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Microplastics in sewage sludge from the wastewater treatment plants in China

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A B S T R A C T

Sludge disposal such as land application is suspected as a significant source of microplastic (MP) pollution in the environment. To examine such a hypothesis, the present study was conducted to investigate the occurrence of MPs in sludge by analyzing 79 sewage sludge samples collected from 28 wastewater treatment plants (WWTPs) in 11 Chinese provinces. MP concentrations in the sludge samples ranged from 1.60–56.4 $\times$ 10^3 particles per kilogram of dry sludge, with an average of 22.7 $\pm$ 12.1 $\times$ 10^3 particles per kilogram of dry sludge. Thereinto, the sludge-based MP contents were greater in eastern China than in western China and varied during different months. Their colors and types were mainly white (59.6%) and fibers (63%), respectively. Microscope Fourier Transform infrared spectroscopy revealed that most of MPs belonged to polyolefin, acrylic fibers, polyethylene and polyamide. Some WWTP parameters, such as servicing area, proportion of industrial wastewater, secondary treatment and sludge dewatering may have affected MP concentrations in sludge. Based on the total sludge production in China, the average amount of sludge-based MPs entering into natural environmental was estimated to be 1.56 $\times$ 10^{14} particles per year. The findings confirmed that sewage sludge discharge is an important source of MP pollution in the environment. Further evaluation of the associated environmental hazards with MPs is deemed necessary.

1. Introduction

Plastic pollution in aquatic habitats has been well studied and given considerable attention for a number of decades (Derraik, 2002; Jambeck et al., 2015; Lebreton et al., 2017; Murphy et al., 2016; Pruter, 1987). In recent years, small plastic particles known as microplastics (MPs) have also started receiving much attention (Andrady, 2011). MPs are plastics which are less than 5 mm in size (Murphy et al., 2016), and are subdivided into primary and secondary MPs. Primary MPs are plastics that are produced and enter the environment with small sizes, such as microbeads in personal care and cosmetics products (Cheung and Fok, 2017; Eerkes-Medrano et al., 2015), whereas secondary MPs originate from the breakdown of larger plastic debris in the environment due to exposure to sunlight, wind, water, and other environment stressors (Murphy et al., 2016; Song et al., 2017).

MPs are ingested by biota and get accumulated within organisms, resulting in physical harm, such as internal abrasions and blockages (Wright et al., 2013). Meanwhile, ingested MPs release toxic contaminants such as monomers and plastic additives, which can lead to carcinogenesis and disrupt the endocrine system (Wright and Kelly, 2017). Furthermore, MPs can adsorb and concentrate hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorinated biphenyls, and heavy metals such as cadmium, zinc, nickel, and lead (Holmes et al., 2012; Koelmans et al., 2013, 2016; Rochman et al., 2014; Wright and Kelly, 2017; Ziajahromi et al., 2016). After ingestion or inhalation of MPs, the accumulated chemical contaminants may be released and leached into the gastrointestinal tract of aquatic organisms or the lungs of humans, adversely

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impacting human health and ecosystems (Wright and Kelly, 2017). In addition, MPs can increase the bioaccumulation of the released contaminants (Besseling et al., 2013), leading to chronic toxicity.

MPs have been widely found in natural environment, including marine, freshwater, sediment and terrestrial environments (Andrady, 2011; Eerkes-Medrano et al., 2015; Lwanga et al., 2016; Rillig, 2012; Van Cauwenberghe et al., 2013), even in polar regions (Lusher et al., 2014). Recent studies showed that effluent of wastewater treatment plant (WWTP) is an important source of MPs (Carr et al., 2016; McCormick et al., 2014; Murphy et al., 2016; Talvitie et al., 2015; Ziajahromi et al., 2016). Microbeads used in facial scrubs, toothpaste, and other personal care products, and synthetic textile fibers from washing of clothes are transported from the raw wastewater to WWTPs, and may bypass the WWTPs and enter the aquatic environment due to their small size (Browne et al., 2011; Chang, 2015; Fendall and Sewell, 2009). Murphy et al. (2016) estimated that a WWTP (population equivalent 650 000) releases 65 million MPs into the receiving water every day. Cheung and Fok (2017) reported that 209.7 trillion microbeads (306.9 tones) are emitted into the aquatic environment in mainland China every year, and more than 80% of the emissions originate from WWTP effluents. In fact, the WWTPs are effective in removing the MPs from municipal effluents, and the removal rate reaches to 98.41% (Murphy et al., 2016). In other words, most of MPs in the raw wastewater retain in sewage sludge (Magnusson and Norén, 2014; Ziajahromi et al., 2016). Studies have found the presence of high concentrations of MPs in WWTP sludge samples (Bayo et al., 2016; Brandsma et al., 2013; Carr et al., 2016; Habib et al., 1998; Lassen et al., 2015; Magnusson and Norén, 2014; Mahon et al., 2017). Mahon et al. (2017) found that the MP concentration isolated from the sludge ranges from 4.20–15.4 $\times$ 10^3 particles kg^{-1} dry sludge. Lassen et al. (2015) reported that sludge from the WWTPs in Germany contains 1.00–24.0 $\times$ 10^3 MP particles ($\geq$10 μm) per kg of dry sludge. However, these reports are often based on limited sludge samples from some WWTPs, and systematic investigation is presently lacking about MP characteristics in dewatered sewage sludge such as its spatial-temporal distribution and possible affecting factors, especially in China.

The total sludge production in China in 2015 was calculated to be around 40 million tons (moisture content 80%). With increase in the daily-wastewater-treatment capacity and the number of WWTPs, the total sludge production has also steadily increased with an annual growth of about 13% (Yang et al., 2015). It has been predicted that it will achieve more than 60 million tons in 2020. Land application is one of the commonest sludge disposal methods, and its development is encouraged by the Ministry of Housing and Urban-Rural Development, China (Yang et al., 2015). However, the widespread application of sewage sludge from WWTPs to farmlands is likely a major input of MPs to soils, with unknown consequences to sustainability and food security (Nizzetto et al., 2016a, 2016b). In addition, research has shown that high proportion of sewage sludge is dumping improperly in China (Yang et al., 2015), leading to high amounts of MPs in the sludge reaching soil and freshwater environment. Mahon et al. (2017) even suggested that sludge after treatment may also introduce MPs in the natural environment. Therefore, it is very significant to investigate the characteristics of MPs in sludge from the WWTPs of China for comprehensively understanding potential risk of sludge-based MPs on soil or other natural pollution and human or livestock health.

The objectives of this study are to (1) analyze the concentration, classification and morphological characteristics of MPs extracted from sewage sludge in 28 WWTPs of China, (2) investigate spatial and temporal distribution of MPs in WWTP sludge, and (3) explore the effect of WWTP parameters such as treatment capacity and secondary treatment on MP concentrations in sewage sludge.

2. Materials and methods

2.1. Sampling and analysis

A total of 79 dewatered sewage sludge samples were collected from 28 WWTPs in 11 provinces of China, during 2014 and 2015. Basic information of the investigated WWTPs in regard to treatment capacity, servicing population, servicing area, proportion of industrial wastewater in the influent, secondary treatment process, discharge standard of the effluent and sludge dewatering process is given in Table S1 of the SI. Spatial distribution and number of sludge samples collected from the WWTPs are shown in Fig. S1 of the SI. In addition, these samples cover each month, although only one sample is collected in November and December. Other information of the sludge samples is outlined in Table S2 of the SI.

After collection, the samples were stored in −20 °C prior to analysis. Total solid content of the sludge samples was determined by drying the samples at 105 °C for 24 h, while volatile solid content was measured by heating the sample at 600 °C for 1 h in a muffle furnace (Li et al., 2014). The total solid contents range from 11.8% to 51.1% and VS contents are 18.2%–72.3% (Table S2 of the SI), implying that properties of the sludge samples are distinctive in different sampling location and time, and the samples can represent characteristics of sewage sludge from WWTPs in China.

2.2. Extraction of MPs in dewatered sewage sludge

All sludge samples were homogenized before subsampling for extraction and before analysis of their dry weights. To extract the MPs, the method of Thompson et al. (2004) was followed with slightly adapted. In brief, 20 g of sludge was added to an Erlenmeyer flask with 300 ml deionized water in which sodium chloride (NaCl) had been added to saturation (1.2 g ml^{-1}). After stirring for 15 min, the mixture was settled for 2 h. Then, the top water layer was filtered in a vacuum filtration unit using a sieve with pore size of 37 μm. The extraction was conducted in triplicate, and thus all the extracts were collected in the sieve. The sieve in the vacuum filtration unit was then washed with more than 600 ml distilled water to remove any salt residues.

The extract in the sieve was sequentially treated with 100 ml hydrogen peroxide solution (H_2O_2, 30%), which was performed overnight, in order to remove the soft and easily disintegrating organic materials. The mixture was poured into 200 ml of distilled water, vacuum-filtrated through glass fiber filters, rinsed again severed time with deionized water, and dried in a desiccator for 3 days (Klein et al., 2015).

2.3. Quantification of MPs in dewatered sewage sludge

Each extract was inspected and counted using a Stemi 508 stereomicroscope (Carl Zeiss Jena, Germany) equipped with an Axiocam 506 color digital camera. The MP particles were classified according to their types into categories “fiber”, “shaft”, “film”, “flake” and “sphere” (Free et al., 2014; Su et al., 2016), and colors into categories “white”, “red”, “green”, “black”, “orange”, “blue” and others. The particle concentration is given as number of particles kg^{-1} dry sludge.

All particles were examined carefully for remaining natural organic during microscopic analysis (Talvitie et al., 2017). Obvious residual natural debris were excluded with microforceps or a dental explorer. Suspected particles was separated with the tip of a dental explorer and determined for hardness.

2.4. Quality assurance and control (QA/QC) of the MP extraction

To assess the separation power of the methods, recovery experiments with clean sludge and polymer standards were performed. Clean sludge was from the sludge after the MPs were extracted. Polystyrene (PS), polyethylene (PE) and polypropylene (PP) were used to simulate the MP portion of the sludge sample. Each polymer was picked two sizes, i.e. 380–830 and 75 μm. Each polymer particle was marked with a blue marker to ensure the accuracy of the determination. Fifty polymer particles were added to 20 g of clean sludge, and spiked for 15 min. Then, the extraction and quantification of polymer particles were conducted according the above methods. The number of particles separated from the sludge matrix was counted and then percentage efficiency of the extraction was determined. Results show that average extraction efficiency for three kinds of MP particles ranged from 67% to 98% (SI Table S4), which increased with increasing particle size. The relative standard deviations were 0.9–4.5%, indicating that the repeatability of the MP measurements was excellent.

During all steps of sample treatment, openings were wrapped using aluminum foil to avoid contamination with other particles or fibers. Synthetic clothing was avoided and working surfaces were cleaned with alcohol prior to use. When analyzing filter papers, a blank filter paper was placed in the open laboratory conditions to evaluate the possibility of air-borne contamination.

2.5. Morphology and identification of MPs

Pictures for representative MP particles were taken with the Axiocam 506 color digital camera. Scanning electron microscopy (SEM) was used to investigate the surface structures of MPs in the sludge samples (Mahon et al., 2017). A selection of MP samples (~10) extracted from the sludge were gold-coated (Emitecg K550, Quorum technologies, Ltd. UK) and were observed using a scanning electron microscope (Hitachi SU-1500, Hitachi High Technologies Corp., Japan) at beam energies between 2 kV and 30 kV. Chemical composition of the MP particles from the sludge samples was analyzed with Microscopes Fourier Transform infrared spectrometer (M-FTIR, IR/NicoletiN10 MX, Thermo Fisher Scientific, MA, USA). About 10% of the potential MP particles were randomly chosen for further identification (Mahon et al., 2017). Particles were hand-sorted from the filters with fine-tip tweezers under the stereomicroscope; they were then carefully rinsed with deionized water to eliminate the attached organic matter (Leslie et al., 2017). After air drying, the rinsed particles were put onto KBr windows for M-FTIR analysis. Thermo Scientific Hummel Polymer and Additives FTIR Library and Synthetic Fibers by Microscope FTIR Library were used to analyze the spectra, and then the MP types were determined and percentage of MP in potential MP particles for each WWTP was estimated.

2.6. Data analysis

The sludge samples were classified to different groups, as required. They were divided into eleven groups based on sampling location (provinces), to explore spatial distribution of MP concentration in the sludge, while the samples were classified into twelve groups on the basis of sampling month, in order to investigate temporal distribution of sludge-based MP contents. In addition, the samples were divided into 3–5 groups according to different WWTP parameters, to investigate effect of the processing parameters on MP concentration in the sludge. Details are given in the SI and Table S3.

To analyze possible factors influencing on spatial and temporal distribution of MP concentration in the sludge, the relevant information of eleven provinces investigated was collected from China statistical yearbook 2015 (NBSC, 2016), which includes population densities, total investment in fixed assets, the area of afforested land, and average temperature and rainfall. Analysis of correlation between average MP concentration and these

Table 1
Microplastic (MP) concentrations in dewatered sewage sludge from 28 WWTPs.

WWTP No.	Total solid content of wet sludge (%)	Range of MP contents ($\times 10^3$ particles kg^{-1} dry sludge)	Average of MP contents ($\times 10^3$ particles kg^{-1} dry sludge)
W1#	25.2	20.0	20.0
W2#	16.9–20.3	11.3–15.1	13.2 ± 1.9
W3#	17.8	13.8	13.8
W4#	14.0–19.2	7.60–26.7	15.9 ± 8.0
W5#	17.2–23.1	23.2–27.3	25.3 ± 2.0
W6#	26.0–26.6	7.00–8.50	7.70 ± 0.8
W7#	17.1–19.4	14.2–20.9	16.9 ± 2.7
W8#	23.9–34.0	10.3–48.2	29.6 ± 15.5
W9#	20.2–27.3	10.9–21.0	14.9 ± 3.7
W10#	18.1–24.1	17.2–39.7	24.8 ± 10.5
W11#	20.1–22.0	18.9–21.3	20.1 ± 1.2
W12#	19.2–30.7	19.3–43.2	29.2 ± 7.9
W13#	16.5–25.9	5.40–23.7	14.3 ± 6.4
W14#	14.8–18.9	18.3–46.2	32.1 ± 11.4
W15#	15.3–25.2	14.3–36.5	23.1 ± 9.1
W16#	15.0–20.7	28.0–49.1	38.5 ± 10.5
W17#	16.9	45.7	45.7
W18#	12.6–37.2	17.1–43.2	24.2 ± 9.8
W19#	20.3	18.0	18.0
W20#	19.1	12.6	12.6
W21#	16.9	37.5	37.5
W22#	16.6–19.2	31.0–54.6	46.0 ± 10.7
W23#	11.8	10.2	10.2
W24#	15.9–19.5	18.9–56.4	37.7 ± 18.7
W25#	17.0–51.1	1.60–20.6	11.1 ± 9.5
W26#	17.4	24.4	24.4
W27#	16.6–25.2	14.1–25.6	19.2 ± 4.8
W28#	13.2–20.0	19.6–23.6	22.2 ± 1.8
Total	11.8–51.1	1.60–56.4	22.7 ± 12.2

Table 2
Comparison of microplastic (MP) concentrations in different study areas as reported in the literatures.

Sample	Environment	Location	Location specification	MP size range	MP concentration (particles kg^{-1} dry sludge [a])	Reference
Sediment	Freshwater	China	Estuary	<5 mm	20–340	Peng et al. (2017)
Sediment	Freshwater	China	Lake	<5 mm	11.0–234.6	Su et al. (2016)
Sediment	Freshwater	China	River littoral zone	<5 mm	178–544	Wang et al. (2017)
Sediment	Freshwater	Germany	River shore	<5 mm	228–3763	Klein et al. (2015)
Sediment	Freshwater	Italy	Lake shoreline	<5 mm	112–266	Fischer et al. (2016)
Sludge	Wastewater	Germany	WWTPs	10 μm–5 mm	1000–24000	Lassen et al. (2015)
Sludge	Wastewater	Ireland	WWTPs	250 μm–4 mm	4196–15385	Mahon et al. (2017)
Sludge	Wastewater	Netherlands	WWTPs	0.7 μm–5 mm	370–950 [b]	Brandsma et al. (2013)
Sludge	Wastewater	Swedish	WWTPs	300 μm–5 mm	$16.7 \pm 1.96 \times 10^3$	Magnusson and Norén (2014)
Sludge	Wastewater	USA	WWTPs	No data	about 1–4 [c]	Zubris and Richards (2005)
Sludge	Wastewater	USA	WWTPs	<5 mm	5 [d]	Carr et al. (2016)
Sludge	Wastewater	China	WWTPs	37 μm–5 mm	1565–56386	present study

[a] DM, dry matter.
[b] The unit is particles kg^{-1} wet weight and the dry weights of the wet sewage sludge samples were all below 1%.
[c] The unit is particles per g.
[d] The unit is particles per 5 g.

parameters was carried out using GraphPad Prism 6 (GraphPad Software Inc., USA).

3. Results and discussion

3.1. Reliability of extraction methods

Ten percent of the suspected MP particles was randomly collected in the extracted particles and further analyzed by M-FTIR, in order to investigate the MP percentage. The result showed that the MP percentages in the samples from the 28 WWTPs ranged from 66.7% to 100% (SI Table S5), and the average was 78.27 ± 9.83%. In general, the current method for MP quantification are acceptable and reliable.

3.2. Characteristics of MPs

The concentrations of MP particles in the sludge samples were $1.60–56.4 \times 10^3$ particles kg^{-1} dry sludge with an average of $22.7 \pm 12.1 \times 10^3$ particles kg^{-1} dry sludge (Table 1). The sludge samples contained one or two orders higher concentrations of MPs than freshwater sediment from China, Germany and Italy (Table 2). That is because wastewater is enriched with vast MPs, and then most of them are retained in the sludge (Carr et al., 2016; Nizzetto et al., 2016a). Previous studies in Europe and the United States obtained MPs extracted from sludge in the range of $0.370–24.0 \times 10^3$ particles kg^{-1} dry sludge (Table 2), which were slightly lower than those obtained in the present study. This is possibly attributed to lower population densities and better waste management systems in high-income countries (e.g., Europe and the United States) than in low-income countries (e.g., China) (Jambeck et al., 2015; Lebreton et al., 2017).

The colors of MPs were white (59.6%), black (17.6%), red (9.0%), orange (3.3%), green (2.3%), blue (1.7%) and others (6.5%) (Fig. 1A). Meanwhile, fibers comprised a predominant portion of the MPs (63%), followed by shafts (15%), films (14%), flakes (7.3%) and spheres (1.3%) (Fig. 1B). They show that the predominance of white and fiber MPs in the present study is similar to the results obtained by Mahon et al. (2017) Talvitie et al. (2015) and Magnusson and Norén (2014). Fibers may have principally originated from washing of clothes and discharge of the fiber manufacturing industry (Mahon et al., 2017), while MP flakes are related to plastic production (Lechner and Ramler, 2015). Therefore, the results imply that laundry and plastic-industry wastewater may be the main source of MPs in the sewage sludge.

The sludge-based MPs are mainly composed of polyolefin (fibers and shafts), acrylic fibers (fibers), polyethylene (films), polyamide (films), alkyd resin (flakes) and polystyrene (spheres) (Fig. 2 and SI Fig. S2). The MPs belong to low-density plastics in this study, because high-density MPs such as polyvinylchloride (PVC; density: 1.14–1.56 g ml^{-1}) or polyethylene terephthalate (PET; density: 1.32–1.41 g ml^{-1}) cannot be extracted using concentrated sodium chloride (NaCl) solution (Klein et al., 2015). In addition, SEM analysis shows that the surface morphologies of the MPs are highly abrasive and the structures appear brittle and hackly (Fig. 3). These findings are consistent with those previously reported (Mahon et al., 2017; Zubris and Richards, 2005). It is well-known that decontamination of sludge is mandatory before disposal due to the presence of organic contaminants, heavy metal and pathogenic

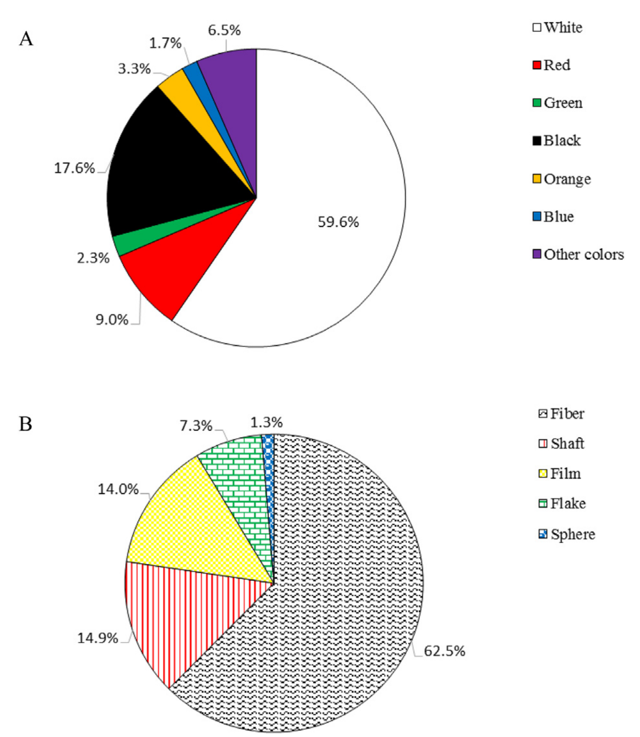

Fig. 1. Average percentages of different color (A) and shape (B) of microplastic (MP) particles in 79 sludge samples from 28 WWTPs in eleven Chinese provinces. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

microorganisms (Liu, 2016). However, the hackly surface of MPs allows the contaminants in sewage sludge to concentrate on the surface (Holmes et al., 2012; Koelmans et al., 2013, 2016; Rochman et al., 2014; Wright and Kelly, 2017; Ziajahromi et al., 2016). The enrichment effect of MPs may enhance the risks of sludge disposal on agricultural land, and this attribute of sludge-based MPs deserves further investigations.

3.3. Spatial and temporal distribution of MPs in sludge

As shown in Fig. 4, the concentrations of MPs are variable with sampling locations. Sewage sludge samples from Jiangsu Province and Shandong Province contained the highest average concentrations of MPs at 29.0×10^3 and 30.7×10^3 particles kg^{-1} dry sludge, respectively, while those from Yunnan Province contained the lowest average MP content, 7.70×10^3 particles kg^{-1} dry sludge in the 11 provinces. The results imply the greater concentrations of MPs in East China than in West China, possibly resulting from higher population density and total investment in fixed assets, and lower area of afforested land (SI Table S6). Correlation analysis between the parameters and average MP concentrations in sludge was carried out on the data from ten provinces except Shanghai city (SI Table S7). Shanghai city is a municipality directly under the Central Government, and its population density and total investment in fixed assets are much higher, but area of afforested land is much lower, compared with other provinces, and thus the data of the three parameters from Shanghai city were excluded for the correlation analysis. Correlation analysis shows that the average MP concentrations in sludge are significantly positively correlated with population density and total investment in fixed assets ($p < 0.05$),

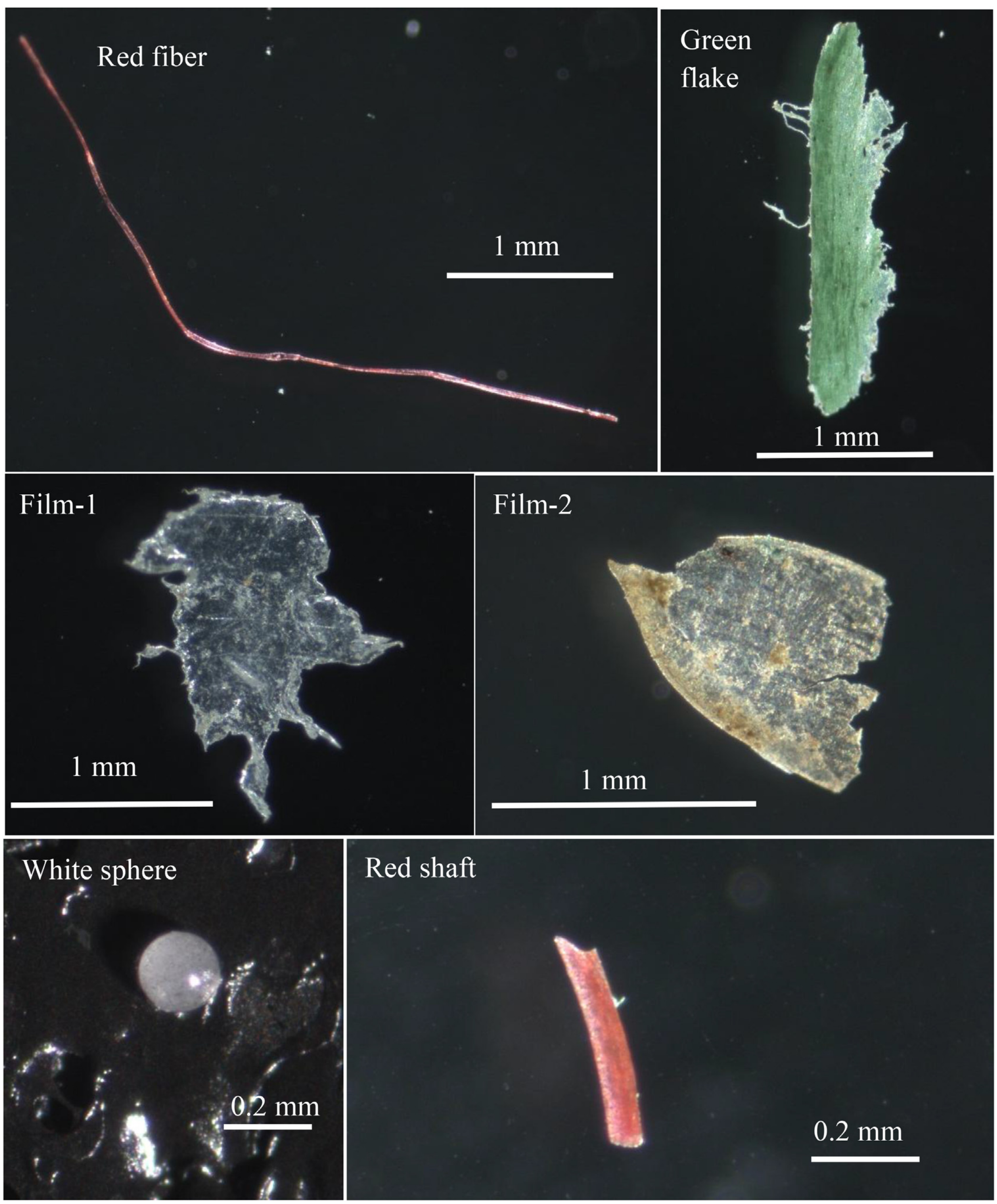

Fig. 2. Stereomicrograph of representative microplastic (MP) particles extracted from the sewage sludge.

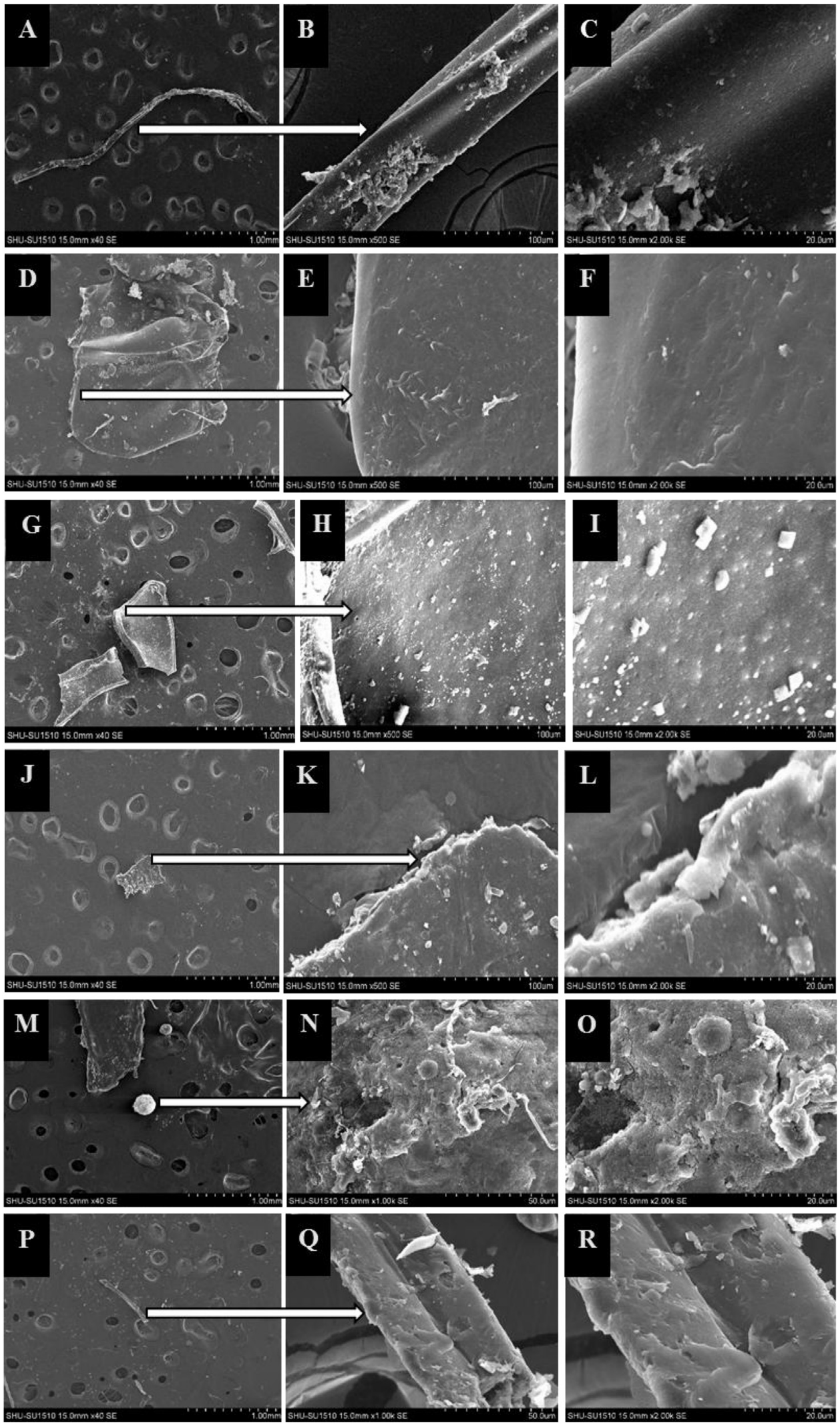

Fig. 3. Scanning electron micrographs of representative microplastics (MPs). A-C, fiber; D-F and G-I, film; J-L, flake; M-O, sphere; P-R, shaft.

but is significantly negatively correlated with area of afforested land ($p < 0.01$). The results indicate that the three parameters have a key influence on the spatial distribution of MP concentration in sludge.

Some studies about coasts, estuaries and rivers have shown that population density is an important factor influencing on MP concentrations (Browne et al., 2011; Jambeck et al., 2015; Lebreton et al., 2017; Yonkos et al., 2014). The possible reason is that higher population density in East China leads to higher consumption of personal care products and larger amount of laundry wastewater, and thus more discharges of MPs (Carr et al., 2016; Jambeck et al., 2015; Talvitie et al., 2015; Ziajahromi et al., 2016). Secondly, higher total investment in fixed assets for East China imply more infrastructure and industrial activity, and thus more industrial MPs from plastic and relevant industries is generated, causing greater amounts of industrial MPs to be discharged and retained in the sewage sludge. In addition, larger afforested land in West China may be related to lower population density, less impervious surfaces and fewer storm drains (Yonkos et al., 2014), implying lower MP concentration in rainwater and lower surface runoff, and thus less discharge of stormwater-based MPs. As most drainage systems within the sampling locations are a combination of wastewater and rainwater drains (Table S1 of SI), larger

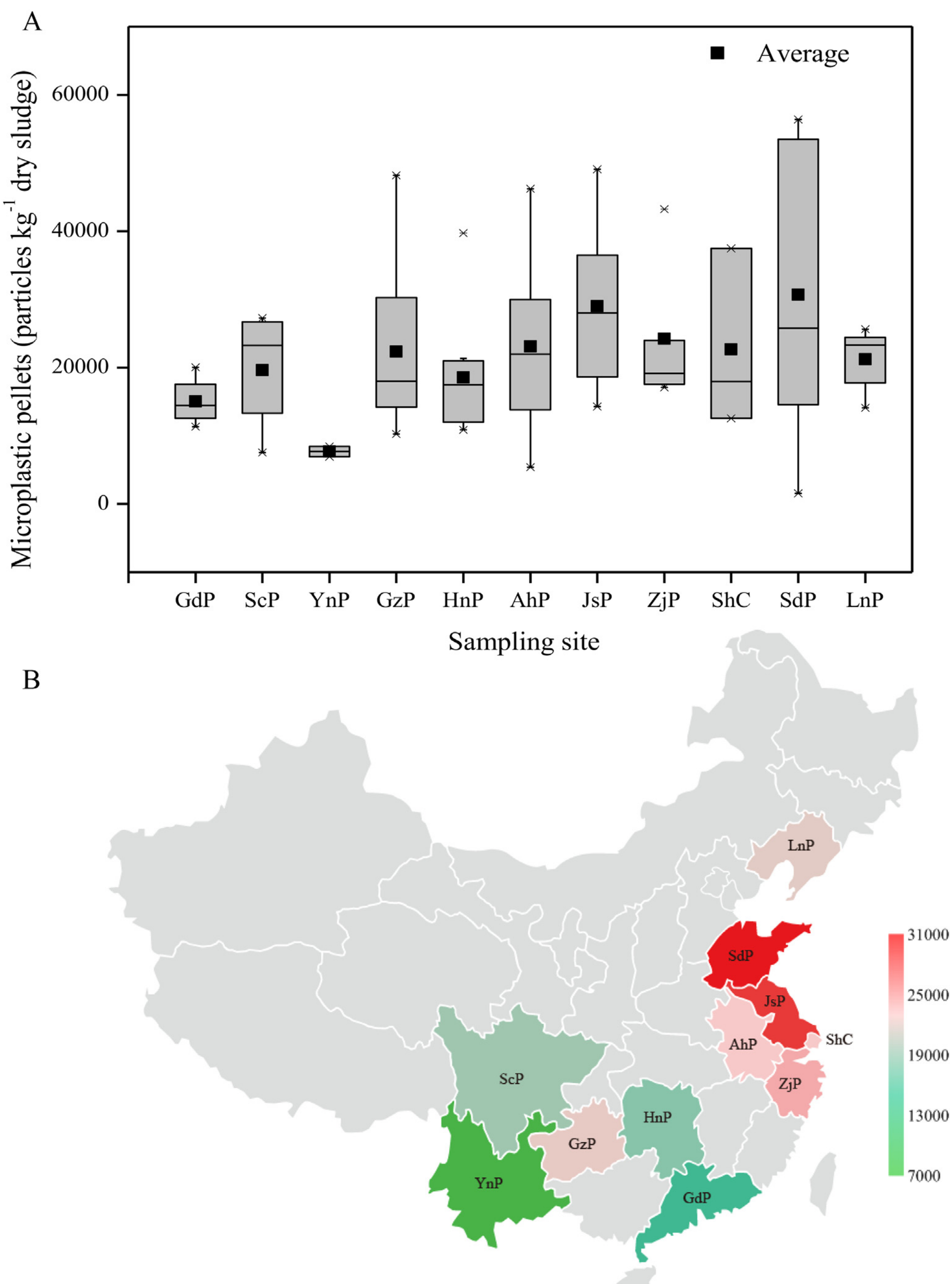

Fig. 4. Box plot (A) and planar graph (B, average) of microplastic (MP) concentration in dewatered sewage sludge from WWTPs in eleven provinces. GdP, Guangdong Province; ScP, Sichuan Province; YnP, Yunnan Province; GzP, Guizhou Province; HnP, Hunan Province; AhP, Anhui Province; JsP, Jiangsu Province; ZjP, Zhejiang Province; ShC, Shanghai city; SdP, Shandong Province; LnP, Liaoning Province.

afforested land may contribute to lower MP contents in sludge from West China. Therefore, the results imply that urbanization, economic prosperity and forest cover as an indicator of urban development in a catchment are controlling factors in the spatial distribution of MP in sludge of China.

Temporal distribution in MP concentration from sewage sludge are shown in Fig. 5. The average MP concentration in sewage sludge increased initially, and then decreased during the year of 2014–2015 except for February and October (SI Fig. S3). The results show that MP contents in sewage sludge are considerably seasonal in China excluding February and October. Meanwhile, monthly temperatures and rainfalls at capitals of the eleven provinces during 2014–2015 are also outlined in SI Table S8 according to China statistical yearbook 2015. Surprisingly, the average temperature and rainfalls have similar changing tendency with average MP concentrations in sludge as the sampling time (SI Fig. S3). If sampling time of all the sludge samples is added by two month, corresponding average MP concentration will be strongly correlated with the average temperature ($p < 0.05$) and rainfall ($p < 0.01$). These results imply that temperature and rainfall have important influence on the temporal variability of MP concentrations in sewage sludge, in accordance to the previous studies about the inputs of river-based plastics to ocean (Andrady, 2011; Lebreton et al., 2017; Yonkos et al., 2014).

The results demonstrate the spatial and temporal variabilities of MP concentrations in sludge. Thus sludge treatment and disposal technologies should be designed to tailor regional and seasonal needs. For example, land application of sludge may be required to reevaluate in regions with high MP concentrations. Additionally, anaerobic digestion can lower MP concentrations in sludge and therefore is necessary before sludge land application (Mahon et al., 2017).

3.4. Effect of WWTP parameters on the MP concentration

The influence of WWTP processes on MP concentration in wastewater has been investigated (Carr et al., 2016; Murphy et al., 2016; Talvitie et al., 2015, 2017), but their effect on MP concentration in sewage sludge remains largely unknown. Mahon et al. (2017) reported that sludge treatment processes can affect MP concentration in the sludge. This suggests that other WWTP parameters may also impact MP concentration in sewage sludge. In this study, the sludge samples were divided into different groups according to the WWTP parameters (SI Table S3), and MP concentrations for each group are shown in Fig. 6.

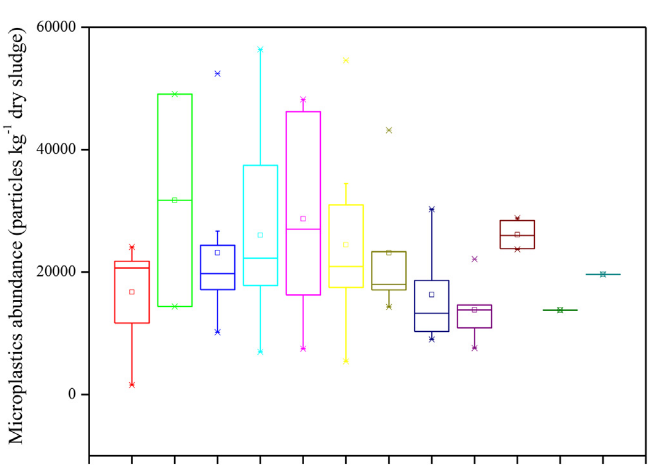

Fig. 5. Temporal distribution in concentration of microplastics (MPs) in the sludge samples. A, box plot; B, average MP concentration, histogram.

There is little difference in average MP concentration among groups by treatment capacity and servicing population (Fig. 6A and B), suggesting that the parameters have limited effect on MP concentration in the sewage sludge. However, they can have an effect on the sludge production, and then indirectly affect the release of sludge-based MPs from WWTPs to soils or other natural environments. In addition, the discharge standard of effluent also has little relation with average MP concentration in the sludge (Fig. 6F). Previous studies found that the majority of MPs in the WWTPs is removed during the early skimming and settling stages of primary treatment (Carr et al., 2016; Murphy et al., 2016; Talvitie et al., 2015). In this study, all the WWTPs have primary and secondary treatment; all the effluents are of high quality, reaching better than second levels according to the Chinese discharge standard of pollutants for municipal wastewater treatment plant (GB 18918–2002); thus the groups based on the discharge standard of effluent are similar in the average MP concentration.

Average MP concentration in sewage sludge has a decreasing tendency with the servicing area, implying that the parameter has an adverse effect on sludge-based MP content (Fig. 6C). It is well-known that the servicing area of the WWTP depends on the servicing population of WWTP and population density of the coverage. If the servicing population of WWTP is certain, the higher population density of coverage is, the less WWTP servicing area will be. As the population density is positively correlated with the MP concentration (Browne et al., 2011; Jambeck et al., 2015; Lebreton et al., 2017; Yonkos et al., 2014), it is reasonable that the average MP concentration decreases with increase in servicing area of WWTP (Fig. 6C). In addition, the average MP concentration tends to increase with increase in the industrial wastewater in WWTP influent (Fig. 6D), implying that the addition of industrial wastewater can cause the enhancement of MP in the sludge. Previous studies reported that one of the primary MP sources entering aquatic systems is industrial manufactures, such as plastic resin powders or pellets used in airblasting, and feedstocks used in manufacturing plastic products (Eerkes-Medrano et al., 2015; Lechner and Ramler, 2015; Ziajahromi et al., 2016). Lechner and Ramler (2015) found that industrial raw materials account for 79% of MPs in the Danube River. The results are additionally supported by the above results that average MP concentrations significantly correlate with total investment in fixed assets relating to infrastructure and industrial manufactures (SI Table S7).

As for secondary treatment, the group that went through anaerobic/aerobic (A/O) processes and their modifications has higher average MP concentrations than the groups that was treated by oxidation ditch and other processes such as sequencing batch reactor (Fig. 6E), showing that different wastewater biological treatment process results in different change in MP concentration in the sludge. Both of the A/O and oxidation-ditch processes have the anaerobic and anoxic zones, in order to gain favorable nitrogen removal efficiency (MOHURD, 2011). A pilot study showed that the plastic can be decomposed to produce biogas in anaerobic digesters (Talvitie et al., 2015), and thus part of MPs may be decomposed by microbe through the activity of exoenzymes (promoting depolymerization) during the A/O and oxidation-ditch processes (Mahon et al., 2017; Shah et al., 2008; Yoshida et al., 2016). In general, compared with the A/O process, the oxidation-ditch process has longer hydraulic retention time (HRT, more than 16 h) and sludge retention time (SRT, more than 15 days), causing that it might have greater influence on sludge-based MPs, and thus the average MP concentration in sludge from the WWTPs with the oxidation-ditch is lower than that using the A/O process (Fig. 6E). In addition, the MP difference between the processes might be also linked to the

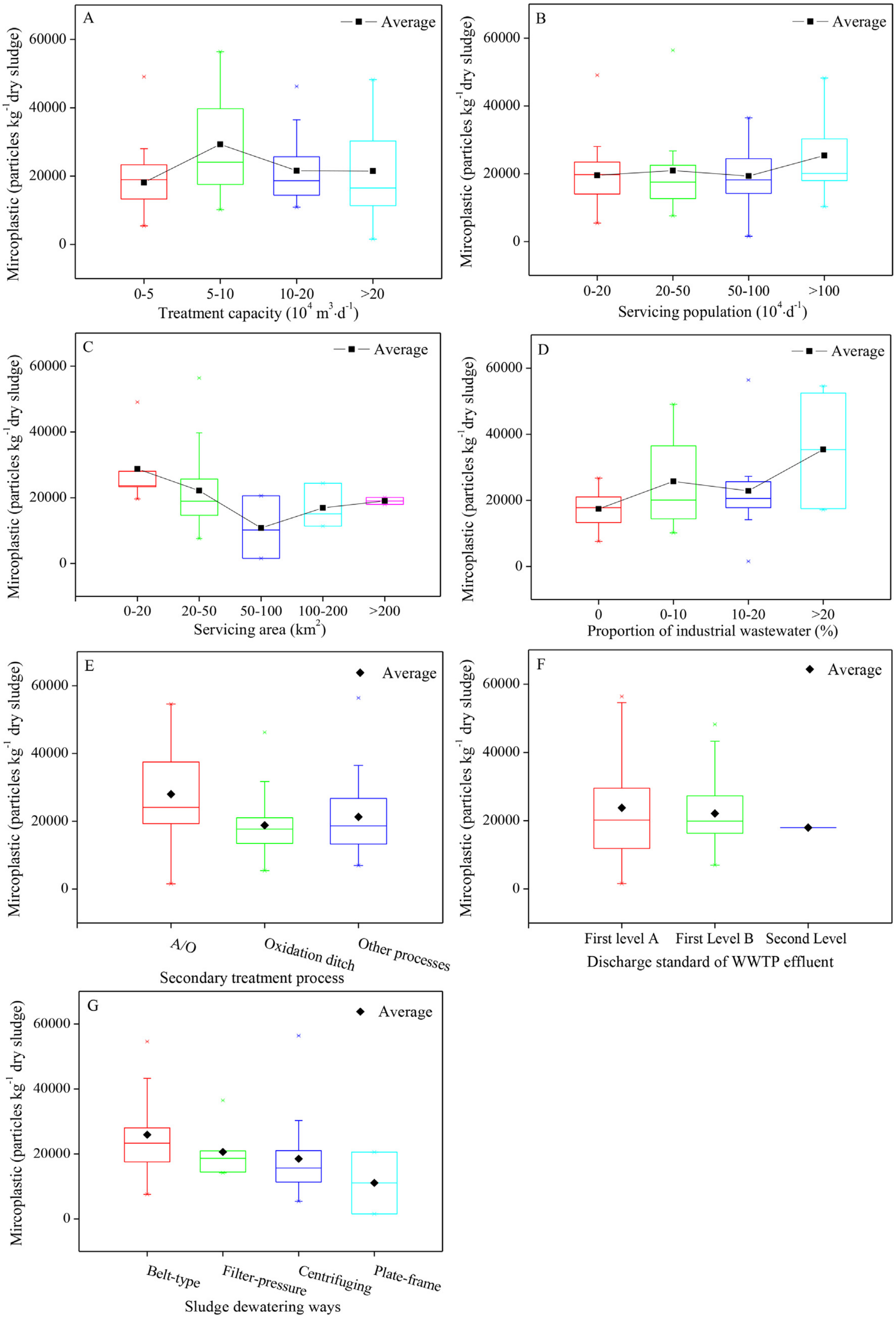

Fig. 6. Effect of WWTP parameters on the concentration of mciroplastics (MPs) in sewage sludge samples. A, treatment capacity; B, servicing population; C, servicing area; D, proportion of industrial wastewater in WWTP influent; E, secondary treatment process; F, discharge standard of the WWTP effluent; G, sludge dewatering process; A/O, including anaerobic/aerobic process and its modification; Oxidation ditch and its modification.

difference in settling efficiencies of sludge due to their diverse SRT. It deserves to further investigate possible reasons through controlled experiment.

Fig. 6G shows that the plate-frame group has lower average MP concentration than the centrifuged group, followed by filter-pressure and belt-type groups, indicating that the sludge from different dewatering has different MP concentration. It is well-known that different sludge dewatering methods have different operating principles. Belt-type, filter-pressure and plate-frame methods remove the water in sewage sludge through extrusion, while centrifugation dewaters sewage sludge based on the density difference between water and sludge. Part of the low-density MPs during centrifugation of the sludge may be released back into the water, thereby causing the sewage sludge using centrifugation dewatering to have lower average MP concentration. In addition, high drying degree of dewatering is often used for emergency treatment of the WWTP sludge by plate-frame filter pressing in China to date. In order to gain low moisture content of sludge (less than 60%), vase lime is often added during the process. The WWTP marked as W25# may have adopted the process. The S71 sludge sample from this WWTP holds hard character and low moisture (51.1%), which supports this assumption. However, the presence of vase lime in the samples may disturb the analysis for the MP concentration, and thus the S71 sample had the lowest concentration of MPs (only 1.60×10^3 particles kg^{-1} dry sludge) in all the sludge samples.

In general, the results show that some WWTP parameters have an important influence on MP concentrations in sewage sludge, indicating that it is possible to control MP pollution in dewatered sewage sludge by improving the WWTP parameters.

3.5. Implication and limitation of this study

It was estimated that eight million tons of dry sludge are generated in China in 2015 (MEPC, 2017). Meanwhile, Yang et al. (2015) reported that 83.6% of the sludge are dumped improperly and 2.4% of the sludge goes to land application; thus, 86.0% of the sludge is released to the soil and other natural environments. Therefore, according to the average MP concentration in the sludge, about 1.56×10^{14} particles of sludge-based MPs are discharged into the soil or other natural environments in 2015. The amount approximates the estimate emission of plastic microbeads from facial scrubs in mainland China (Cheung and Fok, 2017), but surpasses the accumulated number of MP particles (15–51 trillion) entering the global oceans from surface waters (van Sebille et al., 2015). In fact, the MP emission amount will increase with increasing sludge production due to the enhanced wastewater treatment capacity and numbers of WWTPs (Yang et al., 2015). Action plans for preventing and controlling water pollution were issued by the Chinese government in 2015 (MEPC, 2015). One of the aims is to enhance the decontamination rate of sewage sludge in cities up to 90-plus percent by 2020. Therefore, to achieve this goal, it needs to pay much attention to sludge-based MP pollution and its control techniques due to its potential risk to food and human health (Besseling et al., 2013; Holmes et al., 2012; Koelmans et al., 2013, 2016; Rochman et al., 2014; Wright and Kelly, 2017; Wright et al., 2013; Ziajahromi et al., 2016).

The limitations of this study are as follows. First, the MP concentration in the sludge is based on small sampling volumes and the NaCl solution extraction. Although the extraction and quantification method of MPs in dewatered sludge is acceptable in this study, it should be further optimized due to the presence of the bias. Second, the analysis about MP spatial-temporal distribution and the effect of WWTP-parameters on the MP concentrations are conducted through classifying the sludge samples according to the corresponding parameters (SI Table S3). However, each sludge sample contains multiple information, causing that the significant difference is not be found among the groups ($p > 0.05$). Clearly, controlled experiments are needed in the near future, to complement and confirm the findings.

4. Conclusions

MPs in the sewage sludge from WWTPs in China exceed that in freshwater sediment by one or two orders of magnitude, and also are higher than that from sludge in Europe and the United States. Their main source is from laundry and industry applications, and their surface morphology may act as a significant vector for toxic heavy metals and organic pollutants. Spatial distribution of sludge-based MPs is controlled by urbanization, economic prosperity and forest cover in China, while temperature and rainfall may affect MP temporal variability. Sludge treatment and disposal technologies should be designed to tailor regional and seasonal needs in terms of reducing possible MP pollution. In addition, it may be feasible to control MP concentration in sewage sludge through improving some WWTP parameters such as sludge dewatering methods. In China, hundred trillion particles of sludge-based MPs are discharged into the soil or other natural environments per year, and thus significant attention should be paid to sludge-based MP pollution and research effort invested into control techniques.

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Appendix A. Supplementary data

Additional tables and figures as mentioned in the main text. This supporting information is available free of charge via the Internet.

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.05.034.

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