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Microplastic Extraction from Agricultural Soils Using Canola Oil and Unsaturated Sodium Chloride Solution and Evaluation by Incineration Method

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Abstract: Environmental pollution by microplastics (MPs) has become a global problem, but little is known about MPs in soils. This is because MP extraction methods from soils have not yet been standardized. In this study, we tried to establish a simple and economical method to extract soil MPs using the buoyancy of canola oil and the density separation process using sodium chloride (NaCl). In addition, the incineration method was adapted to evaluate the effectiveness of extraction methods precisely. First, the ability and suitability of seven different oils to extract MP from soil were investigated and canola oil was selected. Then, the spiking and recovery test was performed with canola oil and NaCl solution for low-density polyethylene (LDPE), polypropylene (PP), and polyvinylchloride (PVC) as follows: (1) soil and MP mixtures were prepared, (2) 5 g L^{-1} NaCl and canola oil were added and shaken thoroughly, (3) the oil phase containing MPs were separated after sedimentation, (4) the extracted MPs were rinsed with 99.5% ethanol, and (5) the organic adherents to the extracted MPs were digested with hydrogen peroxide. After drying and incineration, the substantial recovery rates were calculated. In the spiking and recovery test for MP particles (<1 mm) from five typical Japanese agricultural soils, the recoveries of LDPE, PP, and PVC were 95.2–98.3%, 95.2–98.7%, and 76.0–80.5%, respectively, higher than those obtained by the density separation using saturated NaCl solution. In conclusion, the method is effective for extracting MPs, especially LDPE and PP, from soils and is less sensitive to soil type, texture, and physicochemical properties.

Keywords: agricultural soil; canola oil; density separation; microplastic; oil extraction; spiking and recovery test

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1. Introduction

Since 1950, global plastic production had been increasing and was estimated to reach 367 million tons per year by the end of 2020 [1]. Apparently, with this growth, the volume of plastic waste is also increasing; however, improper and insufficient waste management leads to the accumulation of large amounts of plastics that can potentially be reused or recycled [2].

Plastics smaller than 5 mm in size are defined as “microplastics (MPs)” [3]. There are two types of MPs found in the environment [4]: primary MPs that are produced for the purpose to use as raw materials or blended forms, (i.e., pellets, microbeads, etc.), and secondary MPs that are the degradation products of plastics in the environment [5]. The size of both primary and secondary MPs particles ranges from 10^{-3} to 5 mm, making them a large cluster of pollutants [6].

Although plastic presence on land can be 4–23 times higher than that in the ocean [7,8], the knowledge about soil pollution of MPs is still lacking. The world's plastic waste is increasing every year [9], and about 79% of the waste is concentrated in landfills and other terrestrial environmental compartments, including agroecosystems [6,10].

Under natural conditions, weathering and microbial degradation increase the hydrophilicity of MPs and change the surface and internal structures [11]. Deteriorated MPs have higher adsorption capacities of potentially toxic elements and inorganic contaminants (Fe, Mn, Al, Pb, Cu, etc.), that cause negative effects on soil biota and even appear in the food chains [8,11–14]. Moreover, plastic particles are considered to interact with a variety of organic pollutants [15–17] and play a role in transporting them, which may enhance the expression of their toxicity [18].

In modern agriculture, various types, shapes, and sizes of plastics are used to protect crops and increase yields [19]. The most common type of plastic used in agriculture is low-density polyethylene (LDPE). LDPE is mainly used as various films for greenhouses, tunnels, mulching, etc. [20,21]. Polypropylene (PP) is the second most common plastic, which is used for pipes, sheets, nets, and ropes. The third one is polyvinylchloride (PVC). PVC is often found in pipes or tubes in agriculture for irrigation systems and in semi-rigid sheets for covering a greenhouse. Accumulation of microplastics on agricultural lands is highly contributed by the application of organic fertilizers produced from municipal solid waste and sewage sludge [22–29]. Since particle size widely varies, MPs are supposed to accumulate not only in plants' root systems but also in edible parts [30]. Hence the task to extract and determine the MPs in agricultural soils is a major challenge for researchers. Although many different methods have been proposed for the separation of MPs from water and sediments [31], they are either not applicable or partially applicable to MPs in soils.

Nowadays, density separation remains to be a popular method for the extraction of MPs. Generally, the density separation has been applied for the MP extraction from water and sediments but has recently been improved for soils [32]. Plastic particles can interact with charged ions, making it possible to apply a variety of salt solutions [33]. Since the optimal density is defined in 1.6–1.8 g cm^{-3} [34], the choice of a solute is a crucial point. Among the safest and the most environment-friendly substances, saturated NaCl solution (1.18 g cm^{-3}) is able to remove low-density types of MPs and is not applicable for high-density plastics such as PVC and PET [35,36], while $CaCl_2$ (1.5 g cm^{-3}) may agglomerate with organic matter [37]. $ZnCl_2$ is toxic to human health; moreover, $ZnCl_2$ is usually mixed with an acid, which may alter the presence, properties, and structure of MPs in samples [12]. NaI has high efficiency in the extraction processes; however, it is expensive to be widely used.

In addition to the conventional density separation, oil separation is getting attention after the use of the oleophilic properties of MPs was proposed [32,38]. Many studies have shown that the application of oils provides higher recovery rates of MPs from soils compared to density separation methods using only salt solutions [38–41]. Castor oil was tested by Mani et al. [39] and showed a high recovery rate (99 $\pm$ 4%) for some polymers in the spiking and recovery test. Scopetani et al. [40] proposed a separation process based on the application of olive oil and reported high recoveries (90–97%) for six polymers. It is important to note that the available techniques may be sensitive to different conditions, such as the equipment used, physicochemical properties of soils, and types and sizes of MPs.

This study aims to develop a cheap and quick method that is less sensitive to the properties of environmental samples. Another aim is to evaluate the effectiveness of extraction methods by incineration for the first time. In this article, we propose an extraction process for MPs from agricultural soils by the force of floatation and sedimentation using a mix of canola oil and NaCl solution. Three types of MPs, LDPE, PP, and PVC, most used in agriculture, and five different soils from several regions of Japan were targeted. The method is represented by two steps: extraction based on a mixture of oil and salt solution, and further filtration. The main criteria for the selection of oil and appliances were the environmental safety of the method, reagents, and wastes during and after the extraction process.

2. Materials and Methods

2.1. Soil and MP Samples

Five different types of soils were collected with a metal shovel from paddy and upland fields in Japan. The soil classifications [42] and physicochemical properties are shown in Table 1. All samples were firstly air-dried under ambient conditions and then heat-dried in an electric oven (ISUZU FR116S, Sanjo, Japan) for 24 h. Soil blocks were crushed, passed through a 1 mm sieve, and stored in zip bags in dark.

Table 1. Soil samples used in this study and the physicochemical properties.

Soil Type (CSCS) *1	Sampling Site	Sampling Date	Land Use	Sand, %	Silt, %	Clay, %	pH (H_2O) *2	EC, mS cm^{-1}	TC *3, mg g^{-1}	TN *3, mg g^{-1}	OM *4, mg g^{-1}	CEC, meq g^{-1}
Gray Fulvic soil	Shibata, Niigata	22 April 2019	Paddy field	63.4	24.4	12.2	5.30	0.084	24.1	2.10	31.4	13.5
Clay Loam soil	Shindori, Niigata	3 October 2019	Paddy field	48.0	24.0	28.0	5.24	0.118	18.6	1.68	50.6	5.54
Pseudogley soil	Agui, Aichi	29 April 2019	Paddy field	37.0	33.8	29.0	5.17	0.078	15.0	1.50	51.8	9.54
Allophanic Andosol	Matsumoto, Nagano	24 April 2019	Paddy field	33.9	24.4	41.5	5.66	0.800	45.7	4.00	68.2	13.2
Sandy Regosol	Ikarashi, Niigata	25 October 2019	Upland field	85.7	8.6	5.7	5.87	0.026	6.20	0.89	24.2	3.23

*1 CSCS—Comprehensive soil classification system of Japan [42], *2 pH(H_2O)—pH measured in soil: distilled water suspension (1:2.5), *3 TC and TN—total carbon and nitrogen, respectively, as measured with a CN coder (MT-700Mark2, Yanaco, Kyoto, Japan), *4 OM—organic matter content digestible by hydrogen peroxide.

In this study, LDPE, PP, and PVC, which are the most prevalent types of plastics for agricultural use in Japan [43], were examined. Commercial LDPE pellets, PP food containers, and a PVC sheet were used to prepare MPs. Plastics were crushed by a laboratory mill (HS-20, 2000 cc., Labnect Co., Ltd., Osaka, Japan) and then passed through 1 mm and 2 mm sieves to prepare large (1–2 mm) and small particles (less than 1 mm). The former was used for oil selection, and both were used for the spiking and recovery test described below.

2.2. Oil Selection

Based on the literature, canola [38,41], rice [44], olive [40], castor [39], turpentine [45] oils, and two types of silicone oils [46] were selected to compare the extraction abilities of MPs from the soil. The prices per 1 L and properties of oils such as density, dynamic and kinematic viscosities are listed in Table 2.

Table 2. Properties of selected oils.

Oil	Manufacturer	Density, g cm^{-3}	Dynamic Viscosity, mPa s	Kinematic Viscosity, mm^2 s^{-1}	Oil–Water Interfacial Tension, mN m^{-1}	Price *, \$ L^{-1}	Reference
Canola (Rapeseed)	J-Oil mills (Tokyo, Japan)	0.916	71.6	78.2	33.47	2	[38,41]
Rice bran	Tsuno Food Industry Co. (Katsuragi, Japan)	0.913	65.8	72.1	22.71	6	[44,47]
Olive	Nisshin OilliO (Tokyo, Japan)	0.911	74.1	81.3	13.15	9	[40,47]
Castor	Fujifilm Wako Pure Chemical (Osaka, Japan)	0.961	852.8	886.6	13.7	34	[39,48]
Turpentine	Ditto	0.86	1.5	1.7	27.2	33	[45,49]
Silicone SE KF-96-100CS	Shin-Etsu Chemical (Tokyo, Japan)	0.965	96.5	100	20.9	23	[46]
Silicone SE KF-96-500CS	Ditto	0.97	485	500	21.1	27	Ditto

* Market prices in Japan as of May 2022.

The experiments were conducted with the gray fulvic soil and the clay loam soil in triplicate. Ten grams of soil sample were placed into a conical flask and mixed with every 10 particles of the big fraction of PE, PP, and PVC. Then, 150 mL of distilled water and 10 mL of oil were poured into the MP-soil mixture. The flask was then covered by Parafilm, evenly shaken, and left for 30 min. The liquid phase containing the extracted MP particles was then transferred into a glass beaker and passed through a filter paper (Whatman No. 41, Cytiva, Marlborough, MA, USA). The MP particles remaining on the filter were then visually counted using a stereomicroscope (SZ61, Olympus Corporation, Tokyo, Japan) equipped with a digital camera (AdvanCam-LP2, AdvanVision Co., Ltd., Tokyo, Japan), and the recovery rates were calculated based on the number of pieces.

2.3. Spiking and Recovery Test for Large Particles

To evaluate the effect of soil type on the MP recovery rate, the spiking and recovery test was conducted using the five different soils in triplicate. The test was performed using the large and small MP particles in order to check the efficiency of the method for different sizes of MPs.

The procedure of the spiking and recovery test is shown in Figure 1, and the actual pictures of the experimental setup are provided in Figure S1. All the solid samples were weighed using an analytical balance (HR-202, A&D, Tokyo, Japan). Each 10 g of soil was contaminated with 0.08 g of MPs and the MP-soil mix was put into a 250 mL glass pear-type funnel. Then, 150 mL of 5 g L^{-1} NaCl solution and 10 mL of canola oil were added into the funnel. The funnel was closed with a cap, rotated into the horizontal position, and evenly shaken thoroughly for 1 min. Then, the funnel was returned to the initial position. The cap and lids were rinsed with distilled water to wash all residues in the mixture. After 30 min sedimentation, the upper phase containing oil and MPs was taken and filtered by a vacuum pump through a glass microfiber filter (grade GF/A, Whatman, Cytiva, Marlborough, MA, USA).

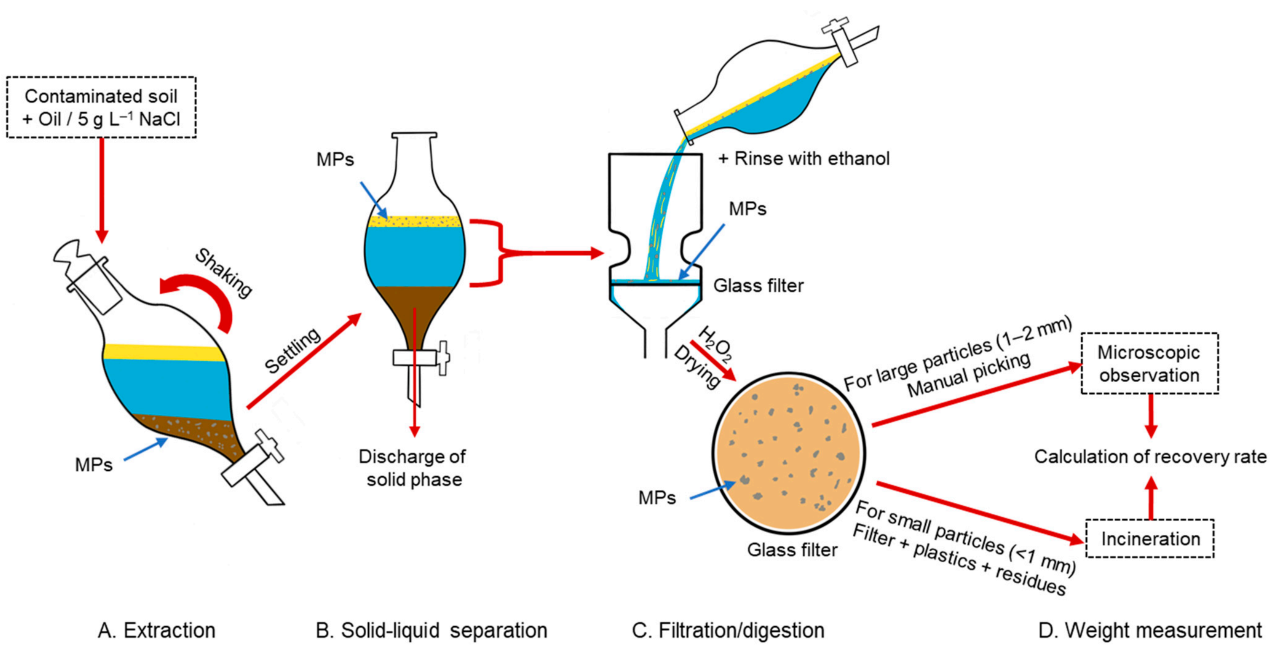

Figure 1. The procedure of the method in this study.

The collected MPs were rinsed with 99.5% ethanol to remove adhered oil and clay particles. Thereafter, a filter was placed onto a Petri dish, and the organic matter adhered to the MPs was digested with 30% hydrogen peroxide (H_2O_2) at 60 °C for 24 h. After particles were manually collected and weighed, the recovery rate was calculated as follows:

$$\eta_L = \frac{W_{LR}}{W_{ini}} \times 100 \quad (1)$$

where η_L—recovery rate (%) of the large MPs; W_{LR}—weight (g) of the large MPs recovered; and W_{ini}—the initial weight (g) of MP particles added.

2.4. Spiking and Recovery Test for Small Particles

For small particles, the manual collection was impossible. Therefore, after extracting plastic particles, we applied the incineration method in an atmosphere electric furnace (FT-101, Full-Tech, Osaka, Japan) to obtain precise recovery rates.

Prior to applying the method to the extracts, the most suitable incineration temperature for the three plastics were determined at 500, 600, and 700 °C. After virgin MPs were placed in the furnace for 30 min at each temperature, the incineration rates were obtained based on the weight loss after incineration. The results showed that the incineration rates of PE and PP were found to be more than 98% at all temperatures examined, while that of PVC was as low as 74% (Table S1). We, therefore, decided to account for the incineration rate in the calculations of the recovery rate of PVC. The optimal temperature for the thermal degradation of polymers is reported to be approximately 500 °C for PE and PP, and approximately 600 °C for PVC [50,51]. Based on this information and our results (Table S1), an operating temperature of 600 °C was adopted for incineration in this study. Blank tests were also conducted on the five soils without artificially contaminated MPs and the results obtained were taken into account in the calculation of the recovery rates.

After applying the incineration method, the weight (g) of the small MPs recovered (W_{SR}) was determined as follows:

$$W_{SR} = W_b - W_a - W_{blank} \quad (2)$$

where W_b—the weight (g) of the extracts before incineration, W_a—the weight (g) of the extracts after incineration, and W_{blank}—the blank test result (g).

In the case of LDPE and PP, the recovery rate of MPs was calculated as follows:

$$\eta_S = \frac{W_{SR}}{W_{ini}} \times 100 \quad (3)$$

where η_S—recovery rate (%) of the small MPs and W_{ini}—the initial weight (g) of MP particles added.

For PVC, Equation (3) was modified as follows:

$$\eta_S = \frac{W_{SR}/(100 - I_{PVC})}{W_{ini}} \times 100 \quad (4)$$

where I_{PVC}—the incineration rate (%) of PVC at 600 °C for 30 min.

2.5. Comparison with the Simple Density Separation

We tried the simple density separation using a saturated NaCl solution with a density of 1.19 g cm^{-3} proposed by Liu et al. [35] and compared the results with those of our method. The soil samples previously contaminated with the small MP particles were mixed with NaCl solution, treated by ultrasonic, and left for 24 h with further decanting of supernatants. The described steps were repeated 3 times. The obtained supernatants were then mixed with 30% H_2O_2 and left on a hot plate (50 °C) for 72 h. The solutions after digestion were filtered and the filters were further dried. As in our method, the filters with the remained MP particles were incinerated at 600 °C for 30 min to determine the effectiveness of the simple density separation. The recovery rates of LDPE, PP, and PVC were calculated using the same formulas as for the oil and density separation.

2.6. Laboratory Precautions and Sample Control

To avoid possible contamination of samples during sample processing, procedural controls were implemented as follows: only metal, ceramic, and glass apparatus rinsed with distilled water and dried at 105 °C were applied. In addition, by wearing a cotton robe, contamination of the samples with plastic fibers from the clothing was avoided. When needed, the samples were stored in an enclosed space until the next analytical step. Since the soils were stored in zip bags, blank tests were performed in triplicate for each soil to ensure no MP contamination from the zip bags.

2.7. Statistics

To investigate the significance of the mean differences between conditions, Student's *t*-test or Tukey–Kramer multiple comparisons test was performed using the R statistical software (version 3.5.2; R Foundation for Statistical Computing, Vienna, Austria).

3. Results and Discussion

3.1. Oil Selection

The extraction capacity of each studied oil was examined on a mixture of LDPE, PP, and PVC. As shown in Table 3, canola, rice, and turpentine oils showed high recoveries of more than 95% in both gray fulvic and clay loam soils. However, turpentine oil is known to dissolve weakly structured plastics, and, therefore, cannot be proposed for further application. Castor oil, whose high efficiency was reported by Mani et al. [39], showed relatively a lower recovery rate for the gray fulvic soil. The results of olive oil and silicon oil KF-96-100CS were relatively lower than the others.

Table 3. Selection of the suitable oil type for plastic separation from soil (LDPE + PP + PVC particle mix, the initial number of pieces was 30 in total).

	Gray Fulvic Soil				Clay Loam Soil			
Oil Type	**LDPE**	**PP**	**PVC**	**Total**	**LDPE**	**PP**	**PVC**	**Total**
Canola oil	100 ± 0	100 ± 0	96.7 ± 2.7	98.9 ± 0.9 a	90 ± 4.7	100 ± 0	100 ± 0	96.7 ± 1.6 a
Rice oil	100 ± 0	96.7 ± 2.7	100 ± 0	98.9 ± 0.9 a	100 ± 0	93.3 ± 2.7	96.7 ± 2.7	96.7 ± 1.6 a
Olive oil	96.7 ± 2.7	86.7 ± 7.2	90 ± 4.7	91.1 ± 4.0 a	93.3 ± 2.7	93.3 ± 2.7	96.7 ± 2.7	94.4 ± 0.9 a
Castor oil	83.3 ± 7.2	86.7 ± 7.2	80 ± 9.4	83.3 ± 5.4 ab	100 ± 0	93.3 ± 2.7	100 ± 0	97.8 ± 0.9 a
Turpentine oil	100 ± 0	93.3 ± 5.4	100 ± 0	97.8 ± 1.8 a	93.3 ± 2.7	100 ± 0	100 ± 0	97.8 ± 0.9 a
Silicon oil KF96-100CS	93.3 ± 2.7	100 ± 0	86.7 ± 2.7	93.3 ± 1.6 a	93.3 ± 5.4	93.3 ± 5.4	96.7 ± 2.7	94.4 ± 2.4 a
Silicon oil KF96-500CS	66.7 ± 11.9	63.3 ± 9.8	76.7 ± 5.4	68.9 ± 2.4 b	83.3 ± 7.2	76.7 ± 7.2	86.7 ± 7.2	82.2 ± 0.9 b

Average ± standard error ($n = 3$). LDPE: Low-density polyethylene, PP: polypropylene, PVC: polyvinyl chloride. Different characters indicate significant differences between the oil types (Tukey–Kramer test, $p < 0.05$).

Theoretically, the most suitable oil for the extraction of MPs from the soil should have a high viscosity enough to catch the MP particles and flotation force enough to float MPs on the liquid surface. However, the silicon oil KF96-500CS, which has the second-highest viscosity, had a significantly lower recovery rate than the others (Tukey–Kramer test, $p < 0.05$). Moreover, it was difficult to fully remove residual silicon oil from labware and MP particles even with strong organic solvents. It was observed that the MP particles formed large agglomerates and sank to the bottom along with the solid phase because this type of oil has a high flotation force but high stickiness. Due to these facts, it was judged that these extractants were unsuitable for our purpose to obtain a simple and quick extraction method.

Lechthaler et al. [41] assumed that attraction between MP particles and canola oil may be related to the lipophilicity of both the hydrocarbon chains and the oil molecules. Kim et al. [52] discussed the relationship between the interfacial tension of the oil and the formation of oil–water emulsions after carrying out the agitation for oil separation of MPs and noted that emulsion formation reduces the stability of the oil layer and the buoyancy of oil-adsorbed MPs, adversely affecting the migration of MPs into the oil layer. In general, oils with high surface tension are less likely to form emulsions. This is probably why canola and rice oils, which have relatively high interfacial tension and low viscosity (Table 2), showed the highest recovery of MPs among the five natural oils examined in this study (Table 3).

Both oils were determined to be useful in the extraction process; however, considering the prices, the less expensive canola oil was chosen as the best oil for soil MP extraction and was used in the spiking and recovery test.

3.2. Spiking and Recovery Test

As a first evaluation, we examined the effectiveness of the extraction of large MP particles from the soils studied. All extracted MP particles were manually separated from the filters and their weights were measured (Table 4). The results revealed that the mixture of canola oil and NaCl solution was suitable for the extraction of LDPE, PP, and PVC at the rates of 96.0–97.9% and 96.6–97.8%, and 96.3–98.4%, respectively.

Table 4. The recovery rates of the large plastic particles (1–2 mm) from the five different soils by the oil and density separation method using a mixture of canola oil and NaCl solution.

Soil Type	LDPE	PP	PVC
Gray Fulvic soil	97.9 ± 0.7	97.3 ± 0.2	97.6 ± 0.4
Clay Loam soil	97.7 ± 0.4	96.6 ± 0.3	98.4 ± 0.4
Pseudogley soil	97.6 ± 0.5	97.7 ± 0.2	96.6 ± 0.4
Allophanic Andosol	96.0 ± 0.4	96.8 ± 0.8	96.3 ± 0.4
Sandy Regosol	97.8 ± 0.3	97.8 ± 0.6	97.4 ± 0.4
Average	97.4 ± 0.3 a	97.3 ± 0.3 a	97.3 ± 0.3 a

Average ± standard error (n = 3). No significant difference was shown between polymer types (Tukey–Kramer test, $p > 0.05$).

Next, the extraction of small particles using the method was evaluated. In the case of the small particles, it was difficult to quantitatively determine the effectiveness using conventional methods such as manual separation, counting, or weighing. For this reason, we used the incineration method to calculate the accurate recovery rates. The results of the recovery rates for the three types of MPs are shown in Table 5. The mean recovery rates of the small particles of LDPE and PP were 95.2–98.3% and 95.2–98.7%, which were similar to those for the large particles (Table 4). When the method was applied to PVC, the recovery ratio ranged between 76.0–80.5%, which was lower than those for the large fractions. This might be because the density of PVC is relatively high (1.35–1.45 g cm^{-3}) and comparable to those of soil particles, therefore, the smaller particles were harder to be separated from the soil. The possibility that dense polymers can get caught by soil particles during the oil separation of MPs from soil has also been noted by Scopetani et al. [40].

Table 5. Comparison of the recovery rates of the small plastic plastics (<1 mm) from the five soils between the oil and density separation method using a mixture of canola oil and NaCl solution and the simple density separation method using saturated NaCl solution.

Soil Type	Separation Method	LDPE		PP		PVC	
Gray Fulvic soil	Oil and density method	95.2 ± 0.4	**	95.2 ± 1.0	**	80.1 ± 2.4	*
	Simple density method	71.4 ± 2.0		83.0 ± 2.2		70.3 ± 2.1	
Clay Loam soil	Oil and density method	96.2 ± 0.8	***	98.4 ± 0.6	**	80.5 ± 0.7	**
	Simple density method	81.5 ± 1.0		75.0 ± 3.4		71.7 ± 0.9	
Pseudogley soil	Oil and density method	95.4 ± 1.1	***	96.0 ± 0.4	***	78.1 ± 1.9	*
	Simple density method	82.8 ± 1.1		74.7 ± 2.4		66.4 ± 2.9	
Allophanic Andosol	Oil and density method	98.1 ± 0.6	***	98.1 ± 0.4	***	76.0 ± 1.9	ns
	Simple density method	71.9 ± 0.4		77.5 ± 1.4		72.3 ± 2.7	
Sandy Regosol	Oil and density method	98.3 ± 0.4	***	98.7 ± 0.5	***	79.0 ± 1.4	*
	Simple density method	70.9 ± 1.0		85.2 ± 1.5		70.7 ± 1.8	
Average	Oil and density method	96.6 ± 0.4 a	***	97.3 ± 0.4 a	***	78.7 ± 0.8 b	***
	Simple density method	75.7 ± 1.5 a		79.1 ± 1.4 a		70.3 ± 1.0 b	

Average ± standard error (n = 3). Asterisk indicates significant differences between the methods (Student's t-test; *, **, and *** mean significant difference at a level of 0.05, 0.01, and 0.001, respectively; ns means not significant). Different characters indicate significant differences between polymer types (Tukey–Kramer test, $p < 0.05$).

Although LDPE and PP were almost completely incinerated at 600 °C for 30 min, the incineration rate of PVC was only 74.0% (Table S1). This implies that when evaluating MP contamination of actual soil samples by the incineration method, it is desirable to evaluate in advance whether the soil contains PVC or not. Then, an appropriate incineration rate should be adopted.

3.3. Comparison with the Simple Density Separation

The simple density separation is the most popular method for extracting MPs from soil samples. Many different solutions have shown high recovery rates and have been suggested as extraction solutions. However, many of them are expensive, harmful to the environment, or hazardous to human health.

For understanding the advantages and disadvantages of our method, we tried the simple density separation using a saturated NaCl solution with a density of 1.19 g cm^{-3} proposed by Liu et al. [35] and compared the results. This method has often been used for the extraction of MPs from the soil; however, there was little information about recovery rates.

As a result, the recovery rates of LDPE, PP, and PVC, calculated using the same formulas as for the oil and density separation, were 70.9–82.8%, 74.7–85.2%, and 66.4–72.3%, respectively, significantly lower than the oil and density method proposed in this study (Student's t-test, $p < 0.001$) (Table 5). The results indicate that saturated NaCl solution has insufficient forces to extract MPs from soils prevalent in Japan. One more disadvantage of using saturated solutions is the possibility that the crystallization process may proceed. It was confirmed that NaCl crystals adhering to the walls of the glassware trapped MPs during the extraction process, inhibiting the complete extraction of MPs and reducing the recovery rates.

3.4. Advantages and Limitations

Oleophilic properties of plastics were supposed as a key feature for developing an effective separation method of MPs from the soil instead of the conventional density separation methods and as a hypothetic solution to the problem of density differences of plastics [38]. Based on the background, we combined the knowledge about canola oil and NaCl solution referred for the application in separation processes.

Since soil properties have a significant impact on the recovery of MPs, the applicability of extraction methods needs to be carefully evaluated. In this study, the extraction method was therefore applied to five different soils collected in Japan. The results showed no significant difference between recovery rates in different soil types. Therefore, it can be concluded that the effect was negligible, and the extraction and quantification methods showed high recovery rates (Tables 4 and 5).

Larger MPs (>1 mm) can be visually collected after extraction with a mixture of canola oil and unsaturated NaCl solution, as was performed in this study; however, it is not easy to apply this method to smaller MPs, (e.g., <1 mm). In the calculation of the recovery rates, it is necessary to consider the amounts of soil and extraction residues remaining after separation and filtration processes; however, this point does not seem to have been recognized as important in the extraction methods proposed to date. Therefore, in this study, the incineration method was used for the small MP particles to obtain more precise recovery rates by eliminating factors that may affect the results. To the best of our knowledge, this is the first attempt to evaluate the recovery rates of MPs using incineration.

Our separation method using canola oil and unsaturated NaCl solution showed high recoveries (>95%) for LDPE and PP with small particle sizes (Table 5). However, the recovery rate is slightly lower at 78.7% for the small-size PVC particles, meaning that the amount of PVC may be underestimated when applied to actual soils. Previous studies proposed the $ZnCl_2$ (1.5 g cm^{-3}) solution as one of the strongest solutions for the extraction of a variety of polymers; however, the recovery for heavier polymers such as PVC was still low [53]. Improving the recovery rate of PVC should be future work.

This study focused on the separation process and the method to obtain accurate recovery rates of MPs. Therefore, the influence of the solvents used on plastic-related chemicals and other contaminants was not considered. If one is interested in contaminants adsorbed on the separated MP, this could be problematic. In addition, it should be noted that ethanol used as a cleaning solvent in this study has been reported to solubilize some plastics such as nylon [54]. Although the use of nylon in agriculture is limited, caution should be exercised when applying this method to soils where nylon contamination is anticipated.

As an alternative to filtration, the use of adsorbents to remove oil is being considered. One possible method is to utilize reusable foams that can easily remove the oil from the extracted MPs [52]. Combining and developing our method with such new technologies may be expected in the future.

4. Conclusions

In this study, a novel separation method using canola oil and unsaturated NaCl solution for the extraction of MPs from the soil was investigated in a precise spiking and recovery test incorporating incineration. The recoveries for <1 mm particles of LDPE, PP, and PVC were 95.2–98.3%, 95.2–98.7%, and 76.0–80.5%, respectively. It was more efficient than 66.4–85.2% obtained by the simple density separation method using a saturated NaCl solution. The extraction method is a promising way to extract MPs, especially LDPE and PP, from agricultural soils since it has the following advantages over the simple density separation: (1) sufficient recovery of MPs is expected, (2) lower sensitivity to plastic types compared to conventional density separation, (3) no dependence on soil properties, (4) expensive and/or toxic to the environment and human health salts such as $ZnCl_2$ and NaI are not used, and (5) the running cost is low.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/soilsystems6020054/s1, Figure S1: Experimental setup, Table S1: Incineration rates of virgin plastics at different temperatures.

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