Conversion of microplastics to flocs during estuarine mixing the Aras River with the Caspian Sea

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Abstract

Microplastics originated from various sources are carried by rivers into oceans, seas and lakes. In the last few years, the accumulation of microplastic particles in marine environments has been on the increase which causes irreversible damages to flora, fauna and human health. One of the most considerable processes in an estuary is the flocculation process. The flocculation process converts pollutants to flocs or greater particles. In the present study, the conversion of microplastics to flocs during estuarine mixing of the Aras River water and the Caspian Sea water is investigated for the first time. The results clearly show that a huge percentage of microplastics (99.95%) are converted to greater particles (> 5mm) due to the flocculation process. The maximum flocculation rate of microplastics (47.37%) is observed at the salinity of 0.25 ppt. Moreover, 35.71% of microplastics are flocculated at the salinity of 29 ppt. Salinity enhances the flocculation of microplastics.

Introduction

Plastics are synthetic organic polymers which can be utilized to manufacture various products (Ferreira et al. 2019; N V Lakshmi Kavya et al. 2020; Mason et al. 2018). Plastic particles smaller than 5 mm can be classified as primary and secondary microplastics (Klemeš and Jiang 2020). Primary microplastics are manufactured at a microscopic size for consumer care products or industrial uses, while secondary microplastics are degraded from larger-sized pieces (Cole et al. 2011; Frias et al. 2020; Han et al. 2020). Microplastics derived from various point sources and non-point sources are eventually carried by rivers into water bodies including oceans, seas and lakes (Bergmann et al. 2015; El Hadri et al. 2020; Thushari and Senevirathna 2020). In the last few years, the accumulation of microplastics in marine ecosystems has been on the increase (Bonanno and Orlando-Bonaca 2020; Fadare et al. 2020). Such pollutants in marine and aquatic environments have long-lasting detrimental effects on marine organisms (Eerkes-Medrano 2015; Jaikumar 2019; Ozturk and Altinok 2020). A wide variety of deadly diseases can be observed in marine and aquatic organisms because of exposure to microplastic particles (Anbumani and Kakkar 2018; Prokić et al. 2019). Microplastics are ingested by marine organisms and transported through the water bodies via the food chain, eventually causing irreparable damages to human health (McGoran et al. 2017; Santana et al. 2017; Susanti et al. 2020). Estuaries are semi-enclosed coastal areas where the mixture of freshwater from the river and saline water from the ocean occur (Heidari 2019). One of the most significant processes in an estuary is the flocculation process (Heidari 2019). A large percentage of pollutants is converted to flocs or greater particles due to the natural and estuarine flocculation process (Karbassi and Heidari 2015). The vital role of the flocculation process in the self-purification of pollutants gives aid to the pollution load of water bodies to be on the decline. In other words, the conditions of marine ecosystems are enriched due to the natural and estuarine flocculation process. In the present investigation, the effect of the flocculation process on converting microplastic particles to greater particles during estuarine mixing of freshwater from the Aras River and saline water from the Caspian Sea is studied for the first time.

Materials And Methods

Aras River with $5323 \times 10^6 \text{ m}^3/\text{year}$ mean annual discharge finds its way into the Caspian Sea. A wide range of marine organisms dwell in the Caspian Sea that is the world's largest lake. The location of sampling is indicated in Fig. 1.

Four Niskin bottles (30 L) were used to sample freshwater and saline water simultaneously (Bagaev et al. 2018). River water samples were collected from the Aras River upstream (Fig. 1). For preventing from the mixture of river water and seawater, saline water samples were collected approximately 20 km away from the Caspian Sea coast (Fig. 1). The HNO_3 and HCl were mixed to acid wash all equipment. Moreover, rinsing was carried out with running Milli-Q water. Collected samples were then passed through a $50 \mu\text{m}$ stainless steel sieve, stored in glass bottles and packed with aluminum foils. 30 L of fresh and saline water samples were filtered through MF-Millipore™ Membrane Filter, $0.45 \mu\text{m}$ pore size. For the flocculation experiments, 30 L of saline water sample was passed through $0.45 \mu\text{m}$ MF-Millipore™ Membrane Filter to ensure that the sample is free of microplastics. Different salinity regimes from 0.5 to 29 ppt were formed by mixing filtered saline water with freshwater at room temperature. Mixed samples were kept for 24 h with occasional stirring. The filters containing the microplastics and flocculated particles were left to dry and transferred to Petri dishes for further experiments. The visual identification technique was used to identify microplastics and flocculated particles preserved on the filters. Microplastic items were measured by a binocular optical microscope (Carl-Zeiss, Weet Germany) (de Lucia et al. 2014). The statistical analysis was done by the weighted pair group (WPG) technique (Karbassi and Heidari 2015). Salinity and electroconductivity were measured by EC/Salinity meter (HI98192). Thermometer DO meter (Inolab WTW) and pH meter (Metrohm 744) were utilized in measuring different parameters including temperature (T), dissolved oxygen (DO) and pH, respectively. Based on the photocatalytic oxidation (PCO) method, dissolved organic carbon (DOC) of samples was determined. The accuracy of the analysis was about $\pm 4\%$.

Results And Discussion

The concentration of flocculants at various values of salinity, dissolved organic carbon (DOC), pH, dissolved oxygen (DO), electroconductivity (EC) and temperature (T) are shown in Table 1. The microplastic abundance in freshwater and saline water is also presented in Table 1.

Table 1 Laboratory flocculation of microplastic particles during estuarine mixing

Sample	Salinity (ppt)	DOC (mg/L)	pH	DO (mg/L)	EC (μS/cm)	T (°C)	Microplastic particles (items/m ³)
River water	0.15	4.51	8.83	6.50	2100.00	21.00	3800.00
Saline water	30.00	N/A	8.27	5.80	58700.00	24.00	1800.00
1	0.25	3.00	8.30	6.90	1200.00	22.41	1800.00
2	1.00	4.20	8.31	6.90	6500.00	22.41	700.00
3	2.00	7.49	8.33	6.90	9800.00	22.41	900.00
4	3.00	10.56	8.36	6.90	10550.00	22.41	1200.00
5	4.00	14.71	8.38	6.90	11100.00	22.41	1000.00
6	5.00	17.86	8.41	6.90	11273.00	22.41	2000.00
7	6.00	20.00	8.44	6.90	11870.00	22.41	1600.00
8	7.00	24.00	8.46	6.90	12300.00	22.41	1200.00
9	8.00	23.00	8.47	6.90	12900.00	22.41	1200.00
10	9.00	22.00	8.49	6.90	13700.00	22.41	1500.00
11	10.00	27.00	8.52	6.90	14650.00	22.41	2000.00
12	11.00	28.00	8.55	6.90	15800.00	22.41	2100.00
13	12.00	29.00	8.56	6.90	16720.00	22.41	1900.00
14	13.00	30.00	8.58	6.90	17860.00	22.41	2160.00
15	14.00	32.00	8.60	6.90	18200.00	22.41	2270.00
16	15.00	31.00	8.62	6.90	18996.00	22.41	2300.00
17	16.00	33.00	8.64	6.90	19700.00	22.41	2300.00
18	17.00	35.00	8.66	6.90	20487.00	22.41	2360.00
19	18.00	37.00	8.67	6.90	21000.00	22.41	2390.00
20	19.00	39.00	8.68	6.90	22540.00	22.41	2300.00
21	20.00	41.00	8.72	6.90	25700.00	22.41	2300.00
22	21.00	43.00	8.74	6.90	27423.00	22.41	2400.00
23	22.00	45.00	8.77	6.90	29600.00	22.41	2410.00
24	23.00	46.00	8.78	6.90	31000.00	22.41	2410.00
25	24.00	47.00	8.79	6.90	32400.00	22.41	2430.00

26	25.00	47.00	8.80	6.90	34600.00	22.41	2441.00
27	26.00	46.00	8.81	6.90	37851.00	22.41	2400.00
28	27.00	48.00	8.82	6.90	40000.00	22.41	2400.00
29	28.00	48.00	8.81	6.90	44000.00	22.41	2420.00
30	29.00	52.00	8.88	6.90	47222.00	22.41	3798.00

According to Table 1, the abundance of microplastics in the Aras River and the Caspian Sea is respectively 3800 and 1800 items/m³. Natural and estuarine flocculation processes may not occur as indicated in Table 1. In other words, at the very first stages of estuarine mixing, some of the microplastic particles are removed from the freshwater in the form of flocculants (Table 2).

Table 2 Actual flocculation of microplastic particles during estuarine mixing

Sample	Salinity (ppt)	DOC (mg/L)	pH	DO (mg/L)	EC (µS/cm)	T (°C)	Microplastic particles (items/m ³)
River water	0.15	4.51	8.83	6.50	2100.00	21.00	3800.00
Saline water	30.00	N/A	8.27	5.80	58700.00	24.00	1800.00
1	0.25	3.00	8.30	6.90	1200.00	22.41	1800.00 (47.37%)
2	1.00	4.20	8.31	6.90	6500.00	22.41	0.00 (0.00%)
3	2.00	7.49	8.33	6.90	9800.00	22.41	0.00 (0.00%)
4	3.00	10.56	8.36	6.90	10550.00	22.41	0.00 (0.00%)
5	4.00	14.71	8.38	6.90	11100.00	22.41	0.00 (0.00%)
6	5.00	17.86	8.41	6.90	11273.00	22.41	200.00 (5.26%)
7	6.00	20.00	8.44	6.90	11870.00	22.41	0.00 (0.00%)
8	7.00	24.00	8.46	6.90	12300.00	22.41	0.00 (0.00%)
9	8.00	23.00	8.47	6.90	12900.00	22.41	0.00 (0.00%)
10	9.00	22.00	8.49	6.90	13700.00	22.41	0.00 (0.00%)
11	10.00	27.00	8.52	6.90	14650.00	22.41	0.00 (0.00%)
12	11.00	28.00	8.55	6.90	15800.00	22.41	100.00 (2.63%)
13	12.00	29.00	8.56	6.90	16720.00	22.41	0.00 (0.00%)
14	13.00	30.00	8.58	6.90	17860.00	22.41	60.00 (1.58%)
15	14.00	32.00	8.60	6.90	18200.00	22.41	110.00 (2.89%)
16	15.00	31.00	8.62	6.90	18996.00	22.41	30.00 (0.79%)
17	16.00	33.00	8.64	6.90	19700.00	22.41	0.00 (0.00%)
18	17.00	35.00	8.66	6.90	20487.00	22.41	60.00 (1.58%)
19	18.00	37.00	8.67	6.90	21000.00	22.41	30.00 (0.79%)
20	19.00	39.00	8.68	6.90	22540.00	22.41	0.00 (0.00%)
21	20.00	41.00	8.72	6.90	25700.00	22.41	0.00 (0.00%)
22	21.00	43.00	8.74	6.90	27423.00	22.41	10.00 (0.26%)
23	22.00	45.00	8.77	6.90	29600.00	22.41	10.00 (0.26%)
24	23.00	46.00	8.78	6.90	31000.00	22.41	0.00 (0.00%)
25	24.00	47.00	8.79	6.90	32400.00	22.41	20.00 (0.53%)

26	25.00	47.00	8.80	6.90	34600.00	22.41	11.00 (0.29%)
27	26.00	46.00	8.81	6.90	37851.00	22.41	0.00 (0.00%)
28	27.00	48.00	8.82	6.90	40000.00	22.41	0.00 (0.00%)
29	28.00	48.00	8.81	6.90	44000.00	22.41	0.00 (0.00%)
30	29.00	52.00	8.88	6.90	47222.00	22.41	1357.00 (35.71%)
Total	3798.00 (99.95 %)						

The values indicated in Table 2 are originated from Table 1 by subtracting the concentration of flocculated microplastics at a specific salinity regime from the previous steps. Based on Table 2, 99.95% of total microplastic particles (3800 items/m³) are converted to greater particles (>5mm) due to the flocculation process during estuarine mixing of the Aras River water and the Caspian Sea water. As a result, the flocculation process gives aid to the self-purification of microplastic particles (Fig. 2).

According to the conceptual model (Fig. 2), microplastic particles derived from point sources and non-point sources find their ways into the Aras River. In the estuary, the formation of flocculation process eliminates 99.95% of microplastics which plays a vital role in enriching the condition of the Caspian Sea in an appropriate manner (Fig. 2). In other words, the mass balance between the Aras River and the Caspian Sea is influenced by natural and estuarine flocculation process. Heidari (2019) clearly showed that trace metals are flocculated during estuarine mixing freshwater from the river with saline water from the sea. The flocculation rate of microplastics at the salinity of 0.25 ppt is 1800 items/m³ (47.37 %) (Table 2). A huge percentage of flocculants are formed at the earlier stages of mixing freshwater from the river with saline water from the sea (Farajnejad et al. 2017). Table 2 shows that 35.71% (1357 items/m³) of microplastics are flocculated at the highest studied salinity (29 ppt). The flocculation rate of microplastic particles at different salinities could be arranged in the following order (Table 2): 47.37% (salinity of 0.25 ppt) > 35.71% (salinity of 29 ppt) > 5.26% (salinity of 6 ppt) > lower than 3% (other studied salinities ppt). The flocculation of microplastic particles is varied during estuarine mixing due to forming various stages of mixing freshwater from the river with saline water from the sea. Such a condition gives aid to the negative net charge of microplastics to be on the decrease. A wide variety of salinity regimes including oligohaline (0.5-5.0 ppt), mesohaline (5.0-18.0 ppt) and polyhaline (18.0-30.0 ppt) can be seen in an estuary (Chang, 2012). The effect of salinity, DOC, pH, DO, EC and T on the flocculation of microplastic particles is illustrated in Fig. 3.

According to Fig. 3, the conversion of microplastics to greater particles (> 5mm) can be controlled by salinity, DOC and EC due to the high similarity coefficient (0.93). Moreover, flocculation of microplastic particles is governed by T, pH and DO with a similarity coefficient of around 0.86 (Fig. 3). Consequently, salinity, DOC, pH, DO, EC and T as effective factors enrich the flocculation of microplastic particles. Heidari (2019) showed that the natural and estuarine flocculation process is influenced by a wide variety

of factors including salinity, pH and dissolved organic carbon (DOC). The flocculation process was governed by dissolved oxygen (DO) (Karbassi and Heidari 2015). Considering the abundance of microplastics in the Aras River water (3800 items/m³) and the mean discharge of the river (5323×10^6 m³ /year), the annual load of microplastics carried by the Aras River into the Caspian Sea would be 2.02×10^{13} items/year. Nevertheless, the results of such a study clearly show that 99.95% of microplastic particles are flocculated during estuarine mixing of the Aras River water and the Caspian Sea water. As a result, the mean annual discharge of microplastics from the Aras River into the Caspian Sea would reduce from 2.02×10^{13} to 1.01×10^{10} items/year.

Conclusion

The results obtained in this study represent that 99.95% of microplastics are flocculated at salinities of 0.5- 29 ppt due to the natural and estuarine flocculation process. At the salinities of 0.5 and 29 ppt, 47.37% and 35.71% of microplastics were respectively converted to greater particles (>5mm) during estuarine mixing freshwater from the Aras River with saline water from the Caspian Sea. Flocculation of microplastics was governed by salinity. Natural and estuarine flocculation process remarkably reduced the microplastic load of the Caspian Sea which plays a vital role in enriching the conditions of marine ecosystems. As a result, the natural and estuarine flocculation process should be applied to eliminate microplastic particles from water bodies (oceans, seas, lakes and rivers) and different types of wastewaters.

Declarations

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Conflicts of interest/Competing interests (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)

Availability of data and material (Not applicable)

Code availability (Not applicable)

Ethics approval (Not applicable)

Consent to participate (Not applicable)

Consent for publication (Not applicable)

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Figures

Figure 1

The location of collecting freshwater and saline water samples

Figure 2

Conceptual model of microplastic particles in Caspian Sea

Figure 3

Cluster analysis of microplastics during estuarine mixing