howell post-hoc test, according to the homogeneity of variances or equal sample sizes, was used to separate the treatment average. In the post-hoc tests, the differences were considered statistically significant for P < 0.05. The extreme values higher than or less than 1.5 times the interquartile range were excluded. The normality of the data and the homogeneity of the variance were tested following the Shapiro-Wilk test and Levene test. Statistical analysis was performed on samples ranging from 7 to 30 values depending on the polymer and the soil layer considered.

3. Results and discussion

3.1. Microplastic characterisation and distribution

Nine different polymers were identified in the 2–5 mm fractions: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyester, polyamide (PA), polycarbonate (PC) and polyurethane (PU) (**Table 1**). No

microplastics were observed in the reference soil. The number of debris impossible to identify was low (N.I, **Table 1**).

Table 1

Amount of each identified polymer

					g Kg⁻¹ Dry						
					Matter						
	MPs	s Polyest									
	tot.	PVC	PP	PS	PE	ΡΑ	PET	er	РС	PU	N.I
		1.76	0.52	0.42		0.04	0.02				0.01
0-5 cm	2.923	3	2	8	0.103	9	4	0.021	0	0	5
15-20		1.86	0.20	0.19			0.00		0.03		0.00
cm	2.544	8	2	9	0.213	0	1	0.029	1	0	2
30-35		0.49	0.20	0.04			0.02			0.00	0.05
cm	0.949	2	8	6	0.106	0	3	0.019	0	1	3

*NI: not identified

The collected microplastics were mainly fragments (83–94%), films (4–14%), and fibres (< 2%). The PVC, PP, PS, and PE accounted for around 90% of the total microplastic, with PVC being the most abundant (52–73%). However, fragments and films present a very different density. PVC is predominant, with 65 to 80% by mass of the fragments are made of PVC. By contrast, 76 to 93% of the films were composed of PE. As shown in Fig. 2, if the plastics are compared by number of particles instead of mass, PVC is no longer predominant, and PE contains equivalent amounts the soil. Therefore, the polymer proportions differ with their shape [38]. Both mass and particle number have thus to be determined to characterise the potential plastic contamination.

In the literature, the most identified polymers in soils are PS, PE, PP and polyester; PVC is much less present [20,27]. To our knowledge, no polymer identification or quantification were provided for soils amended with household compost [26,32]. The abundance of PE, PP, PS, and PET in household waste can easily be explained by their predominant use in packaging [2]. By contrast, PVC mainly originates from the building and construction sectors, and makes up a smaller proportion of recent municipal wastes. Hence, high amounts of PVC in the soil amended with a 30–year-old compost highlights the changing use of plastics over time.



Fig. 2. A) Proportion on a mass basis for microplastics and B). Proportion on a number basis for microplastics. Analysis was made at 3 soil layers: 0–5 cm, 15–20 cm, and 30–35 cm

At the surface layer of the amended soil (the uppermost 5 cm), an average microplastic concentration of 2.92 g kg⁻¹ of dry soil matter was determined for 2–5 mm plastics, which is about 291 plastic particles (films and fragments) kg⁻¹ (**S2**). As mentioned before, other studies performed on soils amended with a household compost did not provide the concentration in recovered microplastics. Fewer microplastics were observed from soils under plastic mulching (**Table 2**, Liu et al. 2018; Hu et al. 2022), but much more was identified from soils under cumulative agricultural practices [15] (**Table 2**). However, many microplastics collected by theses authors were fibres. Here, a majority of fragments and films were extracted; very few fibres were sampled, certainly due to sampling procedure (wet sieving against manual dry sampling). Then, if only fragments and films are considered, Zhang and Liu [15] recovered 75 plastic particles kg⁻¹ dry soil matter. This shows that the soil we studied was much higher in plastic particles, than soils with other agricultural plastic sources.

Table 2.

Concentrations of microplastics from different agricultural soils.

Sources of microplastics	Microplastic concentration Particles kg ⁻¹ dry matter of soil	Microplastic sizes	References	
household compost	291	2–5 mm	This study	
Mulching films	78	1–5 mm	Liu et al., 2018	
Mulching films	154	1–5 mm	Hu et al., 2022	
Greenhouses, irrigation with	038	> 1 mm	Zhang and Liu,	
fertilisation (i.e., sewage sludge)	258	> 1 mm	2018	

In the soil, microplastics were present in the top 35 cm of the profile. Their concentration decreased with depth, except between 20–25 cm, where the concentration was similar to the surface (2.73 and 2.92 g kg⁻¹ soil, respectively, Fig. 3).



Fig. 3. Microplastic distribution with depth. A presents the global average microplastic distribution for the studied plot. B and C present the detailed distribution of fragments and films, respectively. Results are expressed in g of microplastics per kg of soil, from 0–60 cm depth.

Soil ploughing first spreads microplastics through the cultivation area (30–35 cm depth), which explains why the highest concentrations of plastics are on the top and the particle numbers decrease with depth. The variations from 10–30 cm could come from additional vertical mobility occurring during their incubation in the soil matrix. Recent studies suggested that microplastic mobility could be enhanced by bioturbation involved by i) burrowing fauna like earthworms [34,35], ii) collembolans [36], and iii) the action of plant roots [37], even for > 2 mm microplastics [35,37]. Bioactivity also promotes microplastic transfer through attachment to organisms' bodies, ingestion, and indirectly by forming preferential water pathways [61]. A rotary harrow was used several times for seedlings with a working depth of

around 15 cm. It could have rearranged the soil and brought up microplastic particles, decreasing microplastic concentrations in the 10–15 first cm of the soil.

Varying surface roughness was also observed by secondary electronic microscopy with cracks and small holes at the surface of the microplastics (Fig. 4). Clay particles and Fe oxides were identified by Energy Dispersive X-ray spectroscopy (EDX). These soil particles can increase the microplastic density and surface charge, leading to a potential vertical migration [62] controlled by the soil composition and porosity. Zhang et al. (2022) observed that the soil pore size restricted the mobility of the 1–5 mm microplastics while smaller microplastics are mobilised via water flows. The number of wet-dry cycles is also a controlling parameter for vertical particle migration [39]. More information on the soil properties is needed to precisely discuss the vertical migration of the microplastics. For now, a combination of those processes, with varying involvement rates, may be responsible for the vertical distribution observed. As no microplastic was observed below 35 cm depth, microplastics have not penetrated below the cultivation depth. This indicates that their vertical distribution may be mainly due to agricultural practices.

Soil tillage can lead to the formation of a plough sole below the cultivation area, which is a hard layer that is difficult for roots and earthworms to cross by roots. No plough sole was observed in the soil, and earthworm communities confirmed that bioturbation was occurring. The worms were 54% anecic, 45% endogeic and 1% epigeal [63].



Fig. 4. SEM image of 1) a plastic film surface and 2) a fragment surface

Two trends can be observed for microplastic distribution with depth according to their shape (Fig. 2). The concentration of fragments seemed to decrease with depth. By contrast, films present a more homogeneous distribution with similar concentrations at 0–5 cm and 30–35 cm depth, while at 15–20 cm, the concentration was slightly higher.

Various hypotheses may explain the variation of fragments with depth and homogeneous distribution of film.

i) Tillage: When the blades of agricultural tools penetrate the soil, rigid fragments are expected to be spread out while films are more easily captured and carried away. The action of the rotary harrow could promote the film accumulation at the bottom of the working depth, i.e around 15 cm.

ii) Vibrations exerted on the soil surface by the passage of agricultural engines and, to a lesser extent, by heavy ,ain episodes: Such oscillations can lead to the upwelling of large particles, as with gravels, and enhance the downward migration of the smaller microplastics. With this hypothesis, fragments would have vertically migrated towards the surface, explaining a decrease in abundance with depth. By contrast, plastic films could be blocked by root system acting as a net [37]. Plastic films were, indeed, found entangled in the roots (Fig. 5).

iii) Finally, the film distribution could be not the result of an accumulation around 15 cm, but a loss from the surface. Films could be transported by water runoff and soil erosion [43,64] and be preferentially degraded compared to the fragments; films are mostly made of PE (76 to 93%), while fragments are mainly composed of PVC (65 to 80%), less sensitive to degradation [33,65].



Fig. 5. Plastic films (in blue) entangled in ray-grass roots

3.2. Microplastic alteration

Before being spread, the 30–year-old compost was crushed and composted. Microplastics then underwent mechanical degradation (crushing), followed by biochemical degradation [66], before being buried and exposed to the soil matrix for almost 30 years. The plastics were expected to be highly altered. SEM images showed numerous cracks and small holes on microplastic film and fragment surfaces (Fig. 4), which confirmed their alteration, and varied depending on the particle. A better characterisation of the degradation was possible thanks to

ATR-FTIR and the determination of the carbonyl index. The environmental degradation of polymers leads to a break in the polymer chains and the integration of oxygen atoms into the polymeric structure according to multiple reactions [40,41]. The result is the formation of oxygenated functions that can be evaluated by calculating the CI. The 4 main polymers, namely PE, PP, PS and PVC, were investigated.

3.2.1.Description of the raw ATR-FTIR spectra

As generally observed, the ATR-FTIR spectra of microplastics sorted from the soil showed more bands than the references we had for unaltered polymers and plastics (Fig. 6). Several spectra of microplastics (PE, PP, PVC and PS) and plastics standards exhibited bands between 1750 and 1715 cm⁻¹. Spectra of the PE-, PP- and PVC-microplastics showed new bands from 1600–1700 cm⁻¹ as compared to the references (Fig. 6). Several PS-microplastics presented new bands from 1610–1700 cm⁻¹ as compared to the polymers and plastics references. The spectra of PE and PP microplastics showed new bands close to 1030 cm⁻¹ whereas this band was not observed for the PS microplastic spectra (S4). Some PE- and PP-microplastics spectra also presented additional bands from 3200–3500 cm⁻¹. New bands from 1700–1600 cm⁻¹ can mainly be attributed to C=O functions [58,59]. They were not single bands but a large mass of bands from 1600–1700 cm⁻¹, which could correspond to the overlap of several C=O groups from ketone, aldehyde, or carboxylic acid [46] suggesting a complex degradation process coherent with the general mechanism discussed in section 2.3. However, Otake et al. (1995) observed a band at 1640 cm⁻¹ for microplastics buried for 32 years in soil, and assigned this 1640 cm⁻¹ band to unconjugated C=C resulting from biodegradation processes [33]. More recently, Xing et al. [31] made the same interpretation for microplastics sampled in composted sludge, which presented a band at 1600 cm⁻¹. The most important point here was not the band assignment (C=O or C=C) but the polymer degradation process that was mediated by microorganisms.



Fig. 6; Partial ATR-FTIR spectra for the four main polymers (PE, PP, PVC, PS). Sample spectra (A) are compared to the reference spectra (B). Reference spectra correspond to formulated plastics in the dot line and standards in the full line. The orange part in the spectra corresponds to the carbonyl region.

The assignment of the new mass of bands around 1030 cm⁻¹ is an issue (S4, Fig. S4 and Fig. 7). Silicates from soil present Si-O bands in the same range, but their overall shape is different from those observed for the microplastics. Before the analyses, the microplastics were washed with 1M NaOH for 24 h and submitted to two ultrasonic baths. This treatment removed the soil particles; therefore, soils do not explain the 1030 cm⁻¹ band.

This mass of bands might be assigned to residual polysaccharides from a biofilm. The literature reported also the appearance of a similar band as a consequence of plastic alterations creating C–O functions [30,31,33]. These bands were Si-O peaks [67]. Interestingly, this band was not observed for plastics submitted to photodegradation [57,59,68]. Therefore, only based on the description of raw spectra, the present microplastics showed consistent similarities with microplastics exposed to composting or burying in soil, with additional features on PVC that

Journal Pre-proof

were not observed elsewhere under the same conditions. These results suggest that the studied microplastics would be strongly altered compared to the literature data.



Fig. 7. Raw ATR-FTIR spectra of the soil (pink) and of PE-microplastics from the 0–5 cm layer evidencing a mass of bands in the 900–1100 cm⁻¹ range

3.2.2. Carbonyl Index (CI)

The Carbonyl Index (CI) was calculated for the microplastics based on the major polymers, namely PE, PP, PS, and PVC, for soil layers at 0–5 cm, 15–20 cm, and 30–35 cm (Fig. 8) assuming that the 1600–1700 cm⁻¹ range was only due to C=O (and not a superimposition of C=O and unconjugated C=C, see above). For all the layers, CI varied from 0.29 to 1.41 ± 0.09 for PE, from 0.00–0.75 \pm 0.09 for PP, from 0.10–1.18 \pm 0.09 for PS and from 0.07 to $1.86 \pm$ 0.09 for PVC. Comparatively, for PE collected in the North Atlantic gyre, *Ter Halle et al.* (2017) determined CI ranging from 0.13 to 0.74 (92% of PE, 8% PP). From an experimental study, Almond et al. [59] calculated a CI of 0.44 for PE exposed to UVA for 28 days. By contrast, the range of CI determined for PP in this study corresponds to the CI determined by Almond et al. [59] for PP exposed to UVA for only 0–9 days. No comparison is available for PS and PVC carbonyl index [57,69]. Finally, no CI data was reported for composted plastic debris. Except the band intensity, comparing the ATR-FTIR spectra among each type of polymer, no significant difference in the band shape was observed suggesting no significant variation in the degradation state .



Fig. 8. Carbonyl Index according to the depth. Carbonyl indexes were calculated at 0–5 cm, 15–20 cm and 30–35 cm for PE (n=11, 14, 14), PP (n=19, 10, 9), PS (n=25, 9, 7) and PVC (n=29, 22, 21). Different letters indicate significant differences (p < 0.05)

Results first showed that PP debris seemed less altered than PE debris while they are chemically similar. But PE-microplastics were mainly films, while 95% of the PP-microplastics were fragments. This is in accordance with a previous assumption that films are more sensitive to degradation, which is quite logical with respect to the sample thickness and overall accessibility of the surface. However, the possibility that there is an organic coating remaining at the surface of the plastics cannot be excluded. If a coating is truly present, as explained before, it could participate in the functions present in the C=O region and so, increase the CI. However, if no coating remained on the microplastics, the occurrence and diversity of the functional groups observed here with the CI values, suggest that the present microplastics would be more altered than plastic debris from the ocean that were extensively submitted to UV.

Carbonyl indexes of microplastics collected in the studied soil are around 2 times higher than that of Prunier at al. [70]. The variety of the functional groups was also higher in the present study with respect to the C=O band shape..

Finally, CI evolutions for the 4 main polymers were observed with the soil depth (Fig. 8). Carbonyl indexes of PE were significantly higher at 15–20 cm depth (p=0.002 between 0–5 and 15–20 cm and p < 0.001 between 15–20 and 30–35 cm) but no significant differences were obtained between 0–5 and 30–35 cm (p = 0.823). Carbonyl indexes of PP were also significantly higher at 15–20 cm depth (p = 0.012 between 0–5 and 15–20 cm and p = 0.006 between 15–20 and 30–35 cm) and no significant differences were determined between 0–5 and 30–35 cm (p = 0.334). By contrast, the CI of PVC also present no significant differences between 0–5 and 30–35 cm (p = 0.846) but were significantly lower at 15–20 cm depth (p = 0.008 between 0–5 and 15–20 cm and p < 0.001 between 15–20 and 30–35 cm). The CI of PS were not significantly different between 0–5 and 15–20 cm (p = 0.859) but significantly lower at 30–35 cm depth (p = 0.016 between 0–5 and 30–35 cm and p = 0.034 between 15–20 and 30–35 cm).

If the microplastics were only changed by the compost process before being spread on the soil, no difference in CI would be expected within the depth. Hence, CI evolutions highlighted with depth suggest that additional processes likely occurred after burial in the soil; which was expected after almost 30 years.

3.2.3. Parameters influencing the degradation

Sullivan et al. [71] and Otake et al [33] showed that PE and PP change when they are buried in the soil. Otake et al [33] observed no change at all for PS and PVC microplastics after 30 years. The CI evolution of the microplastics suggests, nonetheless, that both degraded in the soil. Very scarce information is available on the degradation of PS and PVC [72], but Sullivan et al. [71] observed PVC degradation n moist sandy soil.

The current highly altered condition of the microplastics was probably mainly due to composting. During the composting process, Xing et al. [31] demonstrated the production of HO° free radicals through Fenton-like reactions promoted by the oxidation of Fe (II) by Feoxidising bacteria. These HO° free radicals promote chain scission and oxidation of the polymers by cleaving the =C-H groups of the microplastic polymer, which results in the formation of carbon-centred tertiary alkyl radicals [31]. This generation of HO° during composting with the reactive oxygen species (ROS) accelerates the oxidative degradation of the microplastics [31,73]. These ROS could be produce by microorganisms and organic components such as humic substances by the composting system [31,74]. Bacterial activity

Journal Pre-proot

during composting produces a few micrometer holes onto microplastics surface [31], similar to the holes observed in Fig. 4. This process is enhanced by high temperature, moisture, and aeration of the compost which stimulate bacterial activity [75,76]. As microplastics are first degraded by composting, they probably become more susceptible to further degradation.

Microplastics are biodegraded by soil microorganisms, affected by bacterial strains[77], which are in turn affected by root exudates, depending on the plant species and the soil composition [78]. In addition, root exudates are composed of organic acids and protons, which could also participate in the degradation of microplastics. Root exudates significantly modify the physicochemical parameters next to the roots such as pH and water quantity that can also affect degradation rates. The pH can modulate the microbial activity impacting their enzyme activity and thus the plastics degradation rate [75,79]. Acidic pH increases in the formation of hydroperoxide and thus accelerate the polymer degradation rate [75,80]. Finally, when the microplastics surface was weakened by a biochemical mechanism, water can enters in the polymer bulk involving a swelling and the release of a small particle [76]. Hence, the rhizosphere might be highly involved in plastic degradation in soils. Its depth varies according to vegetation and land use. The studied soil has been a meadow of ray grass for 15 years. Raygrass roots can reach 25 cm deep [37]. Microplastics within the rhizosphere might have been then preferentially exposed to soil microorganisms and, thus, subjected to biological processes [33,77,81,82]. By contrast, below 25 cm depth, all these processes would be less important and may not be able to alter microplastics.

We expected microplastics in the top 5 cm of soil to be more altered than at depth, in response to UV exposure and other processes. We expected reduced degradation with particle depth. However, PE and PP showed higher oxidation at 15–20 cm depth and no significant difference between the 0–5 and 30–35 cm depths (Fig. 8). Two hypotheses can be made. i) Perhaps photooxidative degradation did not occur, or not substantially at the soil surface. ii) Maybe microplastics have a degraded superficial layer, revealed by oxidised surfaces, which would increase their surface charge and then, their potential for vertical migration [62]. This second effect would increase the average degradation of microplastics in the lower soil layers and the number of particles, which is what is observed for PE microplastics: an accumulation of films (mainly PE) and a higher degradation were observed at 15–20 cm. A degraded superficial layer could also lead to a pulverulent layer that could be lost during the washing or even at the soil surface by abrasion processes via runoff and wind erosion. The microplastics would appear to have changed less if this was the case.

Microplastics made from PVC also present no significant difference between the 0–5 and 30–35 cm depths, but a lower unexpected degradation at 15–20 cm. Finally, the PS microplastic degradation profile suggests that they did not undergo photodegradation at the soil surface and might have only degraded in the rhizosphere.

3.3. Implications, limitations and recommendations

The microplastics in this study originated from household waste. They were crushed and subjected to composting process, speeding up their degradation. The SEM observations show that surface embrittlement increases the specific surface area and causes plastics to release more nanoparticles (Fig. 4). The microplastic embrittlement and the HO° free radical action also promoted microplastic oxidation, formation of surface functional groups [31,83,84], and surface hydrophilicity, which promoted their downward mobility through the soil layers [62].

This plastic-enriched compost was mixed into the soil where the 2–5 mm microplastics remained in the cultivation depth. Although they were not quantified here, we would expect degradation to produce smaller particles in larger numbers [15,27,38]. These smaller particles are prone to downward mobility [85] and could reach deeper soil layers. Microplastic migration in the soil may enhance the release of small microplastics and even nanoplastics, for instance by mechanical abrasion from the altered layer of microplastics. Soil biota, especially earthworms, can also participate in the production of small microplastics and nanoparticles [86]. There were 54% anecic, 45% endogeic and 1% epigeal earthrworms [63]. Hence, the travel of small microplastics and nanoplastics should be further assessed.

The quantified microplastics represent only the tip of the iceberg. In this respect, Zhang and Liu [37] showed that microplastics >1 mm represented only 5% of the total microplastics sampled in Chinese farmland soils; fibres accounted for 92% of the total amount. Quantifying the remaining smaller microplastics and fibres is, therefore, crucial to understand the whole picture. As microplastics degrade, they release additives, especially PVC [30,65,71]. The prevalence of degraded PVC, here, raises the question of the contamination by additives in this soil with all the known negative effects it generates.

A major limit of this study is that it only studied one size category of microplastics (2–5 mm). However, this study has shown that plastic waste degrades over time into smaller particles such as nanoplastics, which can be expected to travel to the deepest soil layers and surrounding shallow groundwaters due to their size and surface reactivity. The extraction and sorting methods were chosen to preserve the integrity of the samples, particularly the metal content,

Journal Pre-proof

for future studies. However, this method prevented the characterization of the entire size continuum and especially the fibers, though getting a measurement on the fibers is much more important than knowing about the fragments or films that we were able to study here. Fibers can represent up to 70% of the microplastics sampled in household waste compost [27]. Furthermore, Han et al. [87] showed that the presence of fibers facilitates the transport of nanoplastics by creating connections between pores. The characterization of meso- and macroplastics is also important to study in the future; they represent a significant part of the plastic waste found on the surface of the soil. Further research should therefore take into account the entire continuum size (from macro to nano) as well as the entire range of particle shapes (fragments, films and fibers) with appropriate methods that will need to be developed.

This study reinforced the general claim about the difficulty of comparing studies to date, as they have not used standardised methods, data treatment, or even units of measurement. It also showed the need to consider both the particle number and masses to characterise the microplastic contamination in the environment. Microplastic particle shape, size, polymer type, and density determine their fate in the environment in terms of mobility, ageing, and environmental impacts.

This study demonstrates the impact that the quality of organic amendments can have on the quality and properties of soils. Here, a single amendment heavily contaminated with plastic waste caused long-term soil contamination (for more than 30 years). Even if the quality control of compost in the future improves, some soils have already received many years of compost amendments that contain plastic debris. As microplastics are not mobile, as demonstrated here, they accumulate in amended soils. Moreover, microplastics slowly degrade to release smaller particles that are expected to be mobile. Therefore, even if modern household compost is held to high plastic-free standards, the long-term impact of the existing plastic in agricultural soils needs to be investigated to preserve and maintain the soil quality.

4. Conclusion

In 1990, to counter the increasing amount of incinerated or landfilled wastes, household compost was promoted to use as organic fertiliser. No pre-sorting was performed, so the compost thus formed contained abundant plastic. Through crushing and other abrasive physical processes, the plastics in the compost became microplastics. We investigated the 2–5 mm microplastic distribution (polymer composition, mass and particle number) with the soil depth and their degree of degradation to evaluate the factor that control their distribution and their potential mobility in the soil matrix. PVC and PE were the most abundant polymers in mass

Journal Pre-proof

and particle numbers. They are followed by PP and PS. PVC, PE, PP, and PS together accounted for 90% of the total identified polymers. Microplastics were only present in the top 40 cm of the soil, which corresponds to the cultivation depth. The 2–5 mm microplastics did not travel deeper in the soil below this limit. Investigations suggested vertical transfer, which is mainly controlled by physical factors such as agricultural tilling. Household waste composting processes have promoted microplastic oxidation and subsequent fragmentation into smaller particles. The 30-year-burial of microplastics, resulting from the soil tilling, also participated in their degradation to a lesser degree. Hence, fertilising the soil with this compost promoted the input of highly degraded microplastics, which could be even more harmful to the physicochemical and biological properties of the soil. Microplastic degradation and fragmentation have added even smaller particles to the soil. More smaller particles are thus expected, which would likely make plastics able to transfer deeper in soils.

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Declaration of interests

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

☑ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Graphical abstract



Highlights

- Household wastes composts are source of plastic debris for agricultural soil
- Microplastics distribution was studied by coupling sorting and ATR-FTIR
- Microplastics are in the cultivated depth but not transferred to the deep soil
- Fragments, films, fibers of PE, PP, PS, PVC accounted for 90% of microplastics
- Advanced degradation has occurred due to composting and soil in-situ processes

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