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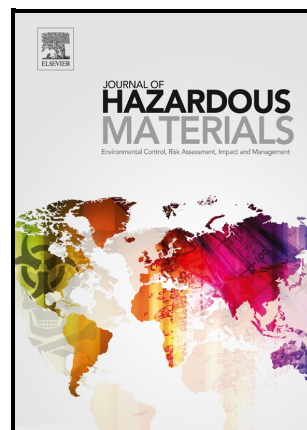
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Nano(micro)plastic mobility in soil : Metallic additives and Sr isotopes as potential tracers

Aurélie Wahl¹, Mélanie Davranche¹, Aline Dia¹, David Vilbert¹, Imane Khatib¹, Maxime Pattier¹, Nataliia Ryzhenko¹, Martine Bouhnik-Le Coz¹, Guénola Peres³, Charlotte Catrouillet¹, Anne-Catherine Pierson-Wickmann¹ and Julien Gigault^{1,2}

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ABSTRACT

Metal contaminants were found in a soil amended with a compost produced from household waste that included plastic debris. A strong correlation between the microplastics (MPs) distribution and the metal concentrations in the soil profile. Metals in the highest concentrations corresponded to the most significant plastic additives. As the total amount of plastic debris and the loss of metals and plastic particles were unknown, it was not possible to conclude that plastic debris is responsible for all of the metal contamination. Amount of calcium (Ca) in MPs (24.5 g kg⁻¹ of MPs) are high in response to its use as filler in plastic formulation. As strontium (Sr) is an analogous of Ca, the potential of ⁸⁷Sr/⁸⁶Sr ratios to quantify MPs and nanoplastics (NPs) was tested. Elemental concentrations (Ca, Cd, Cr Pb, Ni and Sr) coupled with Sr isotopic ratios were compared in both amended soil and a reference soil without amendment. The ⁸⁷Sr/⁸⁶Sr ratios of the amended soil were less radiogenic than for the reference soil (0.724296 ± 0.000010 against 0.726610 ± 0.00009 for the 0-5 cm soil layer, respectively). The Sr isotopic ratio of MPs was also significantly less radiogenic (0.711527 ± 0.000010 for the 0-5 cm soil layer) than for soils. The MPs < 2 mm occurred in the ploughed soil depth with concentration varying from 1.19 to 0.09 mg kg⁻¹. The NPs concentration stayed quite constant from 0 to 55 cm at around 0.25 µg kg⁻¹. The presence of NPs until 55 cm soil depth was attested by the detection of polypropylene NPs by Py-GCMS in the soil solution < 0.8 µm. These results highlighted, for the first time, the NPs mobility throughout the soil depth and their ability to reach hydrosystems. It also demonstrated that Sr could be a potential tracer of the MPs < 2 mm and NPs amount occurring in soils.

Environmental implication

Composted household waste is the source of soil contamination by micro- and nanoplastics. The presence of plastic particles is concomitant with the presence of metals commonly used as additives in the plastic formulation. Nanoplastics are present even beyond the plough sole up to 55 cm in the amended soil, demonstrating the high mobility of nanoplastics and their potential to reach the underlying water tables and, more broadly, the hydrographic network.

Keywords:

Nanoplastics, microplastic, soil, compost, metal, isotope

1. Introduction

Plastics have accumulated in all environmental compartments, and degrade through the action of both abiotic (i.e., UV radiation, mechanical abrasion, thermal degradation) and biotic factors [1–6]. These degradation processes lead to the release of the additives embedded in their polymer matrix following plastic formulation [7–9]. Various kinds of additives (including nano-additives) are used to increase the plastic durability, resistance and other properties. These additives include metals used as UV stabilisers, colourants, heat stabilisers, or flame retardants [10].

Many additives are hazardous to the environment and living organisms [10,11]. In recent years, scientists have studied whether microplastics (MPs) play a role in the increasing heavy metal content in soils. Several studies demonstrated the release of metal additives from plastics (Boyle et al., 2020; Whitt et al., 2016; Nakashima et al., 2012; Long et al., 2011). Various mechanisms control metal particle release from plastic polymer matrices. They can diffuse within the plastic matrices and be released into the aqueous medium. This process is rate-limiting as long as the dissociation rate of potential adsorbed metal complexes is greater [16]. Microplastics are, indeed, able to adsorb external toxins onto their surface, or onto minerals or biofilms coating their surface [17–22]. For example, microplastics can adsorb antibiotics onto attached biofilm [23]. This adsorption depends on the aging and microorganisms strain [24,25].

Polymer degradation is the process the most involved in the additives' release in the environment [9,12,17,26,27]. Additives are trapped in plastic matrices, without any chemical binding between the additives and the polymer [28]. Degradation of the polymer modifies its properties, breaking polymer chains and producing smaller plastic particles, resulting in the release of additives, notably metals, into the environment. Very little is yet known about how these processes affect terrestrial environments. For compost as a source of plastics in soil, Scopetani et al. (2022) investigated the transfer of contaminants, including metals, from plastics to compost. They did not find any significant differences between metal concentrations in composts with or without plastics. However, they could not determine the metal amount released by the composting before the compost was collected. To our knowledge, no data are available to compare soils with and without compost.

Catrouillet et al. (2021) demonstrated that metals adsorbed onto the altered surface of degraded MPs are mainly those additive metals released as plastics degrade. The degraded plastic surface layer is the source of further NPs that will be released in the environment with their metal load as residual additives are adsorbed onto their surface. These metals could thus be further used for tracing NPs. The extraction and identification of NPs in environmental matrices remains challenging due to their carbon-based composition, their size, and their individual properties [30–32], especially when trying to identify NPs in complex heterogeneous soil matrices. NPs identification techniques have so far only determined a few polymers using Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC-MS). However, quantitative data were provided for water treatment effluents and biological samples, using complex

extraction step based on Cloud-Point Extraction (CPE) and pre-concentration combined with Py-GC-MS [33–35].

Therefore, further developments are needed for better NPs detection, including finding reliable tracers to identify the occurrence of NPs in natural media. Metals are interesting candidates, as they are often used as additives and are adsorbed onto the surface of NPs. The combination of the elemental concentration and isotopic composition of specific metallic or inorganic plastic additives could be an asset to develop this type of approach. Conservative isotope compositions can be indeed used to trace sources based on the specific isotopic signature of each involved pool (Drouet et al., 2005; Clow et al., 1997).

There is an undeniable challenge in detecting and quantifying NPs in soils and soil solutions. Nanoplastics are nanosized and behave as colloids, they can therefore be transported in soil solutions through the soil porosity and subsequently reach surface and groundwaters. If authors considered that their mobility is limited by their ability to homo-aggregate or hetero-aggregate with soil components (mainly organic matter) (i.e. Wu et al., 2020), it has been demonstrated that 50 nm-sized NPs remained dispersed in water in presence of vermiculite under convective transport condition [39].

Based on all the considerations mentioned above, this study aims to assess the relationship between plastic and metal contamination to test the potential of metallic additives in quantifying the occurrence and mobility of MPs and NPs in soil. To circumvent the complexity of the existing Py-GC-MS methodology for quantifying MPs and NPs in soils and soil solutions, the potential of using the isotopic composition of inorganic additives (Sr) as a tracer was tested. Isotopic results combined with NPs detection by Py-GC-MS allowed to discuss the mobility of MPs (<2 mm) and NPs in soil.

2. Material and methods

2.1 Soil sampling and geochemical analysis

The sampling site is located in Cléry-Saint-André, in north-central France. The investigated site consists of two contrasted agricultural soils. One received an amendment of household waste (HW) compost in 1990 [40]. Composting, at this date, was not regulated, and manufactured wastes were not sorted from the organic components. Hence, the compost had high amounts of crushed plastic and glass debris, clearly visible on the soil surface and within the first top 30 cm of the soil profile. A non-amended soil, beside the contaminated soil, and thus with the same geochemical background, was sampled as an uncontaminated reference soil. These soils are well-drained cambisol (WRB), enriched in pebbles and developed from alluvial deposits. Each year, the amended-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 grown for 15 years in rotation with sunflower and rye, with annual ploughing. Since 2005, the parcel has been used as a meadow. 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 then performed on each plot from 8 sub-profiles from 0 to 60 cm depth. Sampling was carried out every 5 cm in depth (i.e., 0 to 5 cm, 5 to 10 cm). Hence, three composite soil profiles were sampled. The same protocol was used to sample a

neighboring soil, free of compost, and considered 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 geochemical composition below 40 cm depth. However, the amended soil is enriched in major and trace elements on the first 35 cm of the soil profile (further information are available in - SI ; Table SI 1 and Table SI 2).

Geochemical characterization was performed at the National Analytical Service des Roches et Minéraux (SARM – CNRS, France). Major and trace element concentrations were determined by Inductively Coupled Plasma-Mass Spectrometry (Thermo Elemental X7). Samples were digested by alkaline fusion using lithium metaborate (LiBO_2) as a fusion flux. Analyses used 1 g of the 12 depth samples of the composite soil profile (0–60 cm depth).

2.2 *Microplastic extraction, sorting and analysis*

Microplastics were manually extracted with a binocular loupe from the 5 to 2 mm soil fraction in all the layers of the 3 soil profiles as previously performed in [41]. The MPs sorting was carried out on the sieved soil fractions. The MPs were washed with ultrapure water and an ultrasonic bath for 30 min, then, washed using 1 M NaOH for 24 h at room temperature to remove organic matter [41]. Then, MPs were washed twice with ultrapure water followed by a 30 min ultrasonic bath. Although the Fenton reagent is recognized as the most suitable for removing soil organic matter from MPs [42], such oxidation was not achieved as the addition of Fe^{2+} could modify Fe speciation and impact metals behavior. Microplastics were rinsed with ultrapure water and dried at 50°C for 24 h, and sorted a second time. ATR-FTIR analysis and SEM observations performed in a previous study provided evidence that no residue of organic matter (notably biofilm) persisted after this washing procedure on the MPs surface [41]. They were weighed to determine their distribution in g kg^{-1} soil. Finally, MPs of each layer were mixed to obtain a composite per layer.

2.3 *Water extractions*

To mimic the release of the most exchangeable metals and nanoparticles from rainwater permeation, water extraction experiments (water with rainwater-like ionic strength, 4 mM NaCl) were performed following the procedure described in Wahl et al. (2021) in triplicats. The soil samples were stirred with rain-like water at a 1:4 soil/water ratio (mass) for 24 h. To separate the colloidal fraction, soil solutions were centrifuged at 1422 g force for 15 min and filtered at 0.8 μm (cellulose acetate, Sartorius) to separate the colloidal fraction. Water-extraction experiments were performed for the 12 contaminated soil layers and the 12 reference soil layers. Dissolved organic carbon (DOC) concentrations were determined using a TOC analyzer (Shimadzu TOC-V CSH). The accuracy of the DOC measurements was estimated at $\pm 5\%$ for all samples using a standard solution of potassium hydrogen phthalate. From the

absorbance obtained at 254 nm, the SUVA (Specific UltraViolet Absorbance) was calculated in the soil water extracts, following the equation $SUVA = A_{254 \text{ nm}}/\text{DOC}$.

2.3.1 Trace elements loading of microplastics and soil-water extracts

Acidic digestions were performed to determine the trace element loading of the MPs collected in the contaminated soils [41]. Microplastics were homogenised using cryo-ball milling before acidic digestion. Three replicates per layer (0–5 cm, 15–20 cm, 30–35 cm) of 160 ± 3 mg of MP powder were mixed with 1 mL of ultrapure water and 5 mL 14.6 N HNO_3 in PTFE tubes. Acidic digestions were performed using a microwave (Multiwave 7000, Anton-Paar). The temperature was increased for 35 min at $6.6^\circ\text{C min}^{-1}$ until 250°C , reaching a pressure of 80 bar. The temperature of 250°C was held constant for 25 min and then cooled for approximately 15 min. Blanks were performed to compare for no contamination. Standards (ERM-680 and ERM-681) from the Joint Research Centre of the European Commission (JRC, Ispra, Italy) were used to validate the protocol. For the soil-water extracts, 20 mL of the solution were mixed with 3 mL of 14.6 N HNO_3 in PTFE tubes, and the same protocol was applied. Trace metal concentrations were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, 7700x Model, Agilent). Helium gas was introduced into a collision cell to reduce argon interference. Calibration curves were made and validated using certified references (SLRS-6, National Research Council). An internal standard (rhodium) was used to correct the instrumental drift and potential matrix effects.

2.3.2 Strontium (Sr) isotope ratio analysis

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured for MPs and for the soil samples and soil water extracts (soil solution) relative to the soil depth. An additional soil sample was analysed before and after MP removal. For this, MPs were manually sorted under a binocular magnifier. Soil samples were manually ground with an agate mortar. Triplicates of MPs were mixed to obtain a MP composite of around 450 mg for each of the 0–5, 15–20, and 30–35 cm depths. The soil solutions and the MPs were digested with one-third 14.6 M HNO_3 and two-thirds 23 M HF at 90°C . Soil samples were digested with HNO_3/HCl at same ratios than previously. After complete evaporation, samples were solubilised with 6 M HCl. The Sr separation was carried out by cationic exchange chromatography using a BioRad AG50W-X8 resin. Analyses were performed using a multi-collector Thermal Ionisation Mass Spectrometer (TIMS; Finnigan MAT 262). Samples were analysed with a standard (NBS-987), and their reported $^{87}\text{Sr}/^{86}\text{Sr}$ values were normalised to the standard reference value (0.71025 ± 0.00001). Mass fractionation was monitored and corrected using the value $^{88}\text{Sr}/^{86}\text{Sr} = 8.3752$. All blanks registered were < 300 pg and therefore considered as negligible.

2.3.3 Nanoplastic Py-GCMS detection

The soil solutions were analysed by pyrolysis (PY-3030, Frontier Lab) coupled with Gas Chromatography and Mass Spectrometry (GC-MS, Agilent Technologies). Before analysis, soil solutions were freeze-dried, and 200 µg of crushed powder were introduced into the pyrolysis cup. To assess any polymer contamination during the sample preparation, empty pyrolysis cups were systematically added beside regular samples. The method was set according to Dehaut et al. (2016). Pyrolysis was performed at 600°C, and samples were injected with a split of 20:1 (split-flow: 20.98 mL min⁻¹) into a 60 m DB5 column (Agilent Technologies) with helium as a carrier gas. The temperature of the column was initially set to 50°C for 2 min, increased at a rate of 10°C min⁻¹ until 180°C, then 5° C min⁻¹ until 310°C, and held at this final temperature for 19 min. MS interface temperature was set to 310 °C, the ion source at 230 °C. Separated pyrolysis products were ionized at 70 eV, and their mass spectra were scanned between m/z 35 to 500. Each pyrograms were realized in four replicates. As it is not yet possible to quantify NPs by Py-GCMS, we determined the signal-to-noise ratio (SNR), ranging from 150 to 430, for all performed analyses. Based on the SNR and the mass of NPs (Environmental Protection Agency, 2016), LOD can be estimated from 0.2 to 0.4 mgC L⁻¹. Polymer identification was performed using a total ion current (TIC), first identified using GC-MS data analysis (Mass-Hunter, Agilent), interrogating the NIST database for molecular identification. The identification was established based on spectrum similarities (in %). Under 85-90 %, similarities are not significant. All analysis cups used were brand new and checked before use to prevent any possible contamination. A particular focus has been held on polypropylene (PP) and its markers based on the method developed by Blancho et al., (2021b) that demonstrated that PP has specific markers not produced by natural organic matter (NOM) pyrolysis, such as the 2,4-dimethyl-1-heptene (C12). As NOM mostly dominated the organic carbon concentration, we focused on this particular ion among the PP markers. Analysis was performed on the water extract filtrated at 0.8 µm for the 3 soil layers: 15-20 cm, 30-35 cm and 50-55 cm.

3. Results and discussion

3.1 Metal contamination as a possible asset to fingerprint plastic occurrence

Fig. 1 illustrates the difference in the trace element concentrations between the amended and reference soils. For all the studied soil depths, the amended soil contained higher than usual amounts of 19 trace elements, including metals such as Cr, Co, Ni, Cu, Cd, and Pb.

The most concentrated elements in amended soils were the most concentrated elements in the MPs samples as assessed by Fig. 1 a and b where the average concentrations in metals and other trace elements in MPs are compared to the average enrichment ([Metal in contaminated soil]-[Metal in reference soil]) of these elements in the 3 uppermost soil layers through depth (0-5, 15-20 and 30-35 cm). The most concentrated elements (Ca, Cd, Pb, Cr, and Ni) are common plastic additives [10,27,28,44,45]). For example, Ca is primarily used as filler, Mg, Na, and Al as antioxidants and UV stabilisers, and metals (Cr,

Cu, Fe, Zn, Cd, Pb) as colourants, stabilisers or heat stabilisers in the formulation of plastics [10,28]. The hypothesis is that the extra elements were sourced from the plastic debris in which they occur as additives. When plastic debris degrade into smaller MPs or NPs, part of these metallic additives remains in the soil while another part is released. The released metals are either leached away or adsorbed onto soil particles (mainly organic matter, Fe-oxides, and clays). Therefore, the total concentration of metals in the contaminated soil should correspond to the sum of the soil background (reference soil), the metals in MPs less than 2 mm (soil size sieving), and the metals from plastic degradation adsorbed onto soil components.

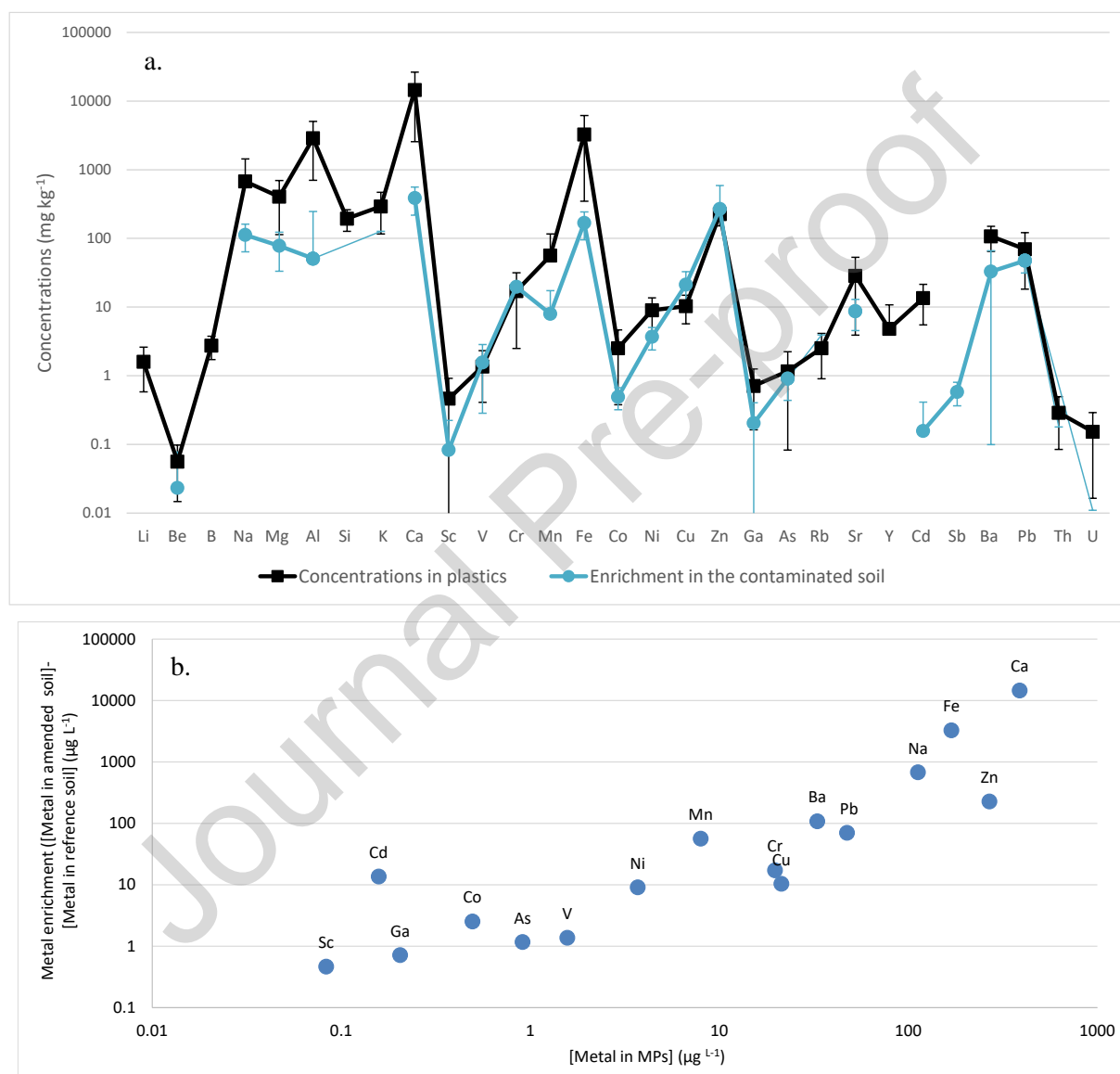


Fig. 1. a. Trace element concentrations in MPs as compared to the trace metal enrichment in the amended soils ($(\text{Avg}([\text{trace elements}]_{\text{amended soil}})_{0-5, 15-20, 30-35 \text{ depth}} - \text{Avg}([\text{trace elements}]_{\text{reference soil}})_{0-5, 15-20, 30-35 \text{ depth}})$, concentrations are expressed in a log scale. **b.** Correlation between the most concentrated metals in MPs and the average enrichment of metal in amended soil.

The correlation between the quantity of MPs (with depth) and the concentration of metals (with depth) were also studied (Fig SI.1). The regression coefficient varies from 0.9 to 0.78, demonstrating a correlation between the amounts of MPs and metals. For most metals, the correlation with MPs is

preserved throughout the soil depth. Metals thus seem to remain primarily associated with the MPs, either as additives trapped within the polymer structure or adsorbed on their oxidized surface. Catrouillet et al. [45] demonstrated that metals adsorbed in high concentrations on the MP surface originate from metal additives present within the plastics.

The highest concentrations in the amended soils occurred in the uppermost 35 cm of depth (Fig. 2). From 40 to 60-cm, the concentrations of the amended and reference soils were rather similar, corresponding to the local geochemical background. The organic carbon (C_{org}) concentrations followed the same evolution (Fig. 2e). The uppermost 35 cm of the amended soil corresponds to the cultivation depth where the compost was tilled and included in the soil matrix. In the amended soil, the concomitant increased amounts of C_{org} and trace metals confirm that HW compost components enriched the soil in micronutrients and metals [13,29,46,47]. Achiba et al. (2009) also observed an increase in Pb, Cd, Ni and Cr in a soil amended with HW compost for 5 years at three different rates (i.e., 40, 80, or 120 t ha⁻¹). In the 0–20 cm soil layer, the differences in measured concentrations between the amended and their reference soil were ranging from 25.2–49.0 mg kg⁻¹ in Pb, 0.2–1.6 mg kg⁻¹ in Cd, 4.7–8.5 mg kg⁻¹ in Ni and 3.3–7.0 in Cr.

In this study, from 0–20 cm, the concentration variation between the amended and the reference soils were 57.2 mg kg⁻¹ for Pb, 0.3 mg kg⁻¹ for Cd, 4.06 mg kg⁻¹ for Ni, and 19.67 mg kg⁻¹ for Cr. Here, the metal inputs are thus similar (Cd, Ni) or higher (Pb, Cr) than in Achiba et al. (2009), where soils were amended for 5 years. Hence, even after 30 years and for only one amendment, the geochemical composition of the soil remains affected by the HW compost addition. Metal contamination can also be assessed by calculating the geo-accumulation index I_{geo} described by Muller (1969) as $I_{geo} = \log_2 (C_n/1.5B_n)$. Where C_n is the measured concentration and B_n is the geochemical background, corresponding here to the concentrations in the reference soil. All the values of I_{geo} calculated for Cd, Cr, Pb, and Ni are < 2, corresponding to a moderately polluted soil. Results also showed that the original compost must have been high in metals, since the present metal levels obtained after only one compost application, 30 years ago, reached equal concentrations measured after 5 years of applications by Achiba et al. (2009). According to the geo-accumulation index, the metal contamination in the amended soil remains moderate [48].

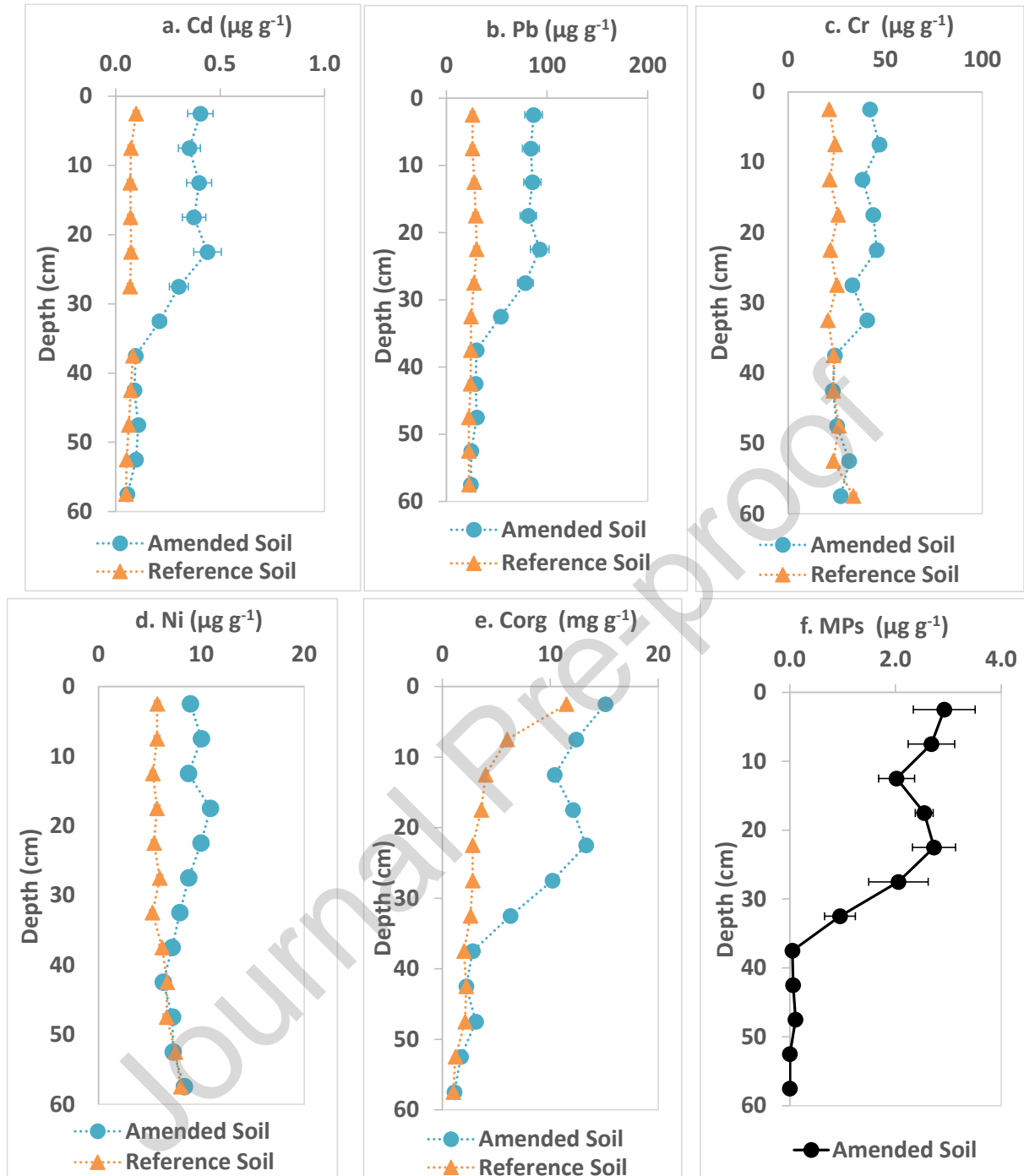


Fig. 2. Concentration evolution of major and trace elements with the soil depth. a–d metal concentration evolutions through depth in the amended and reference soils; e shows the variations in organic carbon (C_{org}), whereas f presents the distribution in MPs through the soil depth. Error bars corresponds to triplicats

The first 35 cm of the soil also corresponds to the accumulation zone of MPs (for 2–5 mm MPs) provided by the HW compost (Fig. 2f; [41]). Wahl et al. (2024) described these MPs as highly degraded and mainly composed of PVC, which has the highest content of heat stabilisers and additives, then rapidly released from the polymer by alteration processes [10,28,49]. Hence, metal contamination could originate from the compost plastic debris load. To estimate the participation of plastic additives in the metal contamination, trace element inputs from the total degradation of plastics were calculated. The estimation

was made considering the complete degradation of the 2–5 mm MPs (considering their masses) and the full release of their metal loading (Table 1).

Table 1. Estimating the metal inputs from the complete MPs (2 - 5 mm) degradation. Results are given in mg kg⁻¹ of dry soil. Values correspond to the average of three replicates for each soil layer.

	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Ni (mg kg ⁻¹)
0–5 cm	0.051 ± 0.002	0.356 ± 0.024	0.015 ± 0.001	0.040 ± 0.052
15–20 cm	0.011 ± 0.001	0.174 ± 0.006	0.085 ± 0.010	0.022 ± 0.001
30–35 cm	0.018 ± 0.001	0.018 ± 0.003	0.012 ± 0.001	0.004 ± 0.0004

The metal content generated from the degradation of the 2–5 mm MPs was negligible as compared to the differences in the concentrations between amended and reference soils (Fig. 1, Table 2). This approach suggested that the additives released cannot explain the soil metal contamination. Scopetani et al. (2022), did not observe any significant differences in metal concentrations between compost with or without plastics. However, their calculations used only the 2–5 mm MPs without considering the biggest or smallest plastic debris. As previously stated by Wahl et al. (2024), the plastic debris were highly degraded, releasing their additive loading and smaller, probably more mobile, particles. Both could have been leached from the soil by the (sub)surface runoff and the rainwater infiltration. Soil surface erosion could also provide a bias in quantifying the plastic debris. Finally, the release rates of additives from plastics are not known. Thereby, the amounts of already lost metal and plastic particles, in the last 30 years, are not possible to determine. Scopetani et al. (2022) estimate has, therefore, to be considered with caution. To state on the metal sources in the amended soil, the metal quantification could be combined with methods specific to the metal source identification such as metal isotope fingerprinting.

Table 2. Differences in concentration between the amended and the reference soils. Results are given in mg kg⁻¹ of dry soil.

	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Ni (mg kg ⁻¹)
0–5 cm	0.308	60.561	20.964	3.238
15–20 cm	0.303	52.335	18.030	5.210
30–35 cm	-0.138	29.484	20.202	2.674

In non-contaminated soils, metals are generally distributed in the residual fraction of the soils, in the Fe-Mn oxides or the soil organic pool. Achiba et al. (2009) recovered less than 6 % of the total metal concentration in the water-soluble fraction. Metals bound to NPs could be significant in the water-soluble fraction and be used for tracing the presence of NPs. As explained in Gigault et al. (2021), due to their size, NPs may present an increased diffusive release of additives, which is expected to be many orders of magnitude greater than for MPs.

[50] observed the presence of TiO₂ nanoparticles, a plastic additive, on the surface of NPs generated from MPs collected on a beach. Catrouillet et al. (2021) demonstrated that most leached additives are re-adsorbed at the degraded MPs surface layer, the one at the origin of the NPs production

and release. Therefore, even if metals are no longer part of their structure, they are expected to be strongly linked to NPs. The Cd, Pb, Cr, and Ni concentrations of the colloidal fraction of the soil solution ($< 0.8 \mu\text{m}$) relative to the soil depth were plotted in Fig. 3. Amended and reference soils exhibited significant differences with higher metals concentrations for the amended soil. Nevertheless, the Cr and Ni concentrations tended to increase through depth, whereas Cd and Pb concentrations tended to be higher within the first 35 cm. Cadmium and Pb showed similar MPs distributions, whereas Cr and Ni distributions differ over depth. These results suggested that (i) the increasing Cr and Ni concentrations through depth are more related to the soil matrix or that (ii) Cr and Ni are less water-extractable (namely as soluble ions, molecules, or colloids) in response to their respective speciation in soil. The concomitant distribution of MPs and Cd and Pb suggested that Cd and Pb could be potential candidates for NPs tracing. Cadmium concentrations in MPs are lower than the other elements. By contrast, Pb was the most prevalent metal in MPs, so we could assess the ability of Pb isotope ratios to fingerprint NPs presence and amount.

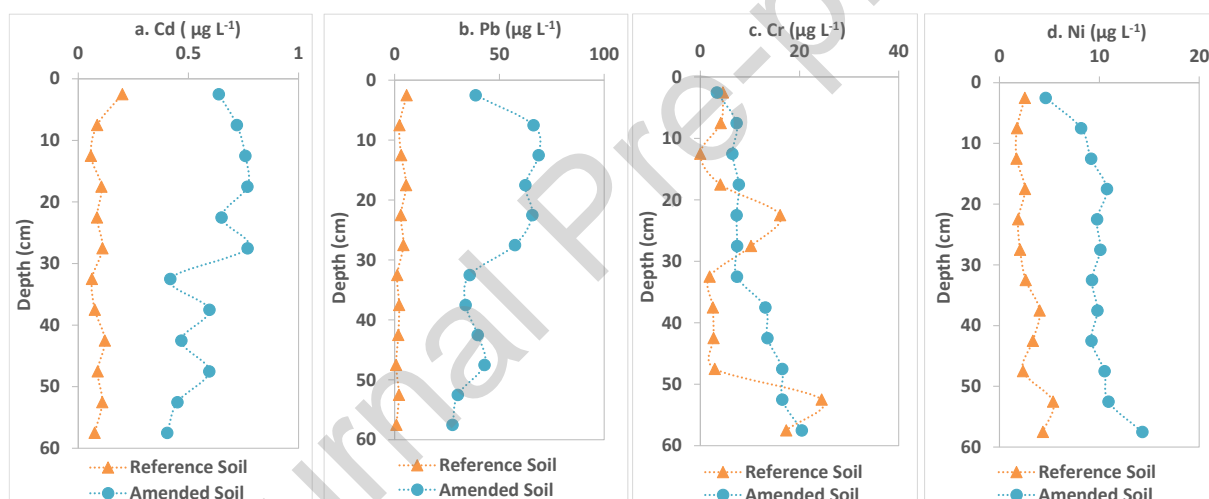


Fig. 3. Trace metal (a-d) profiles in the $< 0.8 \mu\text{m}$ soil solutions. Soil solutions were extracted from the amended soil and the reference soil.

3.2 Sr isotopes as a MPs and NPs tracer

Calcium was the most abundant trace element in MPs (Fig. 1). Up to 24.5 g kg^{-1} of MPs were measured. Calcium is generally accompanied by Sr since Sr, also alkaline earth element, substitutes Ca in crystal lattices. Strontium is therefore considered as an analogue element of Ca [51]. Strontium concentrations ranged from $4.7 - 54.0 \text{ mg kg}^{-1}$ and were higher in the amended soil than in the reference soil, and that considering both the soil matrices and the soil solutions (Fig. 4a). Calcium and Sr distribution with soil depth even followed the MPs distribution. Since Sr isotopes can be used to trace Ca sources [36,37,52], $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were then measured in both MPs, the soils and the soil solutions.

Significant variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were found throughout the soil depth and between the two soils (Fig. 4a). Variations through depth are commonly observed in soils. The uppermost soil layers were enriched in organic matter and allochthonous inputs from water runoff and the atmosphere. By contrast,

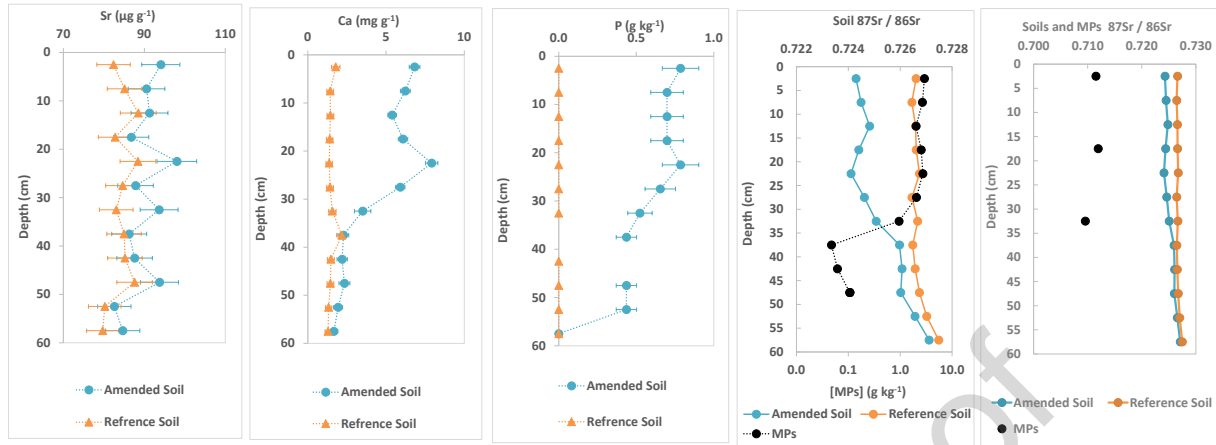
the Sr isotope signature of the deepest soil layers reflects that of the bedrock and the first weathering steps of the pedogenesis [53]. The amended soil $^{87}\text{Sr}/^{86}\text{Sr}$ evolution was more heterogeneous than that of the reference soil (Fig. 4a **Error! Reference source not found.**). All the values are lower in the amended soil, i.e., less radiogenic, especially within the uppermost 35 cm (0.72496 ± 0.00009 - 0.724404 ± 0.000010 for the amended against $>0.72610 \pm 0.000010$ for the reference). Interestingly, the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution in the amended soil was negatively correlated to the MPs distribution (Fig. 4a). Where MPs were the most abundant, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was lower. Below 35 cm depth, where no more MPs (5-2mm) occurred, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the amended soil tended to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the reference soil. Furthermore, the isotopic signature of MPs was much less radiogenic (from 0.709562 ± 0.000010 to 0.711929 ± 0.000010 ; Fig. 4a) than for the soil. The MPs could then be responsible for the $^{87}\text{Sr}/^{86}\text{Sr}$ variations exhibited in the amended soil. In a first approximation, the observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the amended soil could result from a two end-member mixing, involving, as the two end-members: the soil background (represented by the reference soil) and the MPs, respectively, expressed as follows (**Eq. 1**):

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{tot}} \times [\text{Sr}]_{\text{tot}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{reference soil}} \times f[\text{Sr}]_{\text{reference soil}} + (^{87}\text{Sr}/^{86}\text{Sr})_{\text{MPs}} \times (1-f) \times [\text{Sr}]_{\text{MPs}} \quad (\text{Eq.1})$$

With $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{tot}}$ corresponding to the Sr isotope composition measured in the amended soil, $[\text{Sr}]_{\text{tot}}$ the total Sr concentration in the amended soil, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{reference soil}}$ the Sr isotope composition of the reference soil, $[\text{Sr}]_{\text{reference soil}}$ the Sr concentration in the reference soil, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{MPs}}$ the Sr isotope composition of MPs and $[\text{Sr}]_{\text{MPs}}$ the MPs Sr concentration. The variables f and $(1-f)$ are the proportions of the reference soil and MPs, respectively.

We measured the $^{87}\text{Sr}/^{86}\text{Sr}$ for a soil sample (0–5 cm) from which MPs were manually extracted to confirm this result. The expected ratios for a two-end-member mixing were calculated (Table 3). The measured ratios are much lower than the calculated ratios indicating that MPs were not the only allochthonous source responsible for such $^{87}\text{Sr}/^{86}\text{Sr}$ values in the amended soil and especially the lower $^{87}\text{Sr}/^{86}\text{Sr}$ specific signature as compared to that of the reference soil. The MPs-sorted soil $^{87}\text{Sr}/^{86}\text{Sr}$ was 0.724433 ± 0.000010 , higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ of the amended soil with plastics debris but, lower than the $^{87}\text{Sr}/^{86}\text{Sr}$ of the corresponding reference soil with $^{87}\text{Sr}/^{86}\text{Sr} = 0.726610 \pm 0.000010$. Therefore, MPs influenced the $^{87}\text{Sr}/^{86}\text{Sr}$ signature, but since the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio without MPs did not reach the $^{87}\text{Sr}/^{86}\text{Sr}$ of the reference soil, other low radiogenic sources (from other amendments) should occur in the amended soil. Thus, the MPs cannot be the unique source responsible for the low $^{87}\text{Sr}/^{86}\text{Sr}$ signature.

a) Soils



b) Soil solutions

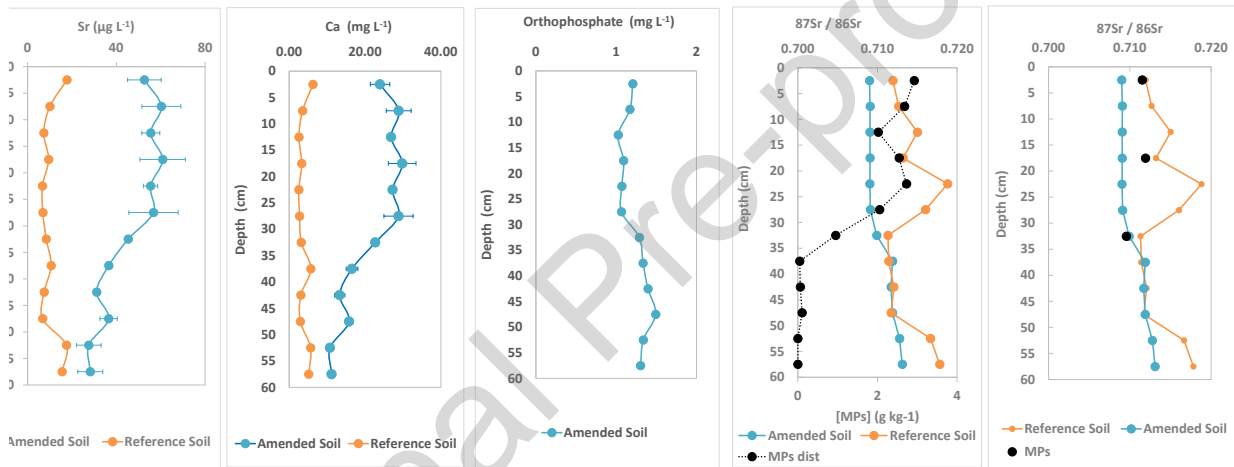


Fig. 4. Evolution of Ca, Sr, P, orthophosphate concentrations, MPs distribution and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, through soil depth for a) the soil and b) the colloidal fraction of the extracted soil water. Error bars corresponds to triplicats

Table 3. Comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ between the measured and calculated values following Eq.1.

Depth	$^{87}\text{Sr}/^{86}\text{Sr}$ calculated from Eq. 1	$^{87}\text{Sr}/^{86}\text{Sr}$ measured in the contaminated soil
0–5 cm	0.726263	0.724296 ± 0.000010
15–20 cm	0.725146	0.724404 ± 0.000010
30–35 cm	0.725581	0.725075 ± 0.000010

The amended soil was fertilized with N-K-P and lime (CaO) for several years until 2005. Both amendments are sources of Ca and Sr. Thomsen and Andreasen, (2019) demonstrated that lime amendment could durably impact the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in soils. The difference noticed in Ca concentrations in between the amended and reference soils (Fig. 4) and the orthophosphate concentration in the amended soil solution confirmed the inputs of both elements (Fig. 4). The $^{87}\text{Sr}/^{86}\text{Sr}$ composition was also determined for the colloidal fraction of the soil solutions (fraction < 0.8 μm) where NPs are expected to occur (Fig. 4b). Globally, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were less radiogenic than in both soils, which can be explained by the low ability of more radiogenic soil minerals to be dissolved by water (namely clay minerals). In the

uppermost 35 cm of soils, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the amended soil solutions were also less radiogenic than those of the reference soil, indicating a less radiogenic pool input. By contrast, below 35 cm, $^{87}\text{Sr}/^{86}\text{Sr}$ of the amended soil solution reached the same values as the reference, showing that the soil background controlled the $^{87}\text{Sr}/^{86}\text{Sr}$ composition at this depth. The $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the water extracts of amended soils evolved inversely with the MPs distribution and the Ca and Sr concentrations (Fig. 4b). However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of MPs being higher than those of the amended soils demonstrated that the Sr signature was also influenced by other anthropogenic Sr sources. The presence of higher orthophosphate concentrations in the amended soils than in the reference soil solutions suggests that N-P-K fertilization could be another contributing source involved in the displayed $^{87}\text{Sr}/^{86}\text{Sr}$ signature (Fig. 4b). Four different sources of Sr, therefore, existed in the soil and in the soil solution, 1) the natural Sr source provided by the reference soil, and the anthropogenic sources corresponding to the CaO, NPK and plastics. The equation Eq. 1 is then modifying to become:

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{tot}} \times [\text{Sr}]_{\text{tot}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{reference soil}} \times f1 \times [\text{Sr}]_{\text{reference soil}} + (^{87}\text{Sr}/^{86}\text{Sr})_{\text{MPs}} \times f2 \times [\text{Sr}]_{\text{MPs}} + (^{87}\text{Sr}/^{86}\text{Sr})_{\text{lime}} \times f3 \times [\text{Sr}]_{\text{lime}} + (^{87}\text{Sr}/^{86}\text{Sr})_{\text{fertilizer}} \times f4 \times [\text{Sr}]_{\text{fertilizer}} \quad (\text{Eq.2})$$

$$\text{With } f1+f2=f3+f4 = 1$$

Unfortunately, information on the specific amounts and the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the N-K-P fertilizer and lime used is lacking. Despite this, the potential of $^{87}\text{Sr}/^{86}\text{Sr}$ to assess the quantity of MPs < 2 mm in the amended soil and NPs present in the experimental soil solution (< 0.8 μm) was explored. Published data on the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of CaO and NPK fertilizer are available [54,55]. By knowing the Sr concentration in CaO and NPK, and the concentrations of Ca and P that do not originate from the bedrock, namely coming from contamination ([Ca in amended soil] - [Ca in reference soil] and [P in amended soil] - [P in reference soil] or in the soil solution), the Sr mass fraction ($f3 \times [\text{Sr}]_{\text{lime}}$ and $f4 \times [\text{Sr}]_{\text{fertilizer}}$) derived from both CaO and N-P-K can be calculated [54–56] (Table 4). Given that $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{tot}}$, $[\text{Sr}]_{\text{tot}}$, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{reference soil}} \times f1 \times [\text{Sr}]_{\text{reference soil}}$ (quantitative isotopic signal of the reference soil), $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{MPs}}$, and $[\text{Sr}]_{\text{MPs}}$ are known, the proportion of Sr ($f2$) originating from plastics in the < 2 mm soil fraction and in the soil solution (Table 4) can be estimated. The objective here is not to determine the exact concentration of MPs in the < 2 mm fraction or of NPs in the soil solution, but rather to evaluate whether Sr can trace their occurrence and provide an estimated range of MPs and NPs quantities in the studied fraction.

Table 4. Values used in calculations to solve Eq. 2

$^{87}\text{Sr}/^{86}\text{Sr}$ r CaO	$\text{Sr } \mu\text{g g}^{-1}$ from CaO (Range: high to low)		$^{87}\text{Sr}/^{86}\text{Sr}$ NKP	$\text{Sr } \text{mg g}^{-1}$ from NKP (Range: high to low)		Natural source	Anthropogenic Sources			Referenc e [54–56]
	high	low		high	low		CaO	NKP	Plastic s	
0.70785	= 757	= 58	0.70820 6	= 12.8 ^a	= 0.18 ^a	Referenc e Soil	CaO	NKP	Plastic s	Referenc e [54–56]

Soil depth (cm)	<i>Sr</i> $\mu\text{g g}^{-1}$ from CaO in Soil ($\mu\text{g g}^{-1}$)		<i>Sr</i> $\mu\text{g g}^{-1}$ from NKP in Soil ($\mu\text{g g}^{-1}$)		% sources ^b in soil high–low				MPs ($\mu\text{g g}^{-1}$) high–low
	high	low	high	low					
0–5	3.98	0.29	11.6	0.16	87.8	4.7–0.3	12.0–0.2	0–11.7	0–2.4
15–20	3.74	0.27	10.3	0.15	95.7	4.4–0.3	11.6–0.2	0–3.8	0–0.7
30–35	3.42	0.25	7.7	0.11	88.8	4.0–0.3	8.1–0.1	0–10.8	0–0.2
	<i>Sr</i> $\mu\text{g g}^{-1}$ from CaO in Soil Solution ($\mu\text{g g}^{-1}$)		<i>Sr</i> $\mu\text{g g}^{-1}$ from NKP in Soil ($\mu\text{g g}^{-1}$)		% sources ^b in soil solution high–low				NPs ($\mu\text{g L}^{-1}$) high–low
	high	low	high	low					
0–5	14.0	1.08	0.80	0.011	33.8	26.7–1.9	1.5–0.02	63.7–36.9	1.2–0.7
15–20	21.1	1.53	14.0	0.198	15.7	34.6–2.5	23.4–0.3	81.5–42.0	1.3–0.7
30–35	15.5	1.17	7.45	0.105	18.7	34.2–2.5	16.9–0.2	78.5–1.7	1.7–0.9
50–55	4.06	0.29	6.76	0.095	63.7	14.6–1.1	24.3–0.34	34.8–0 ^c	0–1.3

^a Sr concentration corresponds to the soluble fraction of Sr given in Vitoria et al. (2004)

^b % calculated with Eq. 2 from the fitting of the $[\text{Sr}]_{\text{plastics}}$ in order that $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{tot}} \times [\text{Sr}]_{\text{tot}} = \sum (^{87}\text{Sr}/^{86}\text{Sr})_{\text{source}_n} \times f_n [\text{Sr}]_{\text{source}_n}$, with $f_n \times [\text{Sr}]_{\text{source}_n}$ deduced from both the literature and analytical datasets.

^c as no MPs were collected at this depth, the plastic Sr isotopic ratio used for this calculation is the average of the Sr isotopic ratios of each studied depth (0–5, 15–20 and 50–55 cm)

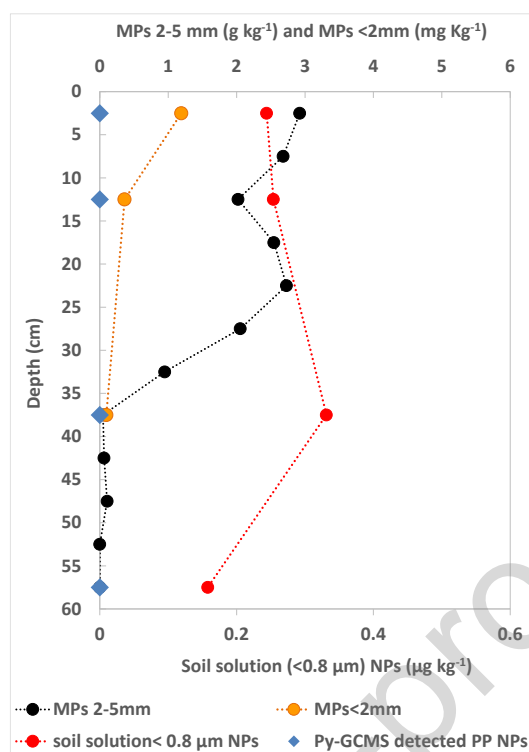


Fig. 5. Distribution of the 2–5 mm MPs (g kg^{-1}), estimated average of < 2 mm MPs (mg kg^{-1}) and NPs in < 0.8 μm soil solution ($\mu\text{g kg}^{-1}$), using the 1:4 ratio of the soil-water extraction experiment; both deduced from Eq. 2. The blue symbols represent the PP NPs that were detected by Py-GC-MS in the < 0.8 μm soil solution.

Calculated amounts of MPs < 2 mm and soil solution NPs are reported in Fig. 5. Results demonstrated that the < 2 mm MPs concentration was about 3 orders of magnitude less than in the 2–5 mm fraction. The < 2 mm MPs follow the same distribution as the largest MPs: high amounts in the uppermost layer of soil and very low amounts at 30–35 cm depth. The 30–35 cm depth corresponds to the plowing depth, and the low amount of MPs < 2 mm confirms that plowing is responsible for the presence of MPs only in the first 35 cm of soil.

The NPs in the soil solution < 0.8 μm are 6 and 3 orders of magnitude less concentrated than the MPs < 2 mm and MPs 2–5 mm until 55 cm depth, respectively (Fig. 5). These amounts do not reflect the effective concentration of NPs in soil but, the concentration of NPs that can be mobilized in the soil solution throughout the depth. This result showed that NPs occurred in the soil at least down to 55 cm of depth. Nanoplastic distribution, unlike that of MPs, remains rather constant through depth. These results suggest that plowing does not affect their distribution.

However, to ensure that NPs were effectively present along the soil depth, Py-GC-MS analyses were performed in the soil solution < 0.8 μm for the 15–20 and 30–35 cm depths. Pyrograms of the m/z 70 obtained for the soil 3 depths allowed to identify the PP marker C12 at $t_R=8.6$ min for the 3 depths of the amended soil, whereas not for the reference soil (Fig. SI 1). For the reference soil, the t_R of the nonene-1-ol marker was close to that of C12 identified for the amended soil but did not overlap. The C12 PP marker signal was also enhanced at the deeper soil depth, where NOM was less abundant and less interfered with

the PY-GCMS signal. This confirms the presence of NPs in the 3 studied soil layers and even at the deeper depth.

4. Implications, Limitations and Perspectives

Combined with the previous results of Wahl et al. (2021), the present data showed that the main 4 polymers used in plastic formulation occurred as NPs in the amended soil. Particularly interesting is that PP NPs were even identified within the deepest soil depth. Nanoplastics are therefore mobile in the soil porosity and transported by the water flow along with the soil profile. This outcome was not intuitive. Nanoplastics, as charged nanoparticles could indeed (1) interact with the opposite charge components (i.e. Fe and Al oxyhydroxides, Wu et al., 2020) or (2) homo and hetero-aggregate which alters their colloidal stability and results in their deposition in the soil porosity. Hetero-aggregation with NOM in the soil is expected to be promoted by the high molecular and colloidal NOM amount. However, Pradel et al. (2021) demonstrated that NOM enhanced NPs stability with various mechanisms depending on the ionic strength and the organic matter sources. At high ionic strength, NPs homo-aggregate and form larger particles, but humic acid provides steric hindrance, keeping them in suspension. At low ionic strength, electrostatic repulsion between the negatively charged NPs and humic acid maintains NPs stable in solution. By contrast, non-humic organic molecules (i.e. alginate) are sorbed onto NPs and stabilized into the solution by steric hindrance. pH slowly impacts these processes. The SUVA value obtained for the amended soil solution varied between 1.7 to 3 from 5 to 55 cm, respectively, suggesting that biologic organic matter prevails in the uppermost soil layers, whereas more terrestrial ones (humic substances) are dominant at 55 cm depth. Therefore, in the amended soil rich in organic matter, whose properties varied between biological and humic organic matter, all the processes described by Pradel et al. (2021) could occur and maintain the NPs in the soil solution. Moreover, NPs are generated by plastics degradation and composting processes [1,6,41,58,59]. In soil, their main source is therefore the uppermost soil layers, where the plastic-enriched compost was inserted by ploughing. However, PP NPs were detected in the deepest soil layers. Furthermore, these PP NPs were extracted with water of ionic strength corresponding to rainwater, demonstrating that a fraction of the NPs present in the deepest soil depth can be mobilized by water flow through the entire soil profile. This water-mobilizable NP fraction could thus reach the water network. These finding highlights a critical environmental concern regarding the mobility of NPs through soil and their potential impact on groundwater contamination, particularly in groundwater recharge zones and alluvial water tables directly connected to surface water. Surface water runoff was known to transport MPs into surface water networks [60–62]. However, our study reveals an additional pathway where NPs can travel through soil porosity with the subsurface water flow, ultimately reaching water tables. Once in the water tables, nanoplastics face could remain in solution due to the low ionic strength of groundwater, allowing them to migrate towards rivers. However, their fate upon reaching the riverbanks, particularly known for Fe-oxides precipitation and elements trapping [63], raises questions. Will these riverbanks act as barriers for NPs, preventing them from further migrating into surface water,

or will they facilitate their transport? Understanding these transport mechanisms and interactions with soil components like Fe-oxides and organic matter is crucial for assessing the potential environmental impacts of NPs contamination. Further research is needed to elucidate how NPs behave in these complex environmental matrices and to develop effective strategies for mitigating their presence and impact on aquatic ecosystems.

Due to the lack of data on the quantities and sources of lime and fertilizers, the use of Sr isotopes did not provide precise quantification of NPs in the soil matrix but, however a range of concentrations. Nevertheless, the provided estimations are supported by Py-GC-MS analyzes which confirmed the presence of NPs even in the deepest depths of the soil. Unfortunately, this concentration range cannot be compared to other data since until now no quantitative values have been ever published for environmental samples, this study being the first. The main reason is that quantifying a carbon-based polymer in an organic matrix is extremely complicated and still more in real samples even with pre-concentration step [35]. However, Okoffo and Thomas (2024) obtained using Py-GC-MS a concentration varying from 27.7 to 9.1 $\mu\text{g L}^{-1}$ for the NPs $<1 \mu\text{m}$ in waste water treatment plant in which water treatment are expected to concentrate particles. Here, the estimated range varied between 0.7 to 1.7 $\mu\text{g L}^{-1}$ in a soil solution, which is not aberrant. The use of additives, particularly through their isotope fingerprinting ability, appears therefore to be a valid alternative as here shown. Although the method certainly requires adjustments, this study clearly demonstrates its feasibility. It could already be applicable in non-agricultural soils and validated, in soils where limestone and phosphate inputs are constrained, such as experimental plots.

5. Conclusion

Elemental analysis revealed correlations between metal concentrations and the distribution of MPs. The highest metal concentrations in the amended soil matched those used as additives in plastic formulations and found in MPs. However, due to the study focus on the 2–5 mm fraction of MPs, estimates from total degradation did not fully explain discrepancies between amended and reference soils. Over 30 years, plastic particles and metals likely underwent losses due to soil erosion driven by water and wind [41].

Both the amended soil and MPs exhibited high Ca and Sr concentrations, with Ca distribution aligning with MPs. Using Sr isotopes as tracers for small MPs ($<2 \text{ mm}$) and NPs, we found that $^{87}\text{Sr}/^{86}\text{Sr}$ values in amended soil were less radiogenic than in reference soil, correlating with MPs distribution. A two-end-member mixing model involving reference soil and MPs partially explained Sr isotope distribution discrepancies, but a four-end-member model, considering fertilizers, lime, and literature values, provided a better fit. In the surface layer of amended soil, Sr isotopes showed that 4.4% on average originated from Sr-MPs $<2\text{mm}$, while NPs ($<0.8 \mu\text{m}$) contributed 42.4% on average in soil solutions. Distribution patterns of MPs $< 2 \text{ mm}$ mirrored those of MPs 2–5 mm, indicating agricultural practices influence small MPs distribution.

This study provides for the first-time information on the consistent distribution of NPs across soil depths by highlighting the mobility of NPs through soil pores. It reveals their potential to penetrate deepest soil layers. This consistent distribution suggests that NPs can travel significant distances from their source. A first quantification range of NPs of mobile NPs in soil was provided for the first time, setting a benchmark for future studies. This contribution is critical for establishing baseline data and comparing future findings. This study also underscores the potential of Strontium (Sr) isotopes as a promising tool for both qualitative and quantitative analysis of NPs occurrence and monitoring their pathways in the environment.

Further research should aim to elucidate the detailed mechanisms by which NPs move through soil matrices. For this, 1) enhanced detection methods should allow to identify and quantify all types of polymers present in soil, including in the deepest layers, and 2) several types of plastic contaminated soil under various pedo-climatic conditions have to be studied. It would also be interesting to collect natural soil solution from this soil to characterize their load in NPs and the NPs themselves.

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References:

- [1] Z. Du, G. Li, S. Ding, W. Song, M. Zhang, R. Jia, W. Chu, Effects of UV-based oxidation processes on the degradation of microplastic: Fragmentation, organic matter release, toxicity and disinfection byproduct formation, (2023). <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85153205600&doi=10.1016%2fj.watres.2023.119983&partnerID=40&md5=ccfd3dd158602c281b8ec43d4aa38dd3>.
- [2] K.N. Fotopoulou, H.K. Karapanagioti, Degradation of Various Plastics in the Environment, in: H. Takada, H.K. Karapanagioti (Eds.), Hazardous Chemicals Associated with Plastics in the Marine Environment, Springer International Publishing, Cham, 2019: pp. 71–92. https://doi.org/10.1007/698_2017_11.

- [3] P. Kaur, K. Singh, B. Singh, Microplastics in soil: Impacts and microbial diversity and degradation, (2022). <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85120918268&doi=10.1016%2fS1002-0160%2821%2960060-7&partnerID=40&md5=5e90c9a5c7b4fd0dce003bdf33954d47>.
- [4] Z. Lin, T. Jin, T. Zou, L. Xu, B. Xi, D. Xu, J. He, L. Xiong, C. Tang, J. Peng, Y. Zhou, J. Fei, Current progress on plastic/microplastic degradation: Fact influences and mechanism, *Environmental Pollution* 304 (2022) 119159. <https://doi.org/10.1016/j.envpol.2022.119159>.
- [5] Y. Otake, T. Kobayashi, H. Asabe, N. Murakami, K. Ono, Biodegradation of low-density polyethylene, polystyrene, polyvinyl chloride, and urea formaldehyde resin buried under soil for over 32 years - Otake - 1995 - *Journal of Applied Polymer Science* - Wiley Online Library, <https://onlinelibrary.wiley.com/doi/epdf/10.1002/app.1995.070561309> (1995). https://onlinelibrary.wiley.com/doi/abs/10.1002/app.1995.070561309?casa_token=zdLRdpw_HpEAAAAA:FW_O4L_aD76t4Y-2DDUFRVry-6LX7nghsKv6FVtegOVJayJh4PnhdIPoE6ipQzZlgF5Z_GB0qbwCtpY (accessed July 19, 2022).
- [6] Y. Sun, X. Ren, E.R. Rene, Z. Wang, L. Zhou, Z. Zhang, Q. Wang, The degradation performance of different microplastics and their effect on microbial community during composting process, *Bioresource Technology* 332 (2021) 125133. <https://doi.org/10.1016/j.biortech.2021.125133>.
- [7] O.S. Alimi, J. Farner Budarz, L.M. Hernandez, N. Tufenkji, Microplastics and Nanoplastics in Aquatic Environments: Aggregation, Deposition, and Enhanced Contaminant Transport, *Environ. Sci. Technol.* 52 (2018) 1704–1724. <https://doi.org/10.1021/acs.est.7b05559>.
- [8] A.A. Horton, A. Walton, D.J. Spurgeon, E. Lahive, C. Svendsen, Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities, *Science of The Total Environment* 586 (2017) 127–141. <https://doi.org/10.1016/j.scitotenv.2017.01.190>.
- [9] A.A. Koelmans, E. Besseling, E.M. Foekema, Leaching of plastic additives to marine organisms, *Environmental Pollution* 187 (2014) 49–54. <https://doi.org/10.1016/j.envpol.2013.12.013>.
- [10] J.N. Hahladakis, C.A. Velis, R. Weber, E. Iacovidou, P. Purnell, An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, *Journal of Hazardous Materials* 344 (2018) 179–199. <https://doi.org/10.1016/j.jhazmat.2017.10.014>.
- [11] A. Stenmarck, E.L. Belleza, A. Frane, N. Busch, A. Larsen, M. Wahlström, Hazardous substances in plastics : ways to increase recycling, Nordic Council of Ministers, 2017.
- [12] D. Boyle, A.I. Catarin, N.J. Clark, T.B. Henry, Polyvinyl chloride (PVC) plastic fragments release Pb additives that are bioavailable in zebrafish, *Environmental Pollution* 263 (2020) 114422. <https://doi.org/10.1016/j.envpol.2020.114422>.
- [13] Y.-Y. Long, D.-S. Shen, H.-T. Wang, W.-J. Lu, Y. Zhao, Heavy metal source analysis in municipal solid waste (MSW): Case study on Cu and Zn, *Journal of Hazardous Materials* 186 (2011) 1082–1087. <https://doi.org/10.1016/j.jhazmat.2010.11.106>.
- [14] E. Nakashima, A. Isobe, S. Kako, T. Itai, S. Takahashi, Quantification of Toxic Metals Derived from Macroplastic Litter on Ookushi Beach, Japan, *Environ. Sci. Technol.* 46 (2012) 10099–10105. <https://doi.org/10.1021/es301362g>.
- [15] M. Whitt, W. Brown, J.E. Danes, K.L. Vorst, Migration of heavy metals from recycled polyethylene terephthalate during storage and microwave heating, *Journal of Plastic Film & Sheeting* 32 (2016) 189–207. <https://doi.org/10.1177/8756087915590190>.
- [16] R.M. Town, H.P. van Leeuwen, R. Blust, Biochemodynamic Features of Metal Ions Bound by Micro- and Nano-Plastics in Aquatic Media, *Front. Chem.* 6 (2018) 627. <https://doi.org/10.3389/fchem.2018.00627>.
- [17] C. Catrouillet, M. Davranche, I. Khatib, C. Fauny, A. Wahl, J. Gigault, Metals in microplastics: determining which are additive, adsorbed, and bioavailable, *Environ. Sci. Processes Impacts* (2021) 6. <https://doi.org/10.1039/d1em00017a>.
- [18] M. Davranche, C. Lory, C.L. Juge, F. Blancho, A. Dia, B. Grassl, H. El Hadri, P.-Y. Pascal, J. Gigault, Nanoplastics on the coast exposed to the North Atlantic Gyre: Evidence and traceability, *NanoImpact* 20 (2020) 100262. <https://doi.org/10.1016/j.impact.2020.100262>.

- [19] L.A. Holmes, A. Turner, R.C. Thompson, Interactions between trace metals and plastic production pellets under estuarine conditions, *Marine Chemistry* 167 (2014) 25–32. <https://doi.org/10.1016/j.marchem.2014.06.001>.
- [20] L.A. Holmes, A. Turner, R.C. Thompson, Adsorption of trace metals to plastic resin pellets in the marine environment, *Environmental Pollution* 160 (2012) 42–48. <https://doi.org/10.1016/j.envpol.2011.08.052>.
- [21] J. Prunier, L. Maurice, E. Perez, J. Gigault, A.-C. Pierson Wickmann, M. Davranche, A. ter Halle, Trace metals in polyethylene debris from the North Atlantic subtropical gyre, *Environmental Pollution* 245 (2019) 371–379. <https://doi.org/10.1016/j.envpol.2018.10.043>.
- [22] A. Turner, L.A. Holmes, Adsorption of trace metals by microplastic pellets in fresh water, *Environ. Chem.* 12 (2015) 600–610. <https://doi.org/10.1071/EN14143>.
- [23] Y. Wang, B. Zhou, H. Chen, R. Yuan, F. Wang, Distribution, biological effects and biofilms of microplastics in freshwater systems - A review, (2022). <https://www.scopus.com/inward/record.uri?eid=2-s2.0-85126975122&doi=10.1016%2fj.chemosphere.2022.134370&partnerID=40&md5=5e768a949a4d863f6ca14bc610121243>.
- [24] J. Wang, X. Guo, J. Xue, Biofilm-Developed Microplastics As Vectors of Pollutants in Aquatic Environments, *Environ. Sci. Technol.* (2021) acs.est.1c04466. <https://doi.org/10.1021/acs.est.1c04466>.
- [25] X. Guo, J. Wang, The chemical behaviors of microplastics in marine environment: A review, *Marine Pollution Bulletin* 142 (2019) 1–14. <https://doi.org/10.1016/j.marpolbul.2019.03.019>.
- [26] S. Sridharan, M. Kumar, M. Saha, M.B. Kirkham, L. Singh, N.S. Bolan, The polymers and their additives in particulate plastics: What makes them hazardous to the fauna?, *Science of The Total Environment* 824 (2022) 153828. <https://doi.org/10.1016/j.scitotenv.2022.153828>.
- [27] A. Turner, M. Filella, Hazardous metal additives in plastics and their environmental impacts, *Environment International* 156 (2021) 106622. <https://doi.org/10.1016/j.envint.2021.106622>.
- [28] M. Bolgar, J. Hubball, J. Groeger, S. Meronek, *Handbook for the Chemical Analysis of Plastic and Polymer Additives*, CRC Press, 2007.
- [29] C. Scopetani, D. Chelazzi, A. Cincinelli, T. Martellini, V. Leiniö, J. Pellinen, Hazardous contaminants in plastics contained in compost and agricultural soil, *Chemosphere* 293 (2022) 133645. <https://doi.org/10.1016/j.chemosphere.2022.133645>.
- [30] F. Blanco, M. Davranche, H.E. Hadri, B. Grassl, J. Gigault, Nanoplastics Identification in Complex Environmental Matrices: Strategies for Polystyrene and Polypropylene, *Environ. Sci. Technol.* 55 (2021) 8753–8759. <https://doi.org/10.1021/acs.est.1c01351>.
- [31] J. Gigault, H. El Hadri, B. Nguyen, B. Grassl, L. Roweczyk, N. Tufenkji, S. Feng, M. Wiesner, Nanoplastics are neither microplastics nor engineered nanoparticles, *Nat. Nanotechnol.* 16 (2021) 501–507. <https://doi.org/10.1038/s41565-021-00886-4>.
- [32] B. Nguyen, D. Claveau-Mallet, L.M. Hernandez, E.G. Xu, J.M. Farner, N. Tufenkji, Separation and Analysis of Microplastics and Nanoplastics in Complex Environmental Samples, *Acc. Chem. Res.* 52 (2019) 858–866. <https://doi.org/10.1021/acs.accounts.8b00602>.
- [33] E.D. Okoffo, K.V. Thomas, Quantitative analysis of nanoplastics in environmental and potable waters by pyrolysis-gas chromatography–mass spectrometry, *Journal of Hazardous Materials* 464 (2024) 133013. <https://doi.org/10.1016/j.jhazmat.2023.133013>.
- [34] C.-Q. Zhou, C.-H. Lu, L. Mai, L.-J. Bao, L.-Y. Liu, E.Y. Zeng, Response of rice (*Oryza sativa* L.) roots to nanoplastic treatment at seedling stage, *Journal of Hazardous Materials* 401 (2021) 123412. <https://doi.org/10.1016/j.jhazmat.2020.123412>.
- [35] X. Zhou, L. Hao, H. Wang, Y. Li, J. Liu, Cloud-Point Extraction Combined with Thermal Degradation for Nanoplastic Analysis Using Pyrolysis Gas Chromatography–Mass Spectrometry, *Anal. Chem.* 91 (2019) 1785–1790. <https://doi.org/10.1021/acs.analchem.8b04729>.
- [36] D.W. Clow, M.A. Mast, T.D. Bullen, J.T. Turk, Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an Alpine/Subalpine Watershed, Loch Vale, Colorado, *Water Resour. Res.* 33 (1997) 1335–1351. <https://doi.org/10.1029/97WR00856>.
- [37] Th. Drouet, J. Herbauts, W. Gruber, D. Demaiffe, Strontium isotope composition as a tracer of calcium sources in two forest ecosystems in Belgium, *Geoderma* 126 (2005) 203–223. <https://doi.org/10.1016/j.geoderma.2004.09.010>.

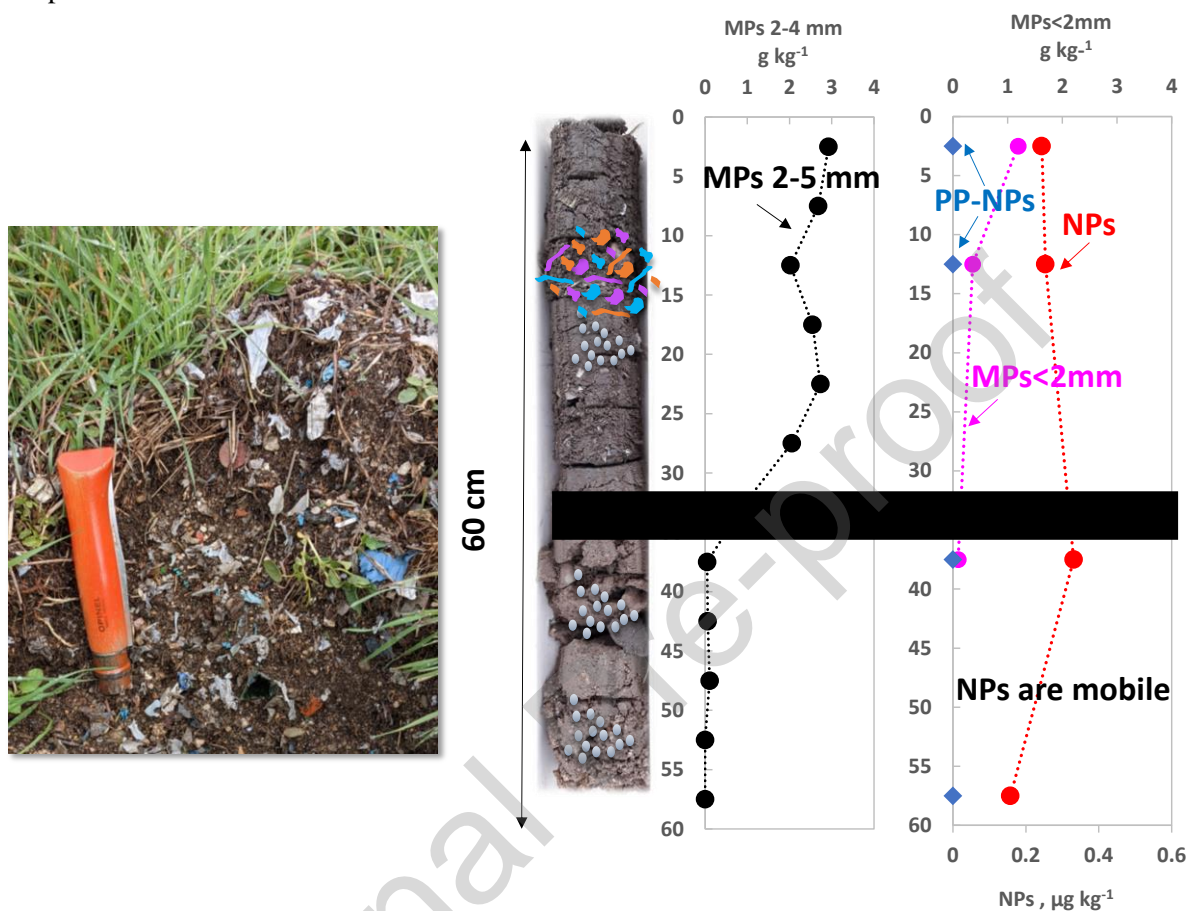
- [38] X. Wu, X. Lyu, Z. Li, B. Gao, X. Zeng, J. Wu, Y. Sun, Transport of polystyrene nanoplastics in natural soils: Effect of soil properties, ionic strength and cation type, *Science of The Total Environment* 707 (2020) 136065. <https://doi.org/10.1016/j.scitotenv.2019.136065>.
- [39] A.F. Astner, D.G. Hayes, S.V. Pingali, H.M. O'Neill, K.C. Littrell, B.R. Evans, V.S. Urban, Effects of soil particles and convective transport on dispersion and aggregation of nanoplastics via small-angle neutron scattering (SANS) and ultra SANS (USANS), *PLOS ONE* 15 (2020) e0235893. <https://doi.org/10.1371/journal.pone.0235893>.
- [40] A. Wahl, Le Juge, Coentini, M. Davranche, El Hadri, Hind, B. Grassl, S. Reynaud, J. Gigault, Nanoplastic occurrence in a soil amended with plastic debris, *Chemosphere* 262 (2021) 7.
- [41] A. Wahl, M. Davranche, M. Rabiller-Baudry, M. Pédrot, I. Khatib, F. Labonne, M. Canté, C. Cuisinier, J. Gigault, Condition of composted microplastics after they have been buried for 30 years: Vertical distribution in the soil and degree of degradation, *Journal of Hazardous Materials* 462 (2024) 132686. <https://doi.org/10.1016/j.jhazmat.2023.132686>.
- [42] D. Thomas, B. Schütze, W.M. Heinze, Z. Steinmetz, Sample Preparation Techniques for the Analysis of Microplastics in Soil—A Review, *Sustainability* 12 (2020) 9074. <https://doi.org/10.3390/su12219074>.
- [43] A. Dehaut, A.-L. Cassone, L. Frère, L. Hermabessiere, C. Himber, E. Rinnert, G. Rivière, C. Lambert, P. Soudant, A. Huvet, G. Duflos, I. Paul-Pont, Microplastics in seafood: Benchmark protocol for their extraction and characterization, *Environmental Pollution* 215 (2016) 223–233. <https://doi.org/10.1016/j.envpol.2016.05.018>.
- [44] E.W. Flick, *Plastics Additives, Volume 1: An Industry Guide*, Elsevier, 2013.
- [45] C. Catrouillet, M. Davranche, I. Khatib, C. Fauny, A. Wahl, J. Gigault, Metals in microplastics: determining which are additive, adsorbed, and bioavailable, *Environmental Science: Processes & Impacts* 23 (2021) 553–558. <https://doi.org/10.1039/D1EM00017A>.
- [46] W.B. Achiba, N. Gabteni, A. Lakhdar, G.D. Laing, M. Verloo, N. Jedidi, T. Gallali, Effects of 5-year application of municipal solid waste compost on the distribution and mobility of heavy metals in a Tunisian calcareous soil, *Agriculture, Ecosystems & Environment* 130 (2009) 156–163. <https://doi.org/10.1016/j.agee.2009.01.001>.
- [47] S. Roghanian, H.M. Hosseini, G. Savaghebi, L. Halajian, M. Jamei, H. Etesami, Effects of composted municipal waste and its leachate on some soil chemical properties and corn plant responses., *International Journal of Agriculture: Research and Review* 2 (2012) 801–814.
- [48] G. Muller, Index of geoaccumulation in sediments of the Rhine River, *Geojournal* 2 (1969) 108–118.
- [49] M. Guillemot, C. Patrascu, *Plastiques, risque et analyse thermique: Les additifs*, INRS, 2019.
- [50] F. Blanco, M. Davranche, F. Fumagalli, G. Ceccone, J. Gigault, A reliable procedure to obtain environmentally relevant nanoplastic proxies, *Environmental Science: Nano* 8 (2021) 3211–3219. <https://doi.org/10.1039/D1EN00395J>.
- [51] T.D. Bullen, S.W. Bailey, Identifying calcium sources at an acid deposition-impacted spruce forest: a strontium isotope, alkaline earth element multi-tracer approach, *Biogeochemistry* 74 (2005) 63–99. <https://doi.org/10.1007/s10533-004-2619-z>.
- [52] J.-M. Brazier, *Rôle des phases minérales des sols en tant que réservoirs de nutriments : approche expérimentale (abiotique), en milieu naturel et multi-isotopique (isotopes stables Ca-Sr)*, phdthesis, Université de Strasbourg, 2018. <https://theses.hal.science/tel-02160035> (accessed May 7, 2024).
- [53] N. Shalev, B. Lazar, L. Halicz, M. Stein, I. Gavrieli, A. Sandler, I. Segal, Strontium Isotope Fractionation in Soils and Pedogenic Processes, *Procedia Earth and Planetary Science* 7 (2013) 790–793. <https://doi.org/10.1016/j.proeps.2013.03.074>.
- [54] E. Thomsen, R. Andreasen, Agricultural lime disturbs natural strontium isotope variations: Implications for provenance and migration studies, *Science Advances* 5 (2019) eaav8083. <https://doi.org/10.1126/sciadv.aav8083>.
- [55] Vitòria, N. Otero, A. Soler, À. Canals, Fertilizer Characterization: Isotopic Data (N, S, O, C, and Sr), *Environ. Sci. Technol.* 38 (2004) 3254–3262. <https://doi.org/10.1021/es0348187>.
- [56] N. Otero, L. Vitòria, A. Soler, A. Canals, Fertiliser characterisation: Major, trace and rare earth elements, *Applied Geochemistry* 20 (2005) 1473–1488. <https://doi.org/10.1016/j.apgeochem.2005.04.002>.

- [57] A. Pradel, S. Ferreres, C. Veclin, H. El Hadri, M. Gautier, B. Grassl, J. Gigault, Stabilization of Fragmental Polystyrene Nanoplastic by Natural Organic Matter: Insight into Mechanisms, *ACS EST Water* 1 (2021) 1198–1208. <https://doi.org/10.1021/acsestwater.0c00283>.
- [58] P.L. Corcoran, Degradation of Microplastics in the Environment, in: T. Rocha-Santos, M.F. Costa, C. Mouneyrac (Eds.), *Handbook of Microplastics in the Environment*, Springer International Publishing, Cham, 2022: pp. 531–542. https://doi.org/10.1007/978-3-030-39041-9_10.
- [59] A.L. Andradý, P.W. Barnes, J.F. Bornman, T. Gouin, S. Madronich, C.C. White, R.G. Zepp, M.A.K. Jansen, Oxidation and fragmentation of plastics in a changing environment; from UV-radiation to biological degradation, *Science of The Total Environment* 851 (2022) 158022. <https://doi.org/10.1016/j.scitotenv.2022.158022>.
- [60] M.B. Alfonso, A.H. Arias, A.C. Ronda, M.C. Piccolo, Continental microplastics: Presence, features, and environmental transport pathways, *Science of The Total Environment* 799 (2021) 149447. <https://doi.org/10.1016/j.scitotenv.2021.149447>.
- [61] V.S. Koutnik, J. Leonard, S. Alkidim, F.J. DePrima, S. Ravi, E.M.V. Hoek, S.K. Mohanty, Distribution of microplastics in soil and freshwater environments: Global analysis and framework for transport modeling, *Environmental Pollution* 274 (2021) 116552. <https://doi.org/10.1016/j.envpol.2021.116552>.
- [62] Fate of microplastics in agricultural soils amended with sewage sludge: Is surface water runoff a relevant environmental pathway? - ScienceDirect, (n.d.). <https://www.sciencedirect.com/science/article/abs/pii/S0269749121021023> (accessed June 21, 2024).
- [63] G. Ratié, D. Vantelon, E. Lotfi Kalahroodi, I. Bihannic, A.C. Pierson-Wickmann, M. Davranche, Iron speciation at the riverbank surface in wetland and potential impact on the mobility of trace metals, *Science of The Total Environment* 651 (2019) 443–455. <https://doi.org/10.1016/j.scitotenv.2018.09.143>.

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.

Graphical abstract



Highlights

- Household wastes composts are source of plastic for agricultural soil
- Strong correlation exists between microplastic and metal in plastic-contaminated soil
- Sr isotopes could trace and quantify the smallest microplastics and nanoplastics in soil
- Nanoplastic concentration stays constant throughout the soil depth
- Nanoplastics are mobile throughout the soil profile