



Identification and quantification of nanoplastics in different crops using pyrolysis gas chromatography-mass spectrometry

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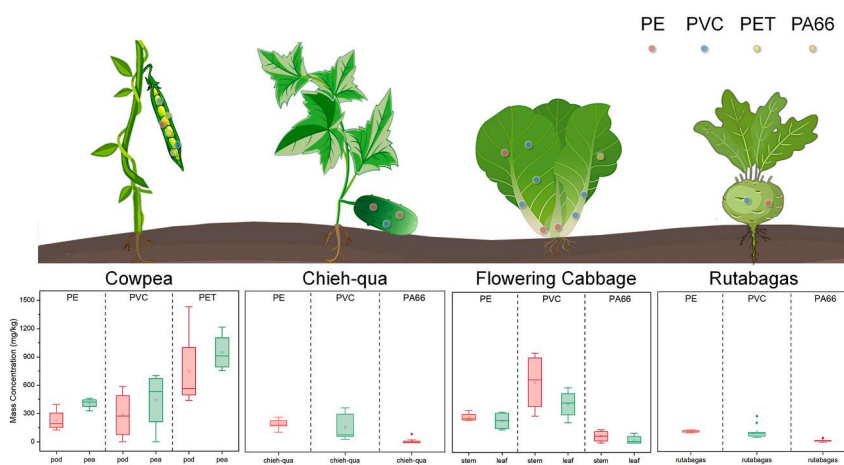
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HIGHLIGHTS

- The actual extent of NP contamination in different types and different parts of crops was revealed.
- PVC and PE were the dominant components in four kinds of crop samples.
- The enrichment degree of NPs in legume crop and leaf crop was greater than that in stem crop and melon crop.
- Notable differences were found in the pollution levels of various edible crop parts.

GRAPHICAL ABSTRACT



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ABSTRACT

Quantitative studies of nanoplastics (NPs) abundance on agricultural crops are crucial for understanding the environmental impact and potential health risks of NPs. However, the actual extent of NP contamination in different crops remains unclear, and therefore insufficient quantitative data are available for adequate exposure assessments. Herein, a method with nitric acid digestion, multiple organic extraction combined with pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) quantification was used to determine the chemical composition and mass concentration of NPs in different crops (cowpea, flowering cabbage, rutabagas, and chieh-qua). Recoveries of 74.2–109.3% were obtained for different NPs in standard products ($N = 6$, $RSD < 9.6\%$). The limit of detection (LOD) and the limit of quantitation (LOQ) were 0.02–0.5 μg and 0.06–1.5 μg , respectively. The detection method for NPs exhibited good external calibration curves and linearity with 0.99. The results showed that poly (vinylchloride) (PVC), poly (ethylene terephthalate) (PET), polyethylene (PE), and

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polyadiohexylenediamine (PA66) NPs could be detected in crop samples, although the accumulation levels associated with the various crops varied significantly. PVC (N.D.–954.3 mg kg⁻¹, dry weight (DW)) and PE (101.3–462.9 mg kg⁻¹, DW) NPs were the dominant components in the samples of all four crop species, while high levels of PET (414.3–1430.1 mg kg⁻¹, DW) NPs were detected in cowpea samples. Furthermore, there were notable differences in the accumulation levels of various edible crop parts, such as stems (60.2%) > leaves (39.8%) in flowering cabbage samples and peas (58.8%) > pods (41.2%) in cowpea samples. This study revealed the actual extent of NP contamination in different types of crops and provided crucial reference data for future research.

1. Introduction

Microplastics (MPs, sizes between 1 µm and 5 mm) and nanoplastics (NPs, sizes <1 µm) have attracted increasing attention and discussion as emerging contaminants in recent years (Ter Halle et al., 2017; Alimi et al., 2018; Dawson et al., 2018; Lehner et al., 2019; Sobhani et al., 2020; MacLeod et al., 2021). Both MPs and NPs originate from a variety of consumer products, such as cosmetics, clothing fibers, agricultural films, and industrial raw materials. They can become secondary products of plastic debris as a result of mechanical, photochemical, and/or biodegradation processes (Besseling et al., 2019; Gigault et al., 2021; Sendra et al., 2021). In general, related to their size, NPs are distinguished from MPs with respect to their transport properties, interactions with environmental media (such as light and natural colloids), bioavailability, and high proportion of particle molecules on the surface (Gigault et al., 2021; Xu et al., 2022). Because Brownian motion predominates, NPs are likely to exhibit more colloidal characteristics than MPs and thus undergo different transport processes (Mitrano et al., 2021). It has also been reported that NPs impose more serious environmental and biological hazards than MPs in soil because of their facility to be uptaken by living beings and transferred across biomembrane structures (Jeong et al., 2016; Luo et al., 2022).

The concentration of NPs in agricultural soil environment is expected to continue to increase, which is one of the potential major threats to agricultural ecosystems (Souza Machado et al., 2018). There is growing proof that NPs can be ingested by field crops as a consequence of widespread exposures from irrigation water or agricultural film (Li et al., 2021a,b,c, 2023), and subsequently transferred widely through the food webs. For example, Jiang et al. (2022) demonstrated that polystyrene nanoplastics (PS-NPs) were translocated from roots and accumulated in the grains at the maturation stage. The application of 250 mg kg⁻¹ PS-NPs negatively affected the quality of peanut and rice, such as lowering the seed-setting rate and the average seed weight. The direct evidence provided by Sun et al. showed a large accumulation of reactive oxygen species and the consequential inhibition in seedling and plant growth of *Arabidopsis thaliana*, with a limited accumulation of positively charged NPs in the root tips (treatment with 300 mg kg⁻¹ in soil) (Sun et al., 2020). By contrast, the negatively charged NPs (treatment with 1000 mg kg⁻¹) were observed commonly in the apoplast and xylem. However, almost all experiments were conducted at designed concentrations of artificial NPs. The concentration of these artificial NPs is usually much different from that in the actual farmland environment, resulting in possible differences between the research data and the actual situation, which may limit the understandings of NP pollution.

The distributions and concentrations of MPs in agricultural environment have been extensively studied (Boots et al., 2019; Lv et al., 2019; Li et al., 2021a,b,c; Chen et al., 2022), as various analytical techniques are available for the determination of MPs in real environmental samples, such as Raman spectroscopy (Araujo et al., 2018), Fourier transform infrared (FTIR) (Liu et al., 2023), and laser direct infrared (LDIR) spectroscopy (Liu et al., 2022a). However, these techniques are no longer effective and accurate once the particles reach the nano-size (Xu et al., 2022), resulting in hardly any data of NPs in real agricultural soils. Not to mention the fact that the detection in biological substrates is more complex, greatly hindering the research of NP

accumulation in actual crop samples. Inductively coupled plasma mass spectrometry (ICP-MS) combined with lanthanide labelling technique is an approach for the quantification of NPs in crop samples, however, it still cannot act as a direct analytical tool to determine NPs in a realistic environment (Luo et al., 2022). Pyrolysis gas chromatography–mass spectrometry (Py-GC/MS) is a promising approach to quantify NPs, which can be applied for reliable identification and quantification of NPs without limitations of particle sizes (Zhou et al., 2019, 2021a,b,c; Seeley and Lynch, 2023). Recently, Py-GC/MS combined with pretreatment has been used in several investigations to quantify NPs in real environmental samples. For example, it is proposed that the Triton X-45 based cloud-point extraction (CPE) extract could be submitted to Py-GC/MS analysis for mass quantification of NPs (Zhou et al., 2019). Alkaline digestion and protein precipitation have recently been suggested as methods for extracting NPs from biological samples, which are then effectively measured using Py-GC/MS (Zhou et al., 2021a,b,c). These efforts have resulted in significant progress in NP research, however, the analysis of NPs is still at the infancy stage and little research on NP pollution in field crops has been published to date.

In this study, four kinds of common crops that located in the same agricultural field were selected for quantitative analysis of NP pollution. To be specific, cowpea (*Vigna unguiculata*), flowering cabbage (*Brassica rapa* var. *chinensis* 'Parachinensis'), rutabagas (*Brassica juncea* var. *napiiformis* Pailleux et Bois), and chieh-qua (*Benincasa hispida* (Thunb.) Cogn. var. *chiehqua* How) were selected to represent the enrichment degree of NPs in different types of crops. Among the crop samples, flowering cabbage and rutabagas were planted without plastic film, while cowpea and chieh-qua were planted with plastic film. Moreover, different edible parts of the crop were measured separately, such as stems and leaves, pods and peas. Overall, this study focuses on the quantitative analysis of NPs in various crops grown in the same field and various crop parts, which is expected to fill the information gaps about actual NP pollution levels.

2. Experimental part

2.1. Chemical and materials

A total of eleven different plastics, including polystyrene (PS), polyethylene (PE), polypropylene (PP), polymethyl methacrylate (PMMA), poly(vinylchloride) (PVC), poly(ethylene terephthalate) (PET), polycarbonate (PC), polyamide 6 (PA6), polyadiohexylenediamine (PA66), polylactic acid (PLA), and poly(butyleneadipate-co-terephthalate) (PBAT) were selected, as these polymers are commonly detected in environments. PS (CAS 9003-53-6) and PMMA (CAS 9011-14-7) were purchased from CHIMEI Co. Ltd (Taiwan, China). PC (CAS 25037-45-0), PLA (CAS 26023-30-3), and PVC (CAS 9002-86-2) were purchased from TEIJIN Limited (Japan). PE (CAS 9002-88-4), PET (CAS 29154-49-2), PP (CAS 9003-07-0), PA6 (CAS 25038-54-4), PA66 (CAS 32131-17-2), and PBAT (CAS 24968-12-5) were purchased from Macklin Biochemical Co. Ltd (Shanghai, China).

2.2. Crop samples collection and processing

The sampling site was located in Kaiping, Jiangmen City (Guangdong

Province, China), where a variety of crops were grown, and the same atmospheric subsidence and water source for irrigation were ensured. In particular, we selected a suitable field for growing cowpea (a type of legume crop), flowering cabbage (a type of leaf crop), rutabagas (a type of stem crop), and chieh-qua (a type of melon crop), two of which were grown with agricultural film while the other two were grown without it over an extended period of time (Fig. 1). This allowed comparisons to be conducted between the impact of various crops and the presence or absence of agricultural film on the level of NP abundance in crops. At each sampling site, a sufficient quantity of the crop samples was collected without the use of any plastic tools. Details about the location and crop type of the sampling sites are provided in the Supporting Information (Fig. S1 and Table S1). All the crop samples were delivered to the laboratory and pretreated within 24 h. The sample collection was conducted on November 16, 2022.

2.3. Pretreatment of different crop samples

At present, the detection of NPs is still in its infancy, and some important literature provides us with method references (Lian et al., 2020; Naidoo et al., 2017; Al-Sid-Cheikh et al., 2018; Li et al., 2021a,b,c; Zhou et al., 2021a,b,c; Gulizia et al., 2022; Jiang et al., 2022; Xu et al., 2022; Seeley and Lynch, 2023). As seen in Fig. 2, each collected crop sample was first passed through a 1 μm membrane filter to exclude the MPs ($>1 \mu\text{m}$). Then, nitric acid digestion followed by multiple organic extraction (chloroform, hexafluoroisopropanol, and methylbenzene) were used to extract NPs. Finally, the extraction solution was transferred into a pyrolysis target cup with a glass pipette, and volatilized to ensure all of the NPs were loaded for subsequent Py-GC/MS measurement. The specific steps in detail are shown in Text S1, Supporting Information.

2.4. Pyrolysis gas chromatography–mass spectrometry analysis

NP detection was carried out with a Multi-Shot PyrolyzerEGA/PY-3030D (Frontier Laboratories, Saikon, Japan) connected to a gas chromatograph mass spectrometer (GCMS-QP2020, Shimadzu, Japan) with a Rtx-5MS chromatographic column (30 m \times 0.25 mm \times 0.25 μm). The samples were pyrolyzed in the single-shot mode at 550 $^{\circ}\text{C}$. The heating procedure of GC conditions with a total duration of 30 min was set to heat from 40 $^{\circ}\text{C}$ (for 2 min) to 320 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$ and held at this temperature for 14 min. The split ratio of the pyrolysis products was 5:1 and helium was used as the carrier gas. The ion source temperature was set at 320 $^{\circ}\text{C}$, and the m/z was in the range of 29–600.

Based on the achievement of predecessors (Nuelle et al., 2014; Dumichen et al., 2017; Fischer and Scholz-Böttcher, 2017; Okoffo et al.,

2020), the chosen polymers were analyzed by Py-GC/MS to identify their characteristic components and ions. PVC, PE, PA66, and PET were detected in this study, and the validation process for the NP types analyzed using actual NP analytical standards are presented in the Supporting Information, Fig. S2–S5. For example, naphthalene (RT = 8.013 min, m/z 128) with high peak intensity and sensitivity was considered as the indicator compound for PVC (Fig. S2). 1-decene (RT = 6.067 min, m/z 140) was chosen as the indicator ion for PE, as it was the most typical and abundant pyrolysis product (Fig. S3). Cyclopentanone (RT = 4.050 min, m/z 84) was selected as an indicator component for PA66 due to its high peak intensity and sensitivity (Fig. S4). Benzoic acid (RT = 7.933 min, m/z 105) was considered as the indicator compound for PET as it was a distinctive and highly sensitive pyrolysis component (Fig. S5). Fig. S6–S12 shows the Py-GCMS spectra and the quantitative curve of other standard products, such as PS, PP, PMMA, PC, PLA, PA6, and PBAT.

The characteristic peak of each sample was identified by comparison with the full-scan mass spectrometry of the analytical pyrolysis library. Through analyzing different amounts of the standard plastics, the external calibration curves were obtained. The calibration range was 0.5–15 μg for PVC, 20–200 μg for PET, 0.5–20 μg for PBAT, 0.05–2 μg for PS, 0.01–20 μg for PMMA, 0.2–2 μg for PC, 0.25–5 μg for PA6 and PA66, 0.1–2 μg for PLA and PP. It could be seen that the external calibration curves based on these indicator ions could reflect the concentration of NPs accurately with acceptable coefficient of determination values ($R^2 > 0.99$). The limit of detection (LOD), defined as 3 times the baseline noise ($S/N = 3$), were 0.02–0.5 μg for different NPs samples; the limit of quantitation (LOQ), defined as 10 times the baseline noise ($S/N = 10$), were 0.06–1.5 μg for different NPs samples, as shown in Table S2, Supporting Information. Six replicates were determined for each standard sample, and RSD was used to evaluate the precision of the determination. The spiking experiments and method validation of standard products were carried out (Text S2 and S3, Supporting Information). Acceptable recoveries were obtained for different NPs, such as, 95.5%–102.8% for PVC, 88.1%–107.1% for PS, 93.5%–102.1% for PP, 74.2%–97.4% for PA66, 89.6%–109.3% for PET, and 94.6%–104.6% for PE (Table S2, $N = 6$, RSD $< 9.6\%$).

2.5. Quality assurance/quality control

Special care needed to be taken to minimize possible contamination during sampling, pretreatment, and testing processes (Xu et al., 2023). To be specific, cotton lab coats and polymer-free nitrile gloves were used throughout the analysis process to prevent any contamination from the plastic items utilized in the experiment. To avoid potential air



Fig. 1. Four different crops, of which flowering cabbage and rutabagas were planted without plastic film, while cowpea and chieh-qua were planted with plastic film.

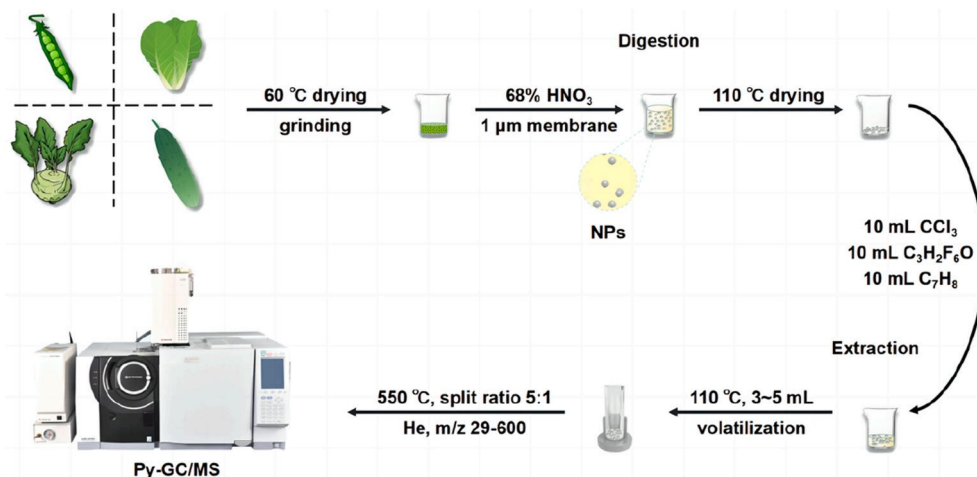


Fig. 2. Extraction of NPs from different crops, followed by determination with Py-GC/MS.

contamination, all experimental consumables used for sample collection and processing were wrapped in aluminum foil. The blank samples were processed using ultra-pure water, and the steps were the same as the sample processing including filtration, digestion, extraction, volatilization, and detection with Py-GC/MS. Fig. S13 shows that no indicator ions associated with the selected polymer were detected in the blank samples, indicating that these pretreatment procedures did not contribute to extra plastic contamination and could ensure the reliability of the results.

3. Results and discussion

3.1. Mass concentration of NPs in different crop samples

The direct identification and quantification of NPs were achieved by sample pretreatment, followed by Py-GC/MS analysis according to the pyrolysis products, characteristic ions, and the corresponding peak areas (Fig. 3).

Based on the similarity analysis of these peaks, PET, PVC, and PE

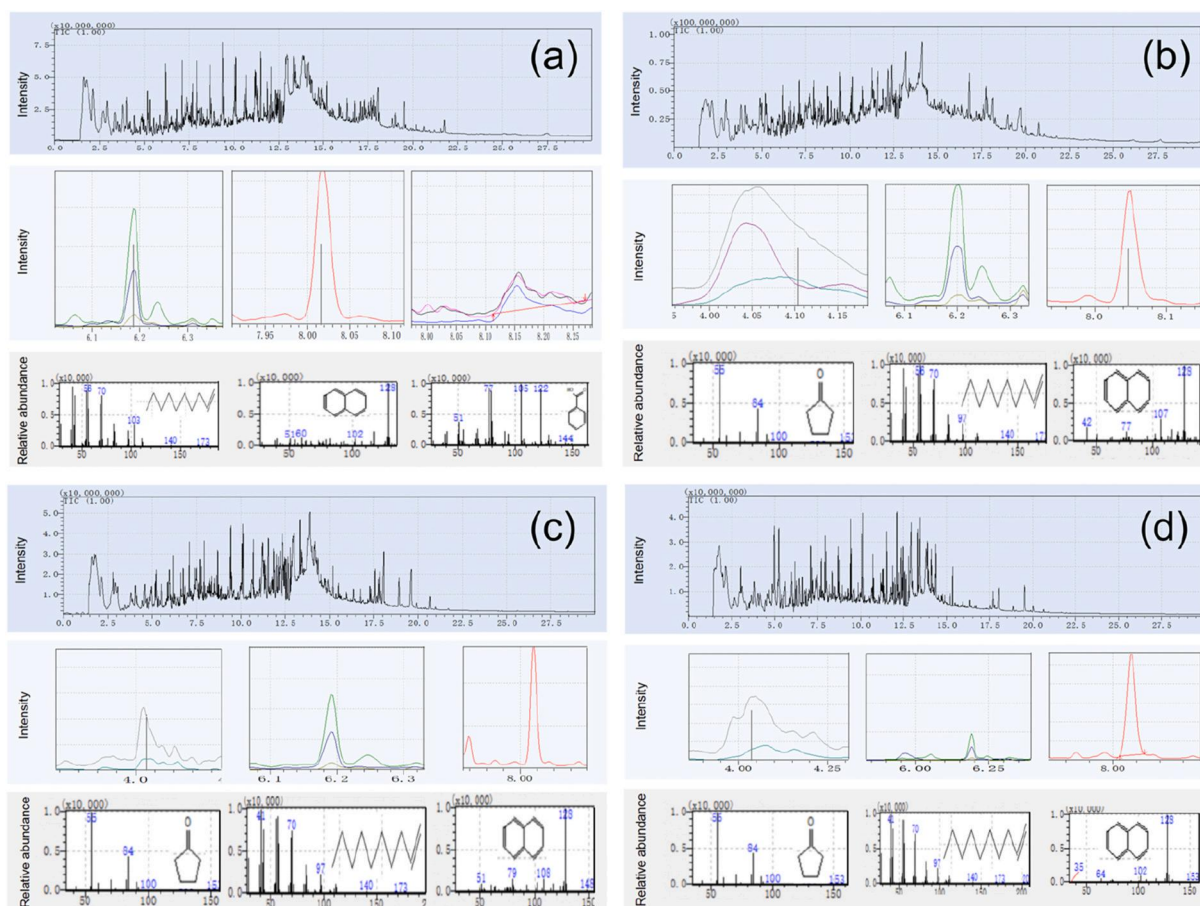


Fig. 3. The Py-GC/MS chromatograms, the extracted ion chromatograms of indicator ions, and the mass spectra of indicator ions of representative (a) cowpea samples; (b) flowering cabbage samples; (c) rutabagas samples; (d) chieh-qu samples.

were identified in cowpea samples. PA66, PVC, and PE were identified in flowering cabbage, rutabagas, and chieh-qua samples, as shown in Fig. 4. The mass concentrations of NPs were quantified according to the corresponding peak areas. For cowpea samples, PET was the highest in mass fraction of total plastic (42.6–72.7%) with the concentrations of 414.3–1430.1 mg kg⁻¹ in dry weight (DW), followed by PVC (N.D.–38.7%, N.D.–703.1 mg kg⁻¹, DW) and PE (14.9–27.6%, 124.8–462.9 mg kg⁻¹, DW). For flowering cabbage samples, the NPs were dominated by PVC (excluding the S1 sample which could only detect PE), which accounted for 39.7–73.4% with the concentrations ranging from 215.1 to 954.3 mg kg⁻¹ (DW), followed by PE (19.5–60.3%, 138.7–345.8 mg kg⁻¹, DW) and PA66 (N.D.–14.0%, N.D.–141.6 mg kg⁻¹, DW). For rutabagas samples, the concentrations of PE and PVC were relatively high, accounting for 29.3–68.4% and 28.3–60.6% with concentrations ranging from 101.3 to 135.1 mg kg⁻¹ and 54.6–279.5 mg kg⁻¹ (DW), respectively. Similarly, in chieh-qua samples, PE (110.8–267.8 mg kg⁻¹, DW) and PVC (35.4–367.9 mg kg⁻¹, DW) remained the dominant NPs, which accounted for 37.1–77.6% and 22.4–59.7%, respectively. The concentrations of PA66 (N.D.–14.6%, N.D.–91.2 mg kg⁻¹, DW) were the lowest. These results confirmed that in the actual field environment, the physical dimensions of NPs enabled them to penetrate biomembrane structures and accumulate in crops. Moreover, the concentration of NPs in crops may be much higher than expected, which is of particular concern as these crops are at the base of food webs and are a crucial part of the human diet.

Fig. 5 shows the mass concentration distributions of the selected NPs in different crops. PET was the highest concentration of NP detected, all of which was found in cowpea samples with an average concentration of 800.6 mg kg⁻¹ in dry weight, however, PET was below the detection limit in other crop samples. Generally, PVC was the NPs with the highest average concentration, followed by PE. The average concentration of PA66 was very low and there were no significant differences in four crop samples. To our knowledge, several studies have analyzed the NP

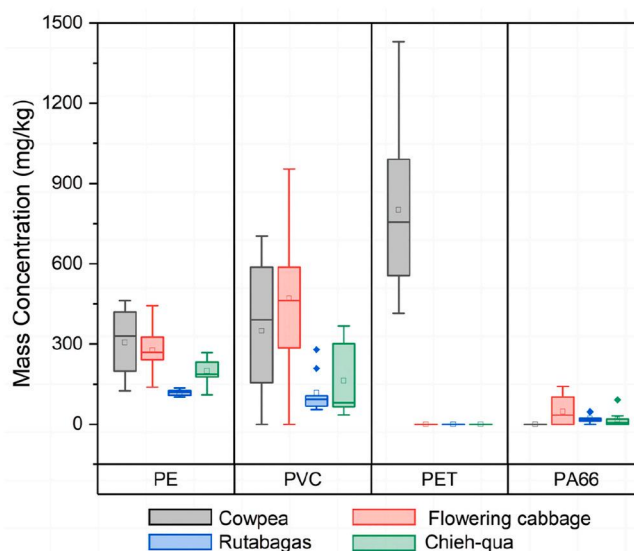


Fig. 5. The boxplot of the mass concentration distributions of the selected NPs in different crops.

concentration and the enrichment rule of designed artificial NPs in crops, however, there are few available data on the NP levels of different crops in actual fields. Although not truly comparable, the types of major plastics in crops are generally consistent with the conclusions of other researches.

Among the four types of crops, the average concentrations of NPs in cowpea (485.1 mg kg⁻¹, DW) and flowering cabbage (264.8 mg kg⁻¹, DW) were significantly higher than those in chieh-qua (126.0 mg kg⁻¹, DW) and rutabagas (85.7 mg kg⁻¹, DW) ($p < 0.001$). These results

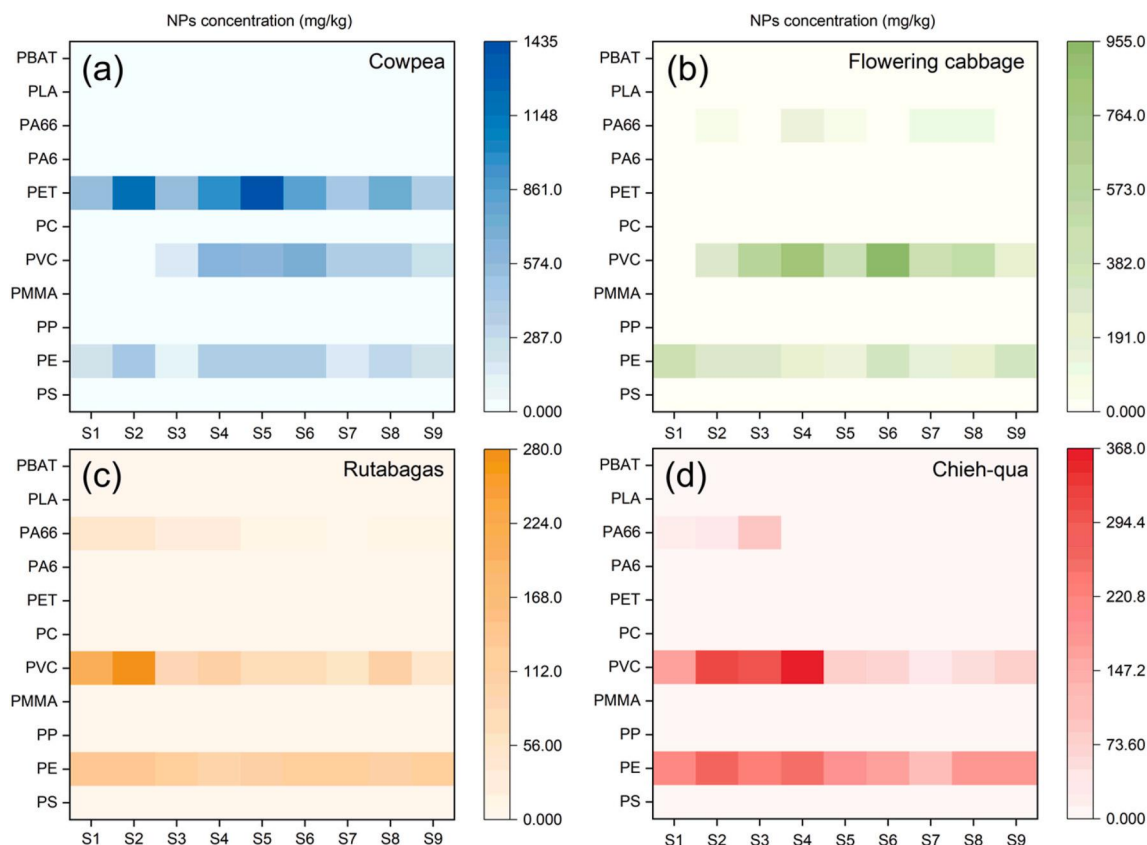


Fig. 4. Heatmaps of NP concentrations in different crop samples (S: sample).

indicated that the enrichment degree of NPs in legume crop and leaf crop was greater than that in stem crop and melon crop, which might be related to the uptake patterns and root size of different crops. During the uptake and transportation in crops, NPs encountered multiple physiological and chemical barriers, which constituted the size-exclusion limits (Eichert et al., 2008). The crop species, growth stages, and environmental factors affected the structure and width of the barriers. It has been reported that large NPs could be taken up by crops despite the small size-exclusion limit of plant roots (Judy et al., 2012). Once NPs entered the roots of crops, they were able to translocate into stems, leaves, and fruits (Jiang et al., 2022). For example, the roots of melon crops (such as cucumber (Li et al., 2021a,b,c)) were capable of uptaking and translocating NP particles through the epidermal root cells. Following that, NPs transported upwards through root pressure and transpiration, and further transported to leaves and fruits through the stems (Lu et al., 2008). For stem crops (such as lettuce (Luo et al., 2022)), NP particles entered the vascular cylinder of the root using the crack-entry mode at sites of lateral root emergence, and then moved along the vascular bundle easily with the flow of water and nutrients, which further transported to the stem and leaves. Studies have proven that transpirational pull was the main driving force of these movement (Li et al., 2020). In general, there are differences in the uptake and transportation of NPs by various types of crops, thus causing the significant differences in the accumulation of NPs, which is consistent with the detection results in the present studies.

3.2. Mass concentration of NPs in different edible parts

It is reasonable to speculate that NPs are absorbed from the soil by the roots of crops and transported upward, so the concentration of NPs in different parts of crops should be different. In order to further analyze the enrichment degree of the selected NPs in different edible parts of crops, stems and leaves of flowering cabbage samples, as well as peas and pods of cowpea samples were separately detected, and the results are shown in Fig. 6. The findings showed that all identified NP levels were considerably higher in the stems (60.2%) of flowering cabbage samples than in the leaves (39.8%) ($p < 0.05$), which indicated that for leaf crops, NPs were absorbed primarily by roots, and transported upwards through root pressure and transpiration, resulting in more NPs accumulation by stems rather than leaves. As expected, the concentrations of all observed NPs were also considerably higher in the peas (58.8%) of cowpea samples than in the pods (41.2%) ($p < 0.05$). It has been reported (Jiang et al., 2022) that the van der Waals interaction with the lipid membrane caused the NPs to adhere to the membrane once inside the crops, and gradually embed themselves in the membrane. Then, NPs were partially encapsulated by the lipid layer by endocytosis. The content of lipid membrane in the peas was more than

that in the pods, which might be responsible for the higher concentration of NPs in peas. This possibility is of particular concern, especially for the crops with higher fat content, such as peanut, oilseed rape, and soybean (Schmidt, 2015), because their rich lipid layer would absorb more NPs, which in turn could be ingested by humans or other animals through the food webs.

3.3. Effects of agricultural films on the concentration of NPs in crops

Identifying the source of NPs in agricultural crops is crucial, and agricultural plastic films are the most intuitive source of plastic pollution. Fig. S14 depicts the concentrations of NPs in various crops in the presence and absence of plastic films. PE is the main component of agricultural plastic films (Xu et al., 2020; Yang et al., 2022), as expected, the mass concentration of PE-NPs in crops grown with plastic films ($251.95 \text{ mg kg}^{-1}$, DW) was higher than that grown without plastic films (197.9 mg kg^{-1} , DW). The result indicated that during the planting and growth of crops, part of PE-NPs was released from the plastics films and adsorbed by the crops. It was discovered that the mass concentration of PVC-NPs in crops (255.7 mg kg^{-1} with plastic films and 293.6 mg kg^{-1} without plastic films, DW) was not directly related to the presence of covering plastic films. As PVC is one of the primary components of plastic pipes, these PVC-NPs may be discharged from irrigation water pipes along with irrigation water or sewage. This hypothesis agrees with previous findings, which reveal that organic fertilizers (Weithmann et al., 2018), wastewater (Murphy et al., 2016), and sewage sludges (Yang et al., 2021) are considered important sources of plastic particles for terrestrial ecosystems. For instance, sewage sludge is thought to be the source of 63,000 to 430,000 tons of plastic particles entering European farmlands each year (Nizzetto et al., 2016). Additionally, a variety of NP particles are produced for industrial uses, including electronics, cosmetics, biomedical products, adhesives, coatings, and paints, some of which are prone to leak into the soil environment (Hernandez et al., 2017; Al-Sid-Cheikh et al., 2018). In summary, the sources of NPs in agricultural land were broad and complicated, and our findings suggested that irrigation water and agricultural films could be the main pollution sources of NPs in this crop field.

4. Conclusion

Agricultural soil is becoming a primary sink for NPs generated from plastic debris. The uptake and accumulation of NPs by crops contaminate the food chain and pose unanticipated risks to the environment and living organisms. Although the fate and ecological risks of NPs in crops were conducted at designed concentrations of artificial NPs, the identification and quantification of NPs in actual field crops remain insufficient. Therefore, this study investigated the main chemical

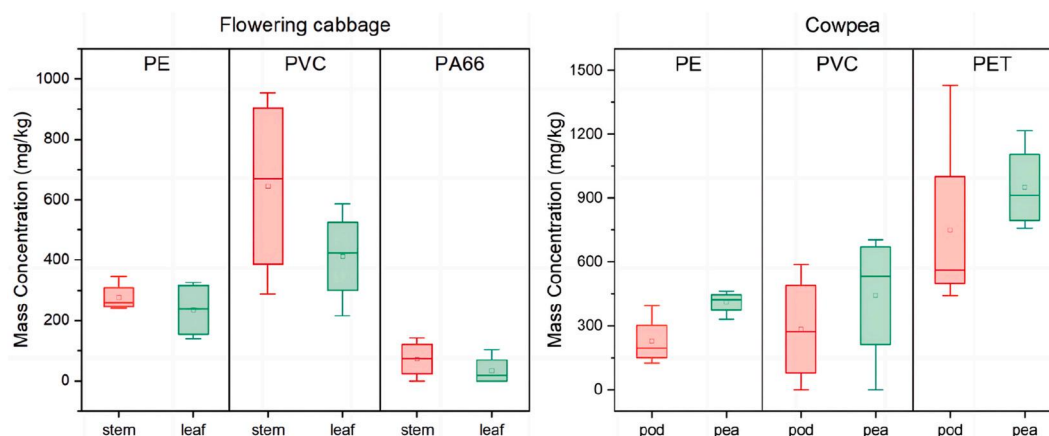


Fig. 6. The boxplot of the NP mass concentration distributions in different edible part of flowering cabbage (left) and cowpea (right).

composition and mass concentration of NPs in actual field crops, including cowpea, flowering cabbage, rutabagas, and chieh-qua. The results showed that four kinds of NPs (PE, PVC, PET, and PA66) were identified and quantified, of which PVC (N.D.–954.3 mg kg⁻¹, DW) and PE (101.3–462.9 mg kg⁻¹, DW) NPs were the dominant components in four kinds of crop samples, and high levels of PET (414.3–1430.1 mg kg⁻¹, DW) NPs were detected in cowpea samples. The concentration of NPs in actual crops may be much higher than expected. This study evaluated the real NP contamination levels in actual field crops, which served as critical reference information for further research. The concentration and type of NPs chosen must accurately reflect the real circumstance in order for any assessment of the pertinent concerns to be valid. For example, the majority of research have studied the fate and transport of NPs in soil or crop media at concentrations far different from the level of NPs measured in this study (Li et al., 2021a,b,c; Zhou et al., 2021a,b,c; Liu et al., 2022b; Luo et al., 2022; Wang et al., 2022). Additionally, commercial PS has been frequently used as the representative NPs when evaluating their environmental behaviors and/or toxicological properties, because it is more easily available in a standardized form from suppliers than other NPs (Lian et al., 2020; Li et al., 2021a,b,c; Wu et al., 2022a,b; Wu et al., 2022a,b); however, our study indicated that PVC and PE were the most prevalent NPs, while PS-NPs were hardly ever detected in crop samples.

Although the current study achieves the identification and quantification of trace NPs in actual crop samples, there is still potential for improvement. For example, the pretreatment process is very complex, which can result in reasonable sample loss and the underestimation of the NPs concentration. Moreover, the response of various NP types in Py-GC/MS is quite different, for example, the response of PS is much better than that of PET, which may cause differences in the detection of various NPs. Method development for NP detection in complex environments or biological media is an ongoing and challenging process. Finally, the mechanisms of NP uptake and transportation by different types of crops still need to be further explored in order to better elucidate the differences in the concentration of NPs in crops.

CRedit authorship contribution statement

Quanyun Ye: Writing – original draft, Data curation. **Yingxin Wu:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Wangrong Liu:** Writing – review & editing. **Xiaorui Ma:** Writing – review & editing. **Dechun He:** Writing – review & editing. **Yuntao Wang:** Writing – review & editing. **Junfei Li:** Writing – review & editing. **Wencheng Wu:** Writing – review & editing, Visualization, Conceptualization.

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.

Data availability

The authors do not have permission to share data.

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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.2024.141689>.

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