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Scopetani, Costanza

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Hazardous contaminants in plastics contained in compost and agricultural soil

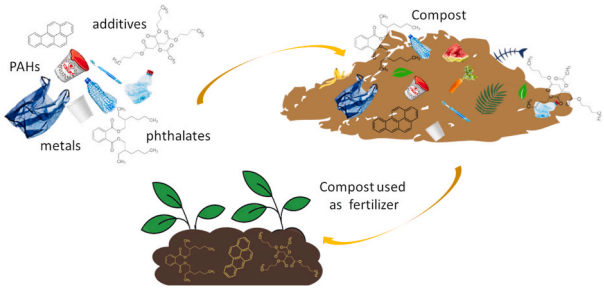
Costanza Scopetani [a,*], David Chelazzi [b], Alessandra Cincinelli [b], Tania Martellini [c], Ville Leiniö [d], Jukka Pellinen [a]

[a] Faculty of Biological and Environmental Sciences, Ecosystems and Environment Research Programme, University of Helsinki, Niemenkatu 73, FI-15140, Lahti, Finland
[b] Department of Chemistry "Ugo Schiff" and CSGI, University of Florence, Sesto Fiorentino, 50019, Florence, Italy
[c] Department of Chemistry "Ugo Schiff", University of Florence, Sesto Fiorentino, 50019, Florence, Italy
[d] Muovipoli Ltd, Niemenkatu 73, 15140, Lahti, Finland

HIGHLIGHTS

- MAPs/MEPs and MPs concentration in the compost: 6.5 g/kg dw and 6.6 ± 1.5 items/g dw.
- MPs load estimation: 4,6 × 10^7 to 2,3 × 10^8 items ha^{-1} yr^{-1} into agricultural soils.
- MAPs/MEPs-containing compost had significantly higher concentration of DEHP.
- Compost can represent a source of plastic contamination to the agricultural fields.

GRAPHICAL ABSTRACT



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ABSTRACT

Macro-, meso- and microplastic (MAP, MEP, MP) occurrence in compost is an environmental issue whose extent and effects are not yet understood. Here, we studied the occurrence of MAPs, MEPs and MPs in compost samples, and the transfer of hazardous contaminants from plastics to compost and soil. MAPs/MEPs and MPs concentrations in compost were 6.5 g/kg and 6.6 ± 1.5 pieces/kg; from common recommendations for compost application, we estimated ~4–23 × 10^7 pieces MPs and 4–29 × 10^4 g MAPs/MEPs ha^{-1} per year ending into agricultural soils fertilized with such compost. Regarding contaminants, bis(ethylhexyl) phthalate, acetyl tributyl citrate, dodecane and nonanal were extracted in higher concentrations from plastics and plastic-contaminated compost than from compost where MAPs/MEPs had been removed prior to extraction and analysis. However, some contaminants were present even after MAPs/MEPs removal, ascribable to short- and long-term release by MAPs/MEPs, and to the presence of MPs. DEHP concentration was higher in soils where compost was applied than in fields where it was not used. These results, along with estimations of plastic load to soil from the use of compost, show that compost application is a source of plastic pollution into agricultural fields, and that plastic might transfer hazardous contaminants to soil.

* Corresponding author.
E-mail address: costanza.scopetani@helsinki.fi (C. Scopetani).

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1. Introduction

Plastic is one of the most used and produced materials in the world (Geyer et al., 2017; Plastics Europe Plastics – the Facts 2020), and has been pointed in the last decades as an emerging pollutant by the scientific community (Carpenter and Smith, 1972; Thompson et al., 2009). Plastic debris is commonly classified in four main categories according to their size, i.e. macroplastics (MAPs ≥25 mm) mesoplastics (MEPs, 5–25 mm) (U.S. Environmental Protection Agency, 2011), microplastics (MPs, 1–5000 μm) (Hartmann et al., 2019) and nanoplastics (<1 μm) (Sendra et al., 2020). Plastics are ubiquitous pollutants, found in the atmosphere, marine, freshwater and terrestrial environments and inside living organisms (Bläsing and Amelung, 2018; Gago et al., 2018; Gasperi et al., 2018; Ivleva et al., 2017; Piarulli, 2019; Scopetani et al., 2018; Scopetani et al., 2020a–c). However, while several studies have focused on MPs aquatic pollution (Avio et al., 2017; Bergmann et al., 2015; Cincinelli et al., 2021; Ivleva et al., 2017; Li et al., 2018; Scopetani, 2021; Scopetani et al., 2019; Suaria et al., 2020), very little is known about their presence and effects in terrestrial environments (de Souza Machado et al., 2018; Fuller and Gautam, 2016; Kuoppamäki et al., 2021; Scheurer and Bigalke, 2018).

The knowledge gap is even larger when it comes to data about the amount of plastics and associated contaminants that agricultural fields receive by the application of recycled fertilizers, like bio-waste and sewage sludge compost (Bläsing and Amelung, 2018; Braun et al., 2021; Weithmann et al., 2018; Zhang et al., 2020). Plastics end up in bio-waste compost due to improper waste disposal and waste management, such as the use of non-biodegradable plastic bags for bio-waste collection (Bläsing and Amelung, 2018; Braun et al., 2021). Sewage sludge retains MPs from water in plants (Carr et al., 2016; Estahbanati and Fahrenfeld, 2016; Mason et al., 2016; Mintenig et al., 2017), and ends up containing around 1000–24,000 plastic items kg^{-1} (Du et al., 2020; Mahon et al., 2017; Mintenig et al., 2017); when sewage sludge is used into agricultural soil, a yearly load of 63,000–430,000 and 44,000–300,000 tons of MPs may end up to European and North American agricultural fields, respectively (Nizzetto et al., 2016). The use of sewage sludge exceeding the legal limits in terms of harmful substances is prohibited but there is no indication about MPs in the EU 86/278/EEC regulation nor in the Code 503 of the USA (Nizzetto et al., 2016). Even in Germany, which has, according to Braun et al. (2021), one of the strictest regulations globally regarding recycled fertilizers ("Düngemittelverordnung"), particles smaller than 2 mm are not regulated.

Overall, considering that general recommendations in agricultural practices suggest a compost application range from 7 to 35 t compost ha^{-1} for agricultural fields, and from 6.48 to 19.44 t ha^{-1} for horticultural soils, Braun et al. (2021) estimated a load of plastics from compost ranging between 84,000–1,610,000, and 77,770–894,240 plastic items ha^{-1} per year, respectively.

Plastic pollution risks are not only linked to soil alteration (de Souza Machado et al., 2018; Wan et al., 2019) and impact on biota (Lin et al., 2020), (Huerta Lwanga et al., 2016; Lei et al., 2018; Zhu et al., 2018) but are also connected to the adsorbed toxic substances that polymers may transport and release during their life cycle. Some of the plasticizers, antioxidants, pigments, flame-retardants and other additives contained by plastic materials, pose a hazard to the environment and human health (Hahladakis et al., 2018). Besides, hydrophobic organic pollutants tend to sorb on plastics from the environment (Hüffer et al., 2018), and might be transported and released to other habitats (Bergmann et al., 2015), or into organisms (Browne et al., 2013; Scopetani et al., 2018). Given the number of plastics that agricultural fields receive by the application of recycled fertilizers, and considering the lack of regulations on plastic content in the latter, it is essential to understand the impact that plastics pollution has on the terrestrial environment, evaluating the possible output of hazardous compounds from plastics.

Coping with these issues, the present research aims to study the occurrence of plastics and MPs in compost and soil samples, as well as the transfer of contaminants from plastics in the compost to the compost itself and to soil. The investigated contaminants were selected based on their documented presence in plastics and on their potential environmental and human toxicity (Cruz, 2013), and comprised PAHs (polycyclic aromatic hydrocarbons), phthalates (especially bis(2-ethylhexyl) phthalate, DEHP), acetyl tributyl citrate (ATBC), cobalt, cadmium and lead, as well dodecane and nonanal (which should not be in plastics but were found in the samples during preliminary screening).

PAHs are a group of compounds considered mutagenic and/or carcinogenic (Andersson and Achten, 2015) and plastic can be listed as a source of these contaminants since PAHs have been found in virgin polystyrene foam with a concentration ranging from 79 to 97 ng/g (Coffin et al., 2020). Plastic can also sorb PAHs from the environment; Indeed, post-consumer plastics fragments were collected in selected ocean sites in California, Hawaii and Mexico to be analyzed for organic contaminants and the total concentration of PAHs ranged from 39 to 1200 ng/g (Rios et al., 2007). Prenatal exposure to Benzo[a]pyrene (B[a]P), recognized as one of the most toxic PAHs, impairs brain development (McCallister et al., 2008); when B[a]P is inhaled by male adult rats, it significantly reduced the components of the steroidogenic and spermatogenic compartments of the testis, decreases testis weight, and reduces plasma total testosterone concentration (Chen et al., 2011; Ramesh et al., 2008). PAHs presence in soils is a serious environmental concern so that in the European Union the cost for soil remediation from PAH is estimated to be up to two billion euros (Luo and Schrader, 2021). The same applies to heavy metals, of which soil is a major sink, that is cytotoxic and able to cause adverse effects on organisms, even at a low concentration level (Long et al., 2021; Lu et al., 2010). Pb, Sn, Ba, Cd, Co, Cu and Zn are commonly added in plastic products as heat stabilizers or organic pigments (Hahladakis et al., 2018).

DEHP is a widely used plasticizer, especially in the production of polyvinylchloride; it forms non-covalent bonds with the polymers and thus, its migration is facilitated over time (Sun et al., 2022). DEHP is recognized as an endocrine disruptor, able to impair the reproduction system and to affect kidney, testicular, ovary, renal and liver function (Liu et al., 2021). Liu et al. (2021) showed that DEHP affects ovarian hormone production and antral follicle development of offspring in lactating mice, while Sun et al. (2022) demonstrated that DEHP exposure to mice disrupts placental growth. Furthermore, it seems that prenatal low-dose DEHP exposure could induce later obesity and metabolic syndrome (Fan et al., 2020). ATBC is a common plastic additive present in food, medical toys and cosmetic plastics, able to leach 10 times more rapidly than DEHP (Malarvannan et al., 2019). ATBC was born as a safer and more environmentally friendly alternative for phthalates in plastic products, but some toxicology studies showed that it might produce detrimental effects on the ovary of mice and suggested that further studies are needed to deepen its impact on the reproductive system (Rasmussen et al., 2017a,b).

Dodecane is a major fuel component (Herbinet et al., 2007) and it is not used as a plastic additive but it was found on plastics recovered from marine waters (Rios et al., 2007) and it shows a strong affinity for polyethylene (Castleman et al., 2021).

Nonanal is used as a flavor agent and similarly to dodecane it should not be contained in plastics but it was found in cling-films for retail use in a concentration ranging from 46.29 to 66.48 μg/g (Panseri et al., 2014) and in plastic debris collected from coastal beaches in South Korea (Rani et al., 2015).

In the present study, we analyzed plastic pollution in compost made of bio-waste and sewage sludge, and soil samples utilizing Fourier transform infrared spectroscopy (FTIR), and then the contaminants were extracted and quantified using gas chromatography-mass spectrometry, to determine if plastics contained in the compost transfer associated contaminants to the soil. We coupled our experimental results with current data on plastic pollution in compost and compost application to soils, providing evaluations for the overall impact of contaminants potentially transferred from compost. To the best of our knowledge, this

is the first time that such an estimation is carried out, and we hope that our data might also provide the basis for following up studies that will have to check if these hazardous substances move further up to the top of the food chain, possibly posing risks for human health.

2. Experimental

2.1. Sampling

A Finnish waste treatment company that collects and treats bio-waste from households, restaurants and industry, and sludge from wastewater treatment plants, provided the compost samples. Their product is a mixture of bio-waste and composted sewage sludge. The name of the company cannot be given because of anonymity reasons. The biowaste to the composting plant comes from households, restaurants, grocery stores, and food industry. The compost, after going through the hygienisation and maturation of composting steps, is transferred to outdoor piles and kept there up to 12 months. There is a steady stream of material to the composting plant throughout the year. Since the quality of biowaste and sewage sludge is relatively constant and the maturing period is so long, seasonal variations are then considered to be low.

Soil samples were collected in November 2020, at the same time as the compost, from four fields in rural areas in Orimattila and Kärkölä, Finland. Two of the selected fields, "BeanC" and "BarleyC" (a horse bean and a barley field), were fertilized in 2020 with the compost produced by the same company that provided us the compost for all the analyses. The fields have been fertilized once a year. A third field, "BarleyS" (a second barley field) was fertilized some years ago with sludge from a wastewater treatment plant in Helsinki. No fertilizers have been used in the fourth field, "Green pea" (pea cultivation). Detailed information about the locations cannot be given because of anonymity reasons. No detailed information about the amount of fertilizers applied to the fields was available.

All the samples were collected using a metal shovel and kept in metal buckets previously rinsed with ultrapure water. Soil and compost samples were preserved in a cold room at 5 °C prior to analysis.

2.2. Chemical reagents

Phthalate mixture (EPA 506 Phthalate Mix) was purchased from Merck (Darmstadt, Germany), the PAH mixture (naphthalene (NAP), chrysene (CHR), anthracene (ANT), and benzo[a]pyrene (B[a]P)) from Phenova (Denver, USA), while dodecane, nonanal and acetyl tributyl citrate (ATBC) from TCI Europe (Zwijndrecht, Belgium). Deuterated solutions of DEHP-d_4 (Sigma-Aldrich), dodecane-d_{26} (Toronto Research Chemicals), acetyl tributyl citrate-d_3 (Toronto Research Chemicals), chrysene-d_{12} (Phenova) were used as internal standards. Metal standards for Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn and the internal standard (In) were purchased from VWR International, as well as hexane and acetone. Glass microfiber filters (GF/A, 45 mm diameter, Whatman) were used to filter the samples after the extraction.

2.3. Extraction and analysis of organic contaminants

A portion of the compost was sieved with a 5 mm mesh metal sieve to remove MAPs and MEPs and collect them for further analyses; henceforth, the acronym for the portion of compost without MAPs/MEPs is CompostW/O while the acronym for the compost left with MAPs and MEPs is CompostW.

Five replicates of the soil samples (BeanC, BarleyC, BarleyS and Green pea), of CompostW/O, Compost/W and the MAPs/MEPs were analyzed for DEHP, dodecane, nonanal, ATBC, CHR, ANT, B[a]P, and NAP determination.

2 g of each replicate was extracted following the procedure described by Aparicio et al. (2007), with slight modifications. Briefly, the samples were lyophilized and transferred to 50 ml glass bottles, and then 20 ml of hexane was added. The bottles were stirred for 30 min (180 rpm) and then sonicated for 60 min. The extraction methodology was repeated thrice. Internal standards were added, and then the combined extracts were filtered through glass fiber filters and evaporated with a gentle flow of nitrogen down to 1 ml in a volumetric flask.

The samples were then analyzed with gas chromatography–mass spectrometry (Shimadzu GC–MS-QP2010 Ultra) system equipped with an AOC-20i autoinjector and a 30-m ZB-5MS column (0.25 mm i.d., 0.25 μm film thickness). The instrument operation conditions were as follows: 250 °C injection temperature, split-less injection mode, 1 μl injection volume, He carrier gas. The temperature program was initially 60 °C hold for 1 min, ramped at 10 °C min−1 to 280 °C and maintained for 6 min. The recovery range of the target compounds was 95–105%. The instrumental limit of quantification (LOQ) was 3.4 ng/g for ANT, 7 ng/g for CHR, 2.4 ng/g for NAP, 8.8 ng/g for B[a]P, 173.6 ng/g for DEHP, 44.1 ng/g for ATBC, 8.7 ng/g for dodecane, and 95.3 ng/g for nonanal. The limit of detection (LOD) was 1 ng/g for ANT, 2.1 ng/g for CHR, 0.7 ng/g for NAP, 2.7 ng/g for B[a]P, 52.6 ng/g for DEHP, 13.4 ng/g for ATBC, 2.6 ng/g for dodecane, and 28.9 ng/g for nonanal.

2.4. Extraction and analysis of metals

CompostW/O, Compost/W, and MAPs/MEPs samples were analyzed in five replicates for Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn, via inductively coupled plasma mass spectrometry (Perkin–Elmer Elan DRC II ICP-MS). Acid digestion was performed following an adapted version of the method US EPA 3050B (Vedolin et al., 2018). Briefly, 200 mg of CompostW/, CompostW/O and MAPs/MEPs samples were digested with 15 ml of concentrated nitric acid and 5 ml of H_2O_2 in a Mars 6 microwave device (CEM corporation) (plant material method). 1 ml of the sample was then diluted with 4 ml of ultrapure water, and 50 μl of indium (1 mg l^{-1}) was added to the diluted sample as the internal standard.

2.5. Extraction of MAPs/MEPs and MPs

MAPs and MEPs were extracted from the compost, sieving 2 kg of compost with a 5 mm mesh size sieve. MAPs and MEPs were visually identified, collected, weighted, and analyzed with FTIR spectroscopy.

MPs were extracted from 5 replicates following the method described by Scopetani et al. (2020). Briefly, 10 g of compost for each replicate was mixed with ultrapure water in polytetrafluoroethylene (PTFE) cylinders. 3 ml of olive oil were added, and after shaking the systems were left to settle for 2 h before being frozen at −40 °C. The ice columns, and the oil layers, were pushed out to filtering funnels and filtered through glass microfiber filters (GF/A, 90 mm diameter, Whatman). After removing the oil traces by rinsing the filters with hexane, the filters were dried in a desiccator and analyzed with FTIR spectroscopy. Each replicate underwent the extraction thrice to maximize the recovery.

2.6. FTIR-ATR analysis

MAPs and MEPs (particle sizes from 5 mm to 15 cm) were investigated with an Agilent Cary 630 FTIR Spectrometer equipped with a diamond crystal ATR (Attenuated Total Reflection) unit. The analyses were carried out in the 4000-650 cm^{-1} spectral range, with a spectral resolution of 4 cm^{-1}, acquiring 32 scans for each spectrum in absorbance mode.

2.7. Microscope FTIR analysis

For the analysis of MPs, the dried filters were investigated through 2D imaging FTIR, using a Cary 620–670 FTIR microscope equipped with an FPA (Focal Plane Array) 128 × 128 detector (Agilent Technologies). This instrument allows FTIR analysis to be carried out directly on the MPs-containing filters, with no pre-treatment. FPA detectors are widely

Table 1
Mean organic contaminants concentrations and standard deviations (n = 5) (ng/g dw). * denotes a significant higher concentration compared to the other sets of samples (p < 0,05). Values in parentheses show the analytical result that was below the Limit of Quantitation, LOQ.

	CHR	NAP	ANT	B[a]P	DEHP	ATBC	Dodecane	Nonanal
Green pea	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ (16)	112 ± 3	224 ± 12
BarleyS	<LOD	<LOD	<LOD	<LOD	<LOQ (27)	<LOQ (30)	110 ± 2	274 ± 22*
BarleyC	<LOD	<LOD	<LOD	<LOD	931 ± 163	207 ± 27	113 ± 3	280 ± 12*
BeanC	<LOD	<LOD	<LOD	<LOD	1080 ± 209	102 ± 21	111 ± 5	256 ± 22*
CompostW	<LOD	<LOD	111 ± 34	<LOD	7090 ± 3240*	<LOQ (28)	183 ± 6*	431 ± 64*
CompostW/O	<LOD	<LOD	108 ± 18	<LOD	2610 ± 1290	<LOD	155 ± 8	340 ± 14
MAPs/MEPs	<LOD	<LOD	651 ± 84*	<LOD	38200 ± 33900*	1100 ± 105	815 ± 19*	1380 ± 31*

used for the detection of MPs, thanks to their high spatial resolution (Andrades et al., 2018; Harrison et al., 2012; Mintenig et al., 2017; Scopetani et al., 2020a,b,c; Simon et al., 2018; Tagg et al., 2015). We operated the system in reflectance mode using an open aperture and a spectral resolution of 8 cm^{-1}, acquiring 128 scans for each spectrum. Each analysis produces a map of 700 × 700 μm^2 (128 × 128 pixels), where each pixel has a dimension of 5.5 × 5.5 μm^2 and provides an independent spectrum. The detection limit of the FPA detector is in the order of 0.02 pg/μm^2 (Mastrangelo et al., 2020). On each filter, MPs were detected and identified in five randomly chosen squares (2 × 2 cm^2), so as to cover 31.4% of the filter area.

2.8. Contamination control

To avoid contamination from organic contaminants, especially from phthalates, all the glassware was rinsed with ultrapure (18.2 MΩ) water, hexane and acetone, and then heated at 200 °C overnight. The risk of MPs self-contamination was also taken into account: items and clothes able to release MPs were avoided, according to Scopetani et al., 2020a,b,c), both during sampling and analyses. All the tools, including the metal buckets, were rinsed with ultrapure (18.2 MΩ) water before covering them with aluminum foil. Field and laboratory blanks were set up in parallel with the samples to check for potential airborne contamination. No MPs were found in any of the blanks.

Procedural blanks for the organic contaminants and metals were performed throughout all steps of the analysis to check for laboratory contamination and interferences. Furthermore, to avoid phthalates contamination, all tools and glassware were rinsed first with ultrapure (18.2 MΩ) water, then acetone and hexane. Since the analytical procedure was free of contamination, no procedural blank correction was applied.

2.9. Statistical analysis

IBM SPSS Statistics version 25 (2017) was used to performed statistical analysis. All data were analyzed with Shapiro-Wilks and Levene's test to check for normality and homogeneity. One-way analysis of variance (ANOVA), followed by Tukey's test, was employed when the data were normally distributed. For not normally distributed data, Dunnett's C test was used to detect differences amongst the treatments. Data were divided in two distinct sets, soil samples (BeanC, BarleyC, BarleyS and Green pea), and compost or plastic samples (CompostW/O, Compost/W and MAPs/MEPs). The two sets were statistically analyzed separately. The results were considered significant at a p value of 0.05.

3. Results and discussion

3.1. Organic contaminants

MAPs/MEPs displayed the highest contaminant concentrations in comparison to soil and compost samples, clearly indicating that plastics are a possible source of pollutants to the compost, and then to agricultural soil. The results are grouped below according to the pollutants. The mean concentration of each contaminant is reported in Table 1.

3.1.1. PAHs (polycyclic aromatic hydrocarbons)

Naphthalene, chrysene and benzo[a]pyrene concentrations were below the detection limit (LOD) in all samples analyzed. ANT, which has a mean concentration of 651 ± 84 ng/g dw in MAPs/MEPs, is also found at lower concentrations in CompostW and CompostW/O (~110 ng/g dw each, with no significant differences, e.g. p = 0.96), while it was below LOQ in all the soil samples.

The sum of analyzed PAHs in compost samples is largely below the limit of 6 mg/kg of compost set by the Regulation EU, 2019/1009 (Regulation EU, 2019), even if this limit concerns the sum of all the 16 PAHs, and our data refer to only four compounds. Brändli et al. (2006) analyzed PAH contents of compost from kitchen and green waste in Switzerland and found PAH concentrations up to four orders of magnitude higher than those detected in the compost analyzed in this study (that is a combination of a mixture of bio-waste and composted sewage sludge). PAHs concentrations in our compost samples were abundantly lower than those found in Poland from raw sewage sludge (Oleszczuk, 2007, 2009) but slightly higher than those detected in composted sewage sludge in Japan by Ozaki et al. (2017).

3.1.2. DEHP (Bis(2-ethylhexyl) phthalate)

DEHP was found in MAPs/MEPs and, at lower concentrations, in all compost and soil samples except for Green pea and BarleyS where the concentrations were lower than the LOD (52.6 ng/g). BarleyC and BeanC samples showed a DEPH concentrations of 931 ± 163 ng/g dw and 1080 ± 209 ng/g dw respectively, and no statistically significant difference was found between them (p = 0.77).

A statistically significant difference was found between Compost/W and CompostW/O (p = 0.043), where the compost samples with MAPs/MEPs presented, as expected, higher DEHP concentrations. MAPs and MEPs had the higher DEHP concentration with an average of 38200 ± 33900 ng/g dw. Overall, our data point to plastics as one source of DEHP in agricultural soils.

The Regulation EU, 2019/1009 (Regulation EU, 2019) does not include limitations of DEHP or other phthalates in compost, but concerns have been expressed about the presence of these contaminants in compost and fertilizers (Huygens et al., 2019). DEHP is one of the most common phthalates added as softeners to plastics products and is often found in concentrations exceeding the limit value of 100 mg/kg fixed by the EU standard for the land application of DEHP containing sewage sludge (Aparicio et al., 2009; Santos et al., 2007). It is recognized as a persistent organic contaminant and an endocrine disruptor able to cause adverse health effects in organisms (Langdon et al., 2019; Sandeep and Rowdhwal, 2018). As far as we know the Danish Decree for the agricultural use of sewage sludge and waste-derived compost is the only regulation that establishes threshold values for DEHP (50 mg/kg) in bio-waste compost. On the contrary, the concentration of DEHP in sewage sludge is regulated by the EU standard for the land application of sewage sludge. The DEHP concentrations we found in compost samples did not exceed the limit value of 100 mg/kg and were lower than those found in the sewage sludge compost produced by a Spanish waste water treatment plant (range 24–124 mg/kg dw and mean 75 mg/kg dw) (Aparicio et al., 2009), but higher than bio-waste compost analyzed by Brändli et al. (2007) (~280 μg kg^{-1}dw). For what concerns soils, our

Table 2
Mean metals concentrations (mg/kg dw) and standard deviation (N = 5). * in MAPs/MEPs data denotes significant difference compared to the compost ($p < 0.05$).

	CompostW	CompostW/O	MAPs/MEPs	Green pea	BarleyS	BarleyC	BeanC
Be	0.38 ± 0.13	0.34 ± 0.09	<0.22 (LOQ)	1.28 ± 0.08	0.85 ± 0.06	1.10 ± 0.19	0.95 ± 0.12
Al	6620 ± 1260	7160 ± 182	518 ± 129*	30400 ± 894	23000 ± 1230	28000 ± 1230	21800 ± 2050
V	18 ± 1.67	18 ± 0.55	<1.7 (LOQ)	102 ± 4.77	103 ± 6.07	89 ± 3,97	75 ± 11
Cr	22 ± 3.19	23 ± 1.10	<8.1 (LOQ)	73 ± 2.88	62 ± 3.27	69 ± 2.77	54 ± 4.80
Fe	54600 ± 6660	55600 ± 3980	1820 ± 466*	38400 ± 1140	34400 ± 1817	35600 ± 1520	31800 ± 5020
Mn	422 ± 31	432 ± 18	14 ± 3.10*	764 ± 80	396 ± 17	750 ± 65	650 ± 130
Co	6.04 ± 0.46	6.34 ± 0.21	<2.2 (LOQ)	21 ± 3.96	13 ± 0.89	17 ± 1.67	15 ± 2.61
Ni	16 ± 1	16 ± 0.55	<6.6 (LOQ)	34 ± 1.22	29 ± 1.30	32 ± 0.89	26 ± 2.35
Cu	128 ± 11	132 ± 16	11 ± 1.73*	29 ± 1.22	32 ± 1.22	36 ± 1.52	37 ± 4.32
Zn	492 ± 90	582 ± 234	1240 ± 354*	152 ± 4.47	<151 (LOQ)	182 ± 8.37	136 ± 11.4
As	<4.2 (LOQ)	<4.2 (LOQ)	<4.2 (LOQ)	<8.4 (LOQ)	<8.4 (LOQ)	<8.4 (LOQ)	<8.4 (LOQ)
Se	<25 (LOQ)	<25 (LOQ)	<25 (LOQ)	<50 (LOQ)	<50 (LOQ)	<50 (LOQ)	<50 (LOQ)
Cd	<1.3 (LOQ)	<1.3 (LOQ)	<1.3 (LOQ)	<2.5 (LOQ)	<2.5 (LOQ)	<2.5 (LOQ)	<2.5 (LOQ)
Pb	9.30 ± 0.42	9.76 ± 1.32	<2.8 (LOQ)	18 ± 0.84	13 ± 0.84	17 ± 0.45	17 ± 2.17

data are comparable to those found by Wang et al. (2013) in suburban vegetable soils in Nanjing (China), but higher than those detected in agricultural soils in the Paris area fertilized with sewage sludge (mean 134 μg/kg) (Tran and Teil, 2015).

3.1.3. ATBC (acetyl tributyl citrate)

As for DEHP, we found ATBC in all samples, the highest values expectedly being in MAPs/MEPs (1100 ± 105 ng/g dw). Similarly to what found for DEHP, ATBC concentrations in Green pea and BarleyS samples were below the LOQ (44.1 ng/g). There was no statistically significant difference between Green pea and BarleyS ($p = 0.597$). Regarding the compost, ATBC concentration in CompostW was below the LOQ but higher than the LOD (13.4 ng/g), while CompostW/O samples showed an ATBC concentration below the LOD. As for DEPH, the results seem to indicate that plastic debris could transfer ATBC to compost, and later on to soil.

As far as we know, the ATBC concentration in compost and agricultural soils is not regulated by any European regulation and there are very few research studies, if any, on its presence in compost and soil. This is probably due to the fact that ATBC is classified as a non-toxic additive (Arrieta et al., 2014; Johnson, 2002), and considered systemically safe up to 1000 mg kg^{-1} day^{-1} (Rasmussen et al., 2017). However, recent findings indicate that long-term exposure to ATBC at environmentally relevant concentration (0.5 μg/l) caused a significant adverse effect on the reproductive system of adult zebrafish (Muhammad et al., 2018). There are evidences indicating that ATBC might disrupt mouse antral follicle function (Rasmussen et al., 2017) and be detrimental to mouse ovarian function at low concentration (10 mg kg^{-1} day^{-1}) (Rasmussen et al., 2017). All these evidences suggest that more information is needed for ATBC risk assessment.

3.1.4. Dodecane

Dodecane was present in all samples, with higher concentrations in MAPs/MEPs and CompostW.

There was no statistically significant difference between soil samples ($p = 0.643$), while CompostW presented a significantly higher dodecane concentration ($p = 0.001$) than CompostW/O.

There are no threshold limits set by the Regulation EU, 2019/1009 (Regulation EU, 2019) for dodecane, a major fuel component (Herbinet et al., 2007). Although it can impair the development of frog embryos (Burýšková et al., 2006) at low doses (0.5 mg l^{-1}), and to induce papillomas in mice (Baxter and Miller, 1987), this substance is not considered toxic as per the International Fragrance Association (IFRA) Environmental Standards (Api et al., 2020). To our knowledge, there are only few studies where dodecane occurrence was investigated and detected (but not quantified) in compost tea, green waste compost and sludge mixed with palm waste (El Fels et al., 2016; Ezz El-Din and Hendawy, 2010; Medicinal and Residues, 2014). The same applies to studies regarding dodecane presence in soil and agricultural fields (Barrutia et al., 2011; Hempfling et al., 1991). Given the high affinity of dodecane for plastic (PE in particular) (Castleman et al., 2021), we can speculate that dodecane was adsorbed on the polymers' surface from the environment and that plastic is not a primary source of this contaminant. Our analyses evidenced the presence of several other aliphatic hydrocarbons, mainly alkanes, both in soil, compost and plastic samples. Further research is needed to understand the source of such compounds and the risks associated with their presence in compost products and agricultural fields.

3.1.5. Nonanal

Similarly to dodecane, nonanal was present in all samples, with higher concentrations in MAPs/MEPs and CompostW. There was no statistically significant difference between the soil samples ($p \geq 0.181$) except for Green pea, where nonanal concentration was statistically lower ($p \leq 0.02$) than in other soils; it must be noticed that nonanal is not a plastic additive and, besides being used in perfumery and as a flavoring agent, can also be directly emitted from vegetation and be present in some wax on the surface of plants (Bowman et al., 2003).

Overall, the data indicate that plastics pollution might represent a source of contaminant for fertilizers and agricultural soils.

As far as we know, the occurrence of nonanal in compost and agricultural soils is not regulated by any European law, and there are no studies regarding its presence in agricultural soils. Published research studies assessing the occurrence of nonanal in compost are scarce but the compound was detected in garden waste compost (López et al., 2016) and in the emissions of municipal solid waste compost maturation treatment (Dorado et al., 2014).

3.2. Metals

Metals analyses were performed on compost soil samples and MEPs and MAPs.

The mean concentration for each metal is reported in Table 2. As, Se and Cd concentrations were below the limit of quantification (LOQ) in all samples, while MAPs/MEPs had values below LOQ for Be, V, Cr, Co, Ni and Pb. Statistical analyses did not show significant differences ($p > 0.05$) between CompostW and CompostW/O.

In comparison to the compost samples, MAPs and MEPs showed a significantly ($p < 0.05$) lower concentration of all metals analyzed except for Zn, which was found in a significantly higher amount in plastics ($p = 0.003$). However, as stated before the compost with and without MAPs/MEPs did not differ significantly in terms of Zn content, indicating that the transfer of Zn from the plastics to the compost could be negligible. The metals concentrations in all the compost samples were similar to those found by Dimambro et al. (2007), and below the limit value levels established by the European Compost Network-European Quality Assurance Scheme for Compost and Digestate (European Compost Network, 2014). In comparison to plastics, soil samples

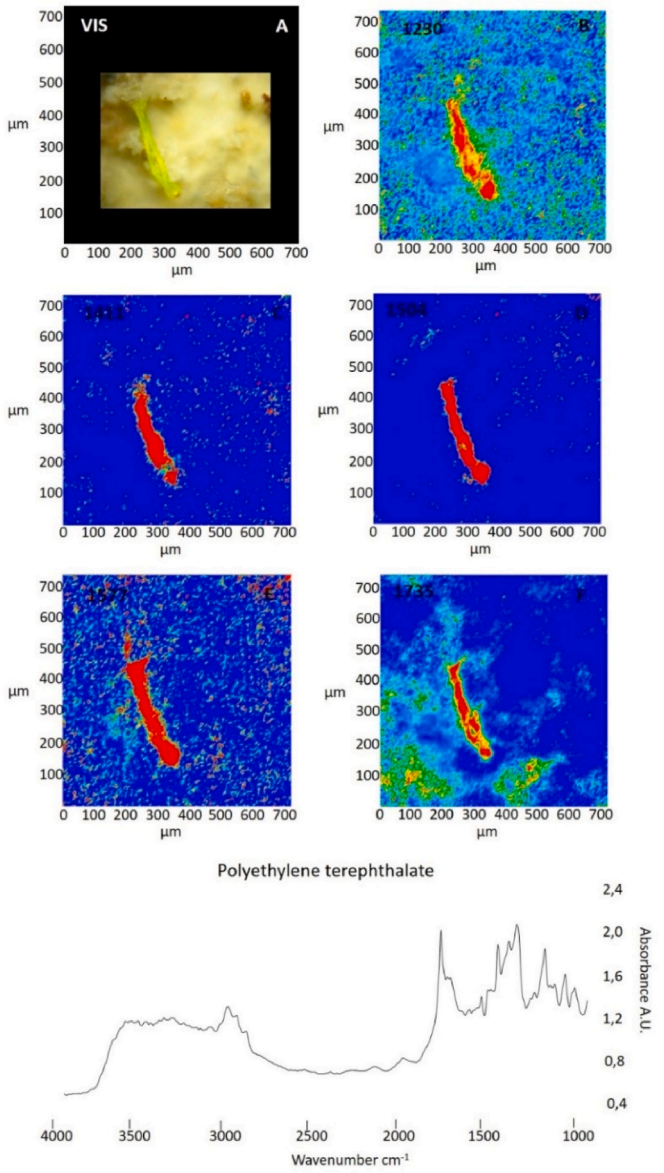

Fig. 1. 2D FITR imaging of a plastic fiber found in the compost. (A) Visible light image of the fiber. (B–F) 2D FTIR Imaging maps (700 × 700 µm^2), showing the intensity of the following bands: (B) 1230 cm−1 (CO stretching); (C) 1411 cm−1 (aromatic skeleton stretching); (D) 1504 cm−1 (aromatic C═C stretching); (E) 1577 cm−1 (aromatic C═C stretching); (F) 1735 cm−1 (CO stretching). The absorbance intensity of the bands is shown in false colors: blue < green, < yellow < red. The bottom panel shows the FTIR Reflectance spectrum of the plastic fiber, relating to a single pixel (5.5 × 5.5 µm^2) of the 2D Imaging map. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

showed significantly higher concentrations ($p \leq 0.02$) of all metals except for Zn, where the opposite result was found ($p < 0.001$). Cu, Fe and Zn concentrations were significantly lower ($p \leq 0.01$) in soil samples in comparison to compost samples, while all the other metals concentrations were significantly higher ($p \leq 0.04$) except for Mn in Barley S samples.

Considering these data, it seems that no transfer of metals occurred from the plastics to the compost. However, we cannot exclude that some of the metals had already transferred from the plastics to the compost during the composting process before our analyses were performed.

3.3. MPs, MEPs and MAPs FTIR analysis

36 MAPs/MEPs were collected from the compost and identified. Polypropylene (PP) (58.3%) and polyethylene (PE) (36.1%) were the most abundant polymers found in the samples, followed by acrylonitrile butadiene styrene (ABS) (2.8%) and polyethylene terephthalate (PET) (2.8%). MAPs + MEPs concentration in the compost was 6.53 g/kg dw. These data are in agreement with those found by Watteau et al. (2018). The authors analyzed plastics >5 mm in two municipal solid waste compost samples, finding concentrations ranging between 1 and 15.3 g/kg dw (Watteau et al., 2018).

MPs were detected in all the compost replicates. The relative abundance of each type of plastics analyzed was as follows: polyethylene terephthalate (PET) (44.2%), PE (25%), acrylates (9.6%), ABS (7.7%), PP (5.8%), polystyrene (PS) (3.9%), acrylonitrile (1.9%), polyurethane (PU) (1.9%). MPs mean concentration found in the compost was 6.6 ± 1.5 items/g dw.

Fig. 1 shows an example of a yellow fiber (ca. 300 µm long) that was analyzed through FTIR microscopy using the FPA detector, and identified as polyethylene terephthalate due to intense absorption peaks at 3000–2800 (aromatic and aliphatic CH stretching region), 1735 (C═O stretching), 1230 cm^{-1} (C–O stretching), 1577 and 1504 (aromatic C═C stretching), 1411 (aromatic skeleton stretching) (Z. Chen et al., 2012; Jung et al., 2018; Pereira et al., 2009).

In the supplementary materials, Figures S1-S7 show the different polymers found in the samples.

The lack of information on the abundance of MPs in compost is a gap in the scientific literature that needs to be filled (Scopetani et al., 2020a, b,c). Only few studies have investigated MPs pollution in recycled fertilizers so far. Among them, Gui et al. (2021) studied MPs (0,05-5 mm) in compost from rural domestic waste finding an average concentration of 2.4 ± 0.4 items/g dw with polyester, PP and PE being the most common polymers (Gui et al., 2021). These findings comply with our results.

EL Hayany et al. (2020) quantified MPs in fresh and in dewatered sewage sludge with mean concentrations of 40.5 ± 11.9 particles/g and 36.0 ± 9,7 particles/g, respectively (EL Hayany et al., 2020), about one order of magnitude higher than our results. Instead, lower MPs concentrations were detected in compost samples by Schwinghammer et al. (2020) and Braun et al. (2021) ranging from 39 to 102 items/kg, and from 12 ± 8 to 46 ± 8 items/kg, respectively (Schwinghammer et al., 2020; Braun et al., 2021). Braun et al. (2021) estimated that compost application to agricultural fields includes a plastic load of 84,000 to 1, 610,000 plastic items ha per year (Braun et al., 2021). This calculation was made taking into account the common recommendations in composting practice that establish an application rate ranging from 7 to 35 t compost ha^{-1} per year.

Applying the same estimate to the MPs and MAPs/MEPs concentrations we found in compost, we obtained a MPs load of 4.62 × 10^7 to 2.31 × 10^8 items ha^{-1} per year and a MAPs/MEPs load of 4.57 × 10^4 to 2.29 × 10^5 g ha^{-1} per year. This indicates that the input of plastics coming from the application of compost to agricultural soil might be higher than previously estimated (Braun et al., 2021).

Thus, our data shows that compost can be a source of plastic contamination to agricultural fields and that technical strategies aimed to minimize the presence of polymers in recycled fertilizers are needed.

4. Conclusions

The purpose of this research was to study the occurrence of MAPs, MEPs and MPs in compost and soil samples, as well as evaluate the transfer of selected contaminants from the plastics contained in the compost to the compost itself, and later on to the soil.

MAPs/MEPs and MPs concentrations in compost were 6.5 g/kg and 6.6 ± 1.5 items/kg respectively, based on which we estimated a MAPs/MEPs load of 4.57 × 10^4 to 2.29 × 10^5 g ha^{-1} per year, and a MPs load of 4.62 × 10^7 to 2.31 × 10^8 items ha^{-1} per year into agricultural soils. We

can thus consider compost as a source of plastic contamination to agricultural fields. MAPs/MEPs had the highest concentrations of all contaminants (except for metals) in comparison to soil and compost samples, indicating that they are a source of potential pollutants transfer from the plastics to the compost and soil. Indeed, MAPs/MEPs-containing compost had significantly higher concentrations of DEHP, ATBC, dodecane and nonanal than compost where these plastics had been removed before contaminants' extraction and analysis. Besides, higher concentrations of DEHP, ATBC and nonanal were also found in the soil samples that had been fertilized with compost, supporting the hypothesis of a contaminant transfer chain from plastics to compost, and then to soil.

A significant transfer of metals from the plastics seems unlikely since plastics had lower metals concentrations than compost and soil samples. However, we cannot exclude that some of the metals had already transferred from the plastics to the compost during the composting process.

Our data indicate that there are risks associated with the presence of plastics in recycled fertilizers and, therefore, regulatory guidelines are needed to ensure the good quality of the final agricultural products. Furthermore, different crops might have diverse capability of fixating and accumulating contaminants. This aspect should be further investigated in future studies to better understand the risks of the presence of plastics in agricultural fields to humans.

Credit author statement

Costanza Scopetani – Experimental design, Sampling, Samples treatment, Measurements, MPs characterization, Data analysis and interpretation, Figures, Writing of the article. David Chelazzi – MPs characterization, Data analysis and interpretation, Revising Text and Figures. Tania Martellini – Revising Text and figures. Alessandra Cincinelli– Revising Text and Figures. Ville Leiniö – Macroplastics characterization. Jukka Pellinen – Experimental design, Data discussion and Revising Text and Figures.

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Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.133645.

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