Seasonal Variations of Microplastic Contamination in Surface Water of The Krishna River, Telangana

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Abstract
The distributions, chemical compositions and fate of plastics in aqua thabitats are still poorly understood, even though research on plastic contamination in freshwater and marinesystems is ongoing. This study aims to investigate the polymers of microplastic contamination in surface waters in the Krishna River. In this study, the occurrence, abundance and distribution, of micro-plastics were assessed in the surface water of Krishna River. In the Krishna River, the sites were sampled using a 50µm mesh-sized student plankton net and were analysed for micro-plastics. All the micro-plastics were secondary being derived from plastic materials utilized by the community. Plastic varieties that are found in the Krishna River, are polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS) and nylon 66 (N-66).

The occurrence of micro-plastics derived from the degradation of large plastic debris implies that proper plastic waste management measures be implemented in the communities operating on the lake and in its vicinity to safeguard the ecosystem benefits derived from the lake. The description and application of analytical methods include estimations of ambient contamination during sample collecting and processing. To measure and detect micro-plastic particles, Fourier Transform Infrared Spectroscopy (FTIR) and Pyrolysis-gas Chromatography (PyrGC/MS) were used.

Keywords: Microplastics, Irrigation, Ecosystem, Krishna River.

Introduction

Plastic particles less than 5 mm in size are referred to as microplastics[14]. Primary and secondary microplastics are the main sources of microplastics. The use of fishing nets and other fishing implements in aquatic aquaculture and the use of plastic films in agricultural cultivation are all potential sources of microplastic pollution[10]. Microplastics have drawn the attention of experts since it was discovered in 1972 that tiny plastic waste particles were present in the water[12]. Plastic products are easy to produce and utilize regularly. However, because of the severe pollution issue brought on by the inappropriate treatment of plastic trash, white pollution has come to be synonymous with plastic pollution[18]. Microplastics have been found in the deep sea as well as at the north and south poles. Microplastics can be found in deep water, sediment, soil and living things in addition to surface water[8].

Because of their unique sizes and stable characteristics, microplastics serve as both contaminant transporters and breeding grounds for microorganisms[5]. To enhance their functionality, plastic items are treated with flame retardants, plasticizers and other chemicals[21]. Microplastics have the potential to release these substances into the environment, posing serious ecological hazards[1]. Only two rivers, the Ganga River and the Nethravati River, with size ranges of 0.063–5 mm and 0.3–5 mm respectively have been the subject of field-based investigations on microplastics in rivers[12]. The sources and inflow processes of microplastics in rivers need to be better understood to efficiently prevent the release of microplastics in aquatic environments. For instance, the inflow processes from non-point sources of microplastics, as well as their point sources[1] should be discussed considering river pollutants. Rivers are the primary mode of conveyance for microplastic in the ocean[2,5].

Throughout the world, rivers allow 1.15 to 2.41 million tonnes of plastic waste to enter the ocean annually. 5.25 trillion plastic shards weighing more than 250000 tonnes are found in the world's oceans[8,22]. Because of their interactions with other contaminants in the environment and the subsequent exposure of these chemicals to living things, microplastics in the environment are a major cause for cancer[4]. As a result, animals are harmed chemically and physically when they swallow microplastic[3,13,20]. After the Ganga, Godavari and Brahmaputra, the Krishna River ranks fourth in India in terms of water inputs and river basin area[18]. The river spans around 800 miles (1,288 km).

Krishnaveni is another name for the river. For Telangana, Karnataka and Maharashtra, it is one of the main sources of irrigation. The Mahbubnagar district occupies 2,737.00 square kilometres (1,056.76 square miles)[7,16,19]. The Krishna River also flows through the regian in addition to the Tungabhadra. Their meeting place is Sangameshwaram. Research has demonstrated that the Krishna river is a primary source of microplastic pollution.

The main sources of microplastic pollution are untreated sewage water, religious presents and cultural festivals. Sewage water enters the river from the nearby communities. One of the primary human endeavours that contribute to the microplastic pollution in the Krishna river is the dumping of waste[15]. These materials have been reduced to microparticles. Because of its extreme verity and complexity, most of the mechanism under laying metal adsorption on microplastic is not known.

As a result, an effort should be made to comprehend the complex mixture of pollutants connected to this item. Studying the intractions between microplastic and other contaminants in freshwater is crucial to define the ecological importance of microplastic as a multiple stressor[17]. The fish pollution of the Krishna River in the Mahabubnager district is well known for its diversity, abundance and dispersion.

Study Area

The Krishna river rises roughly 1,300 meters (4,300 feet) in the Western Ghats, close to Mahabaleshwar, in the State of Maharashtra. It flows eastward from Mahabaleshwar to the town of Wai, where it empties into the Bay of Bengal. The Indian States of Maharashtra, Karnataka, Andhra Pradesh and Telangana are traversed by the Krishna river. It flows across Maharashtra (305 km/190 km), Karnataka (483 km/300 mi) and Andhra Pradesh (612 km/380 mi). It is approximately 1,400 km (870 mi) in length. The Krishna river, which flows through the Deccan plateau, is India's third-longest river after the Ganges and the Godavari. After the Ganges, Indus and Godavari, it is also the fourth-largest river basin in water inflows. The river, also known as Krishnaveni, has a total length of 1,400 km (870 mi), of which 282 km are in Maharashtra. Maharashtra, Karnataka, Telangana and Andhra Pradesh in India rely heavily on it as a source of irrigation.

The river Krishna starts from Maharashtra and flows through Jurala in Telangana. The Priyadarshini Jurala project, also known as the Jurala project, is a dam on the Krishna river that is located approximately 15 kilometres from Gadwal in the Jogulamba Gadwal district. Atmakur, in the Wanaparthy district of Telangana, India, is approximately 29 km away from the Jurala project. It is located at 16º20'15"N; 77º42'16"E. It passes through the Koilsagar and Beechupally. Koilsager is 65 km long from Jurala and Beechupally is 38 km long from Jurala. The water samples are collected from three selected sites (S1, S2 and S3) in January, May and September 2022.

Sampling and Precautions: The collection of water sample was carried out according to the seasons of Telangana which are four in number. According to Government of India, Ministry of Earth Sciences, Indian Meteorological Department, the period of November to February is of winter season while March to May is the summer season, followed by southeast monsoon as June to September. October and November constitute the post monsoon season of the Telangana region. All equipments were stored in dust dust-free environment. All the sampling bottles were labelled. The water samples were taken from surface water at a depth of 10 - 15cm. Before sampling, the temperature of air and water was checked.

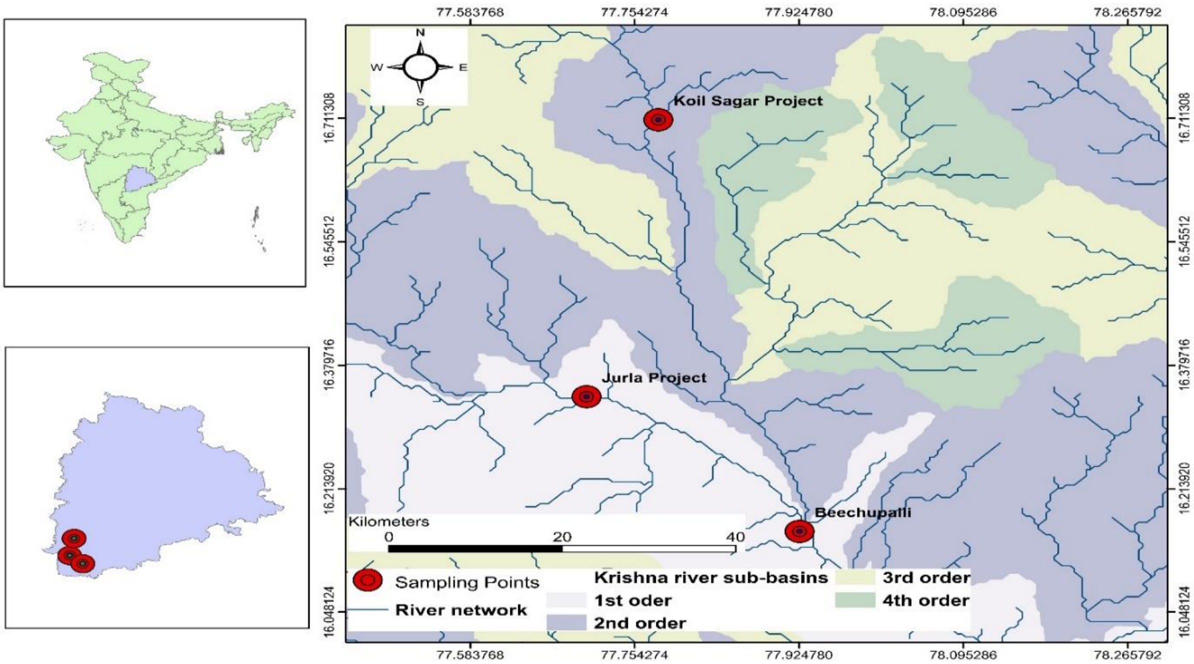


Fig. 1: **Krishna River showing sample collection sites S1, S2 and S3**

Table 1
Locations of water sampling stations of Krishna River

S.N.	Sampling stations	Latitude	Longitude
S1	Jurala	16º20'15"N	77º42'16"E
S2	Koilsager	16°42'33.73"N	77°46'44.08"E
S3	Beechupally	16º09'32.7"N	77º55'43.2"E

Laboratory sample processing: In a glass trough, the plankton net was cleaned using distilled water. In a lab setting, 40, 100 and 250 µm sieves were used to filter the net wash off in order to segregate microplastics according to size. To break down organic materials, an oxidation process was carried out with 30% hydrogen peroxide. Whatmann filter paper was used to filter the samples and subsequently cleaned with distilled water. For density separation, each 10 ml sample is mixed with 40 ml of potassium iodide. Lighter plastic particles are separated using density separation. At 3200 rpm, samples are centrifuged[6]. A Petri plate is used to collect the supernatant. Particles are subjected to visual inspection followed by hot needle test, FTIR and pyrolysis GC-MS techniques for identification and chemical analysis.

Fourier Transform Infrared Spectroscopy (FTIR): Plastic polymer particles can be accurately identified using Fourier-transform infrared (FTIR) spectroscopy based on their distinctive infrared spectra[11]. Infrared light causes molecular vibrations to be excited when it interacts with a sample. Excitable vibrations are wavelength-specific and rely on a substance's molecular makeup and structure. It is possible to detect distinctive infrared spectra because the energy of the infrared radiation that causes a certain vibration on the wave length, will be absorbed to a given extent. IR spectroscopy is an ideal method for identifying microplastics since plastic polymers have IR spectra that are extremely unique and have different band patterns.

Pyr-GC/MS analysis: Pyr-GC is used to analyse the products of heat degradation of macromolecules and to gain structural information about them by combining it with mass spectrometry (MS). Analysing identical samples under various circumstances such as raising the pyrolysis temperature, is known as sequential pyrolysis[9]. A database of programs was also created by analysing ten distinct varieties of the most used standard polymers. The analytical conditions for the Py-GC/MS system are: the column flow rate 0.25mm, length of 40m.df 0.25µm which detects the rate of sample flow at the mobile phase. Column oven temperature was 40^0C – 32^0C. 20^0C/min. 1min hold is a temperature program. It helps the separation of a compound. The mass range measure was m/z 29 - 400^0C which gives us a range at which we want to record our mass spectra. The detector temperature (MS) was 230^0C used for data recording, The Interference temperature was 300^0C which gives a temperature between GC and MS and GC temperature program was 40^0C – 180^0C at 15^0C /min and then to 300^0C at 5^0C/min, held for 12min.

Results and Discussion

FTIR Determination: FTIR analysis helped to identify the type of polymer present in the samples and to ascertain whether microplastic was present in them[11]. The microplastics listed polymer types were polystyrene, polypropylene and nylon-6. FTIR analysis of the samples of three sites showed a spectrum that was most consistent with nylon-6, polystyrene and polypropylene. In the winter season, FTIR spectra of particles (Fig. 2), S1 nylon-6 has one strong and sharp bond located at 3452.53 cm^{-1}. Polystyrene has one strong bond located at 1599.18 cm^{-1}. The additional peaks are known to be characteristic of polypropylene, with peak at 1358.03 cm^{-1}.

In the S2 FTIR spectra of particles, nylon-6 has two strong and sharp bonds located at 3451.73 cm^{-1} and 1603.00 cm^{-1}. The additional peaks are known to be characteristic of polypropylene. A peak at 1359.39 cm^{-1}. In S3 FTIR spectra of particles nylon-6 has two strong and sharp bonds located at 3442.76 cm^{-1} and 1604.58 cm^{-1} and polyethylene has one strong bond located at 1481.93 cm^{-1}. In the summer season, FTIR spectra of particles (Fig. 3), S1 nylon-6 has one strong and sharp bond located at 3442.72 cm^{-1}. Polystyrene has one strong bond located at 1630.44 cm^{-1}. The additional peaks are known to be characteristic of polypropylene, a peak at 1481.90 cm^{-1}. In the S2 FTIR spectra, nylon-6 has two strong and sharp bonds located at 3453.33 cm^{-1} and 1596.45 cm^{-1}.

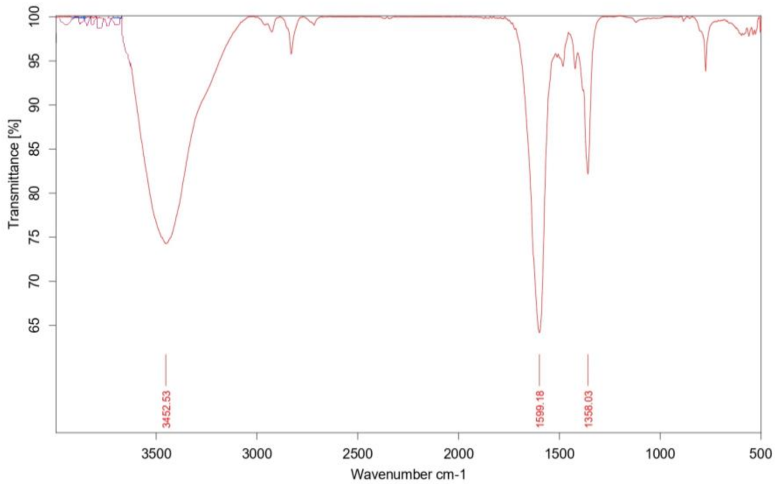
Table 2
Weight of sample residues (mg) in different mesh size filter cloth

Mesh size	S1 W	S2 W	S3 W	S1 S	S2 S	S3 S	S1 M	S2 M	S3 M	S1 PM	S2 PM	S3 PM
40µm	1.4	1.2	1.6	1.8	2.1	2.6	2.4	1.5	2.5	1.6	1.3	2.6
100 µm	2.1	1.4	2.3	2.7	1.8	2	1.8	1.2	2.2	1.3	1.7	2.3
250 µm	1.8	1.5	2.3	2.4	2.1	2.5	1.6	1.3	1.7	1.6	1.3	2.4

S1- Site 1, S2- Site 2, S3- Site 3, W – Winter, S – Summer, M – Monsoon, PM – Postmonsoon

Table 3
Statistical output of different sites and season

Mesh size	Winter season	Summer season	Monsoon season	Postmonsoon season
40	1.4 ± 0.2	2.2 ± 0.4	2.13 ± 0.55	1.83 ± 0.68
100	1.93 ± 0.47	2.16 ± 0.47	1.73 ± 0.50	1.76 ± 0.50
250	1.86 ± 0.40	2.33 ± 0.20	1.53 ± 0.20	1.76 ± 0.56



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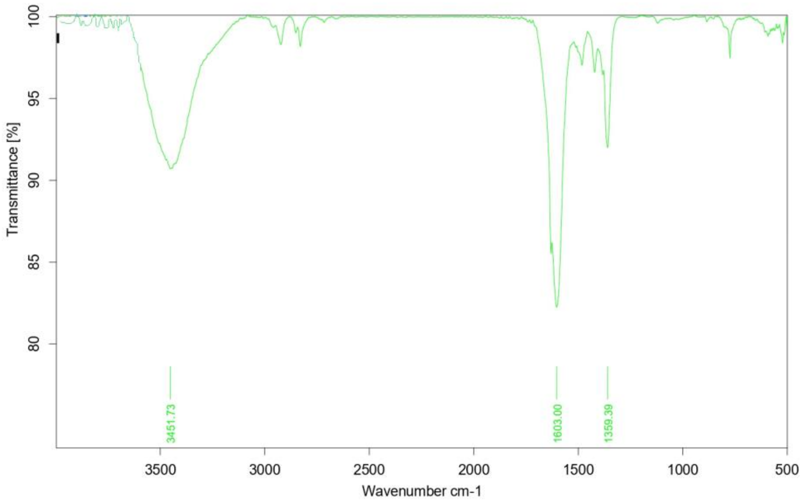

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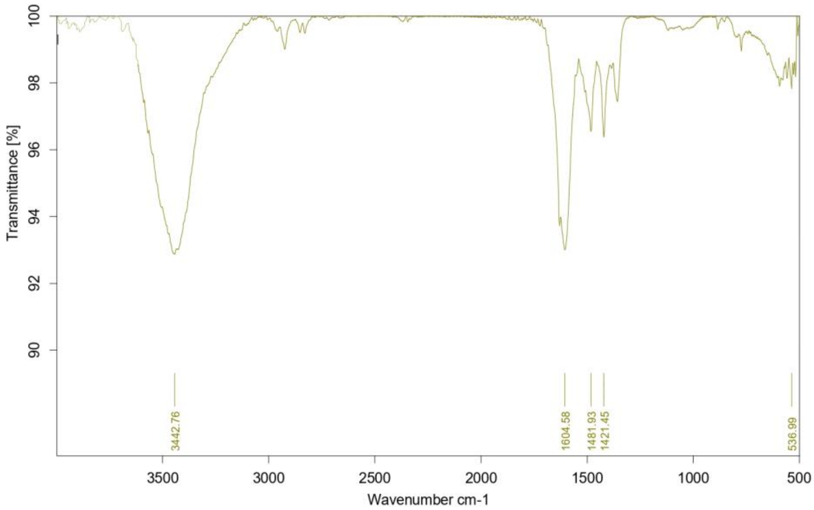

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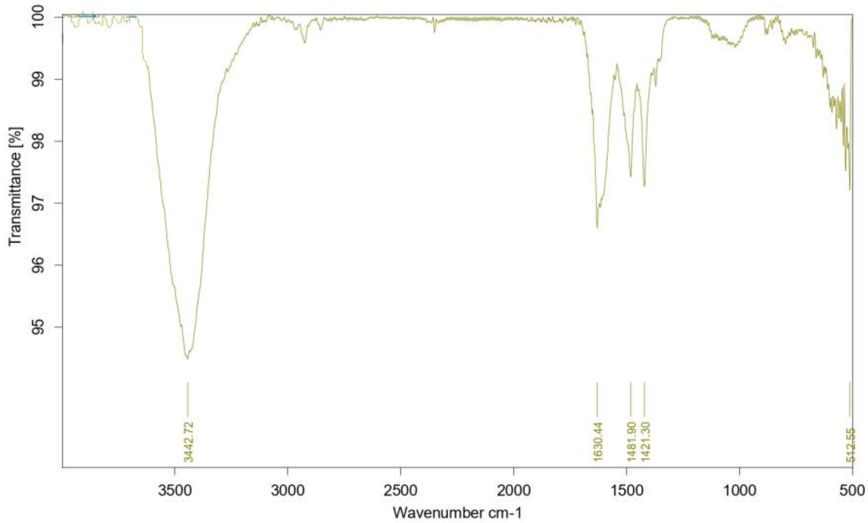
Fig. 2: FTIR Spectra of Particle of Winter Season (a- site 1, b- site 2, c- site 3)

The additional peaks are known to be characteristic of polypropylene a peak at 1352.78 cm^{-1}. In S3 FTIR spectra of particles, nylon-6 has two strong and sharp bonds located at 3451.77 cm^{-1} and 1599.14 cm^{-1}, polyethylene has one strong bond located at 1356.58 cm^{-1}. In the monsoon season, FTIR spectra of particles (Fig. 4) S1 nylon-6 has one strong and sharp bond located at 3450.79 cm^{-1}. Polystyrene has one strong bond located at 1600.51 cm^{-1}. The additional peaks are known to be characteristic of polypropylene, with peak at 1364.13 cm^{-1}. In S2 FTIR spectra of particles nylon-6 has one strong and sharp bond located at 3451.73 cm^{-1}. Polystyrene has one strong bond located at 1603.00 cm^{-1}. The additional peaks are known to be characteristic of polypropylene. In S3 FTIR spectra of particles, nylon-6 has one strong and sharp bond located at 3452.99 cm^{-1}. Polystyrene has one strong bond located at 1607.73 cm^{-1}. The additional peaks are known to be characteristic of polypropylene with peak at 1365.87 cm^{-1}.



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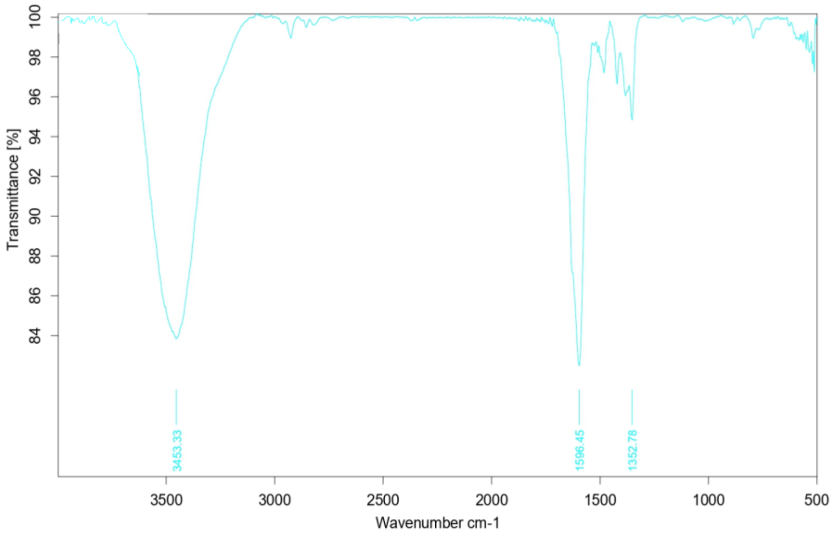

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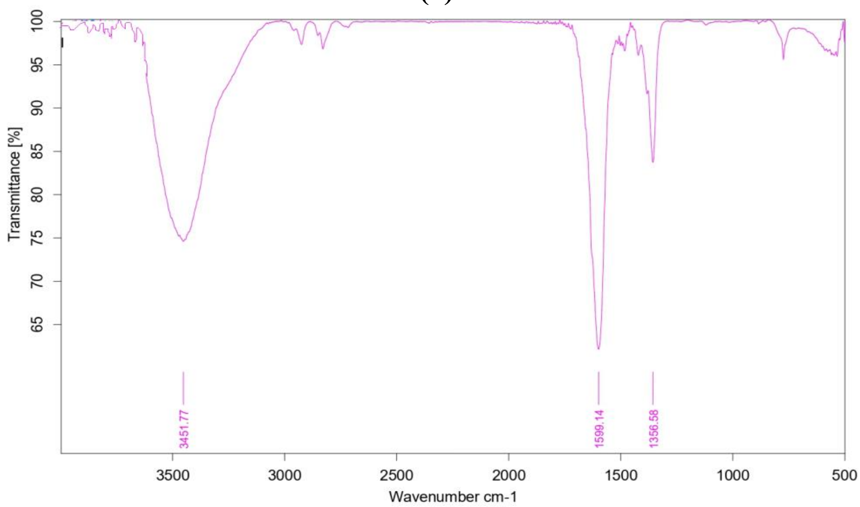

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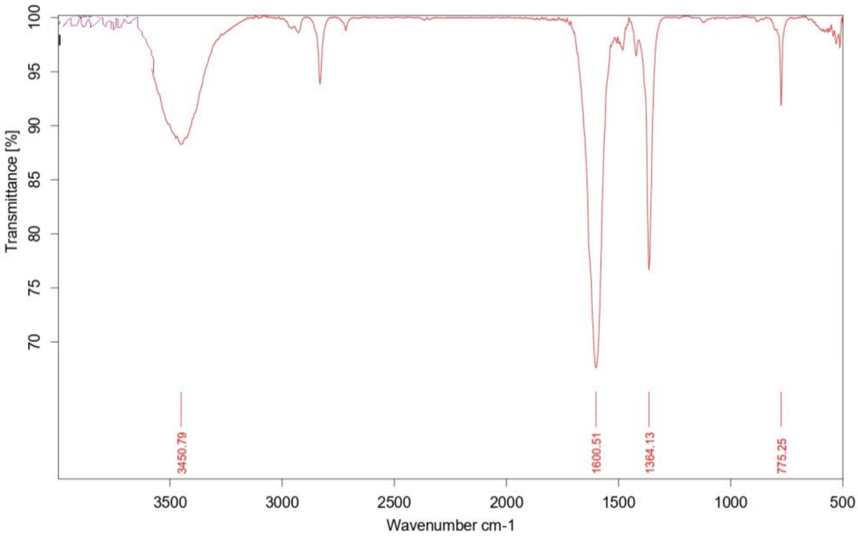
Fig. 3: FTIR Spectra of Particle of Summer Season (a- site 1, b- site 2, c- site 3)



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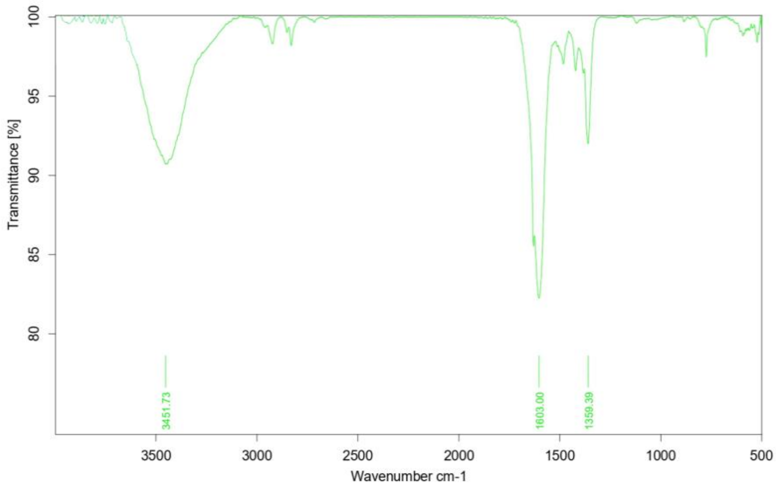

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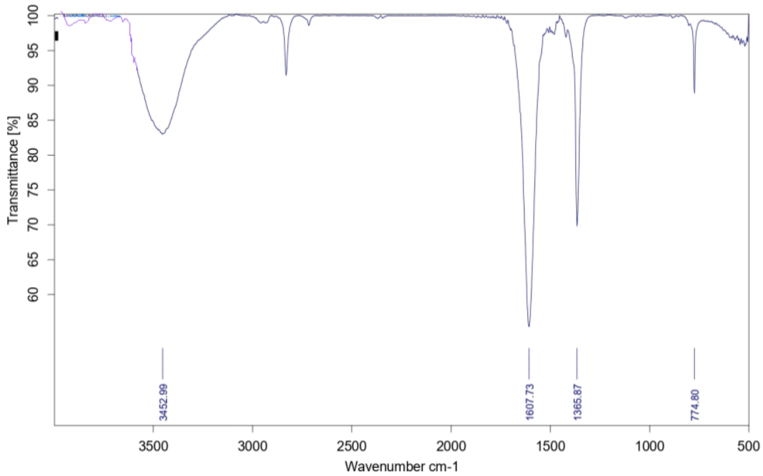

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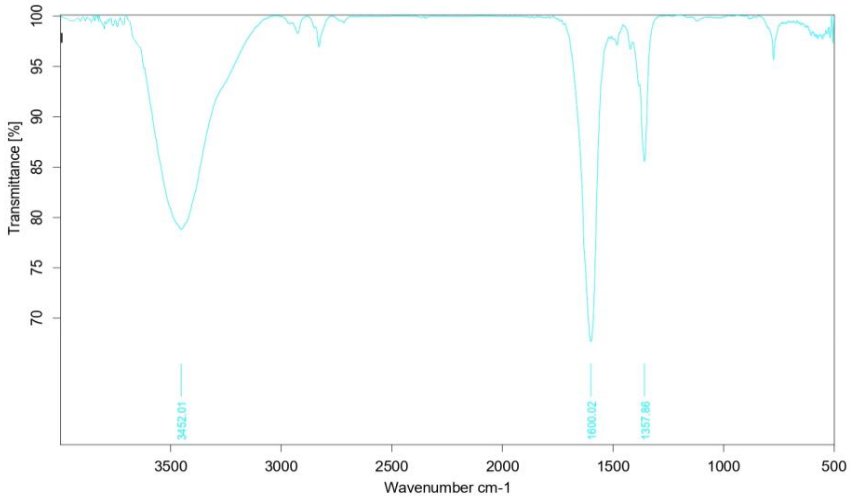
Fig. 4: FTIR Spectra of Particle of Monsoon season (a- site 1, b- site 2, c- site 3)

In post-monsoon season, FTIR spectra of particles (Fig. 5), S1 nylon-6 have one strong and sharp bond located at 3458.01 cm^{-1}. Polystyrene has one strong bond located at 1600.02 cm^{-1}. The additional peaks are known to be characteristic of polypropylene with peak at 1357.86 cm^{-1}. In S2 FTIR spectra of particles, nylon-6 has one strong and sharp bond located at 3445.62 cm^{-1}. Polystyrene has one strong bond located at 1604.97 cm^{-1}. The additional peaks are known to be characteristic of polypropylene with peak at 1361.95 cm^{-1}. In S3 FTIR spectra of particles nylon-6 has one strong and sharp bond located at 3443.52 cm^{-1}. Polystyrene has one strong bond located at 16604.35 cm^{-1}. The additional peaks are known to be characteristic of polypropylene with a peak at 1359.19 cm^{-1}.



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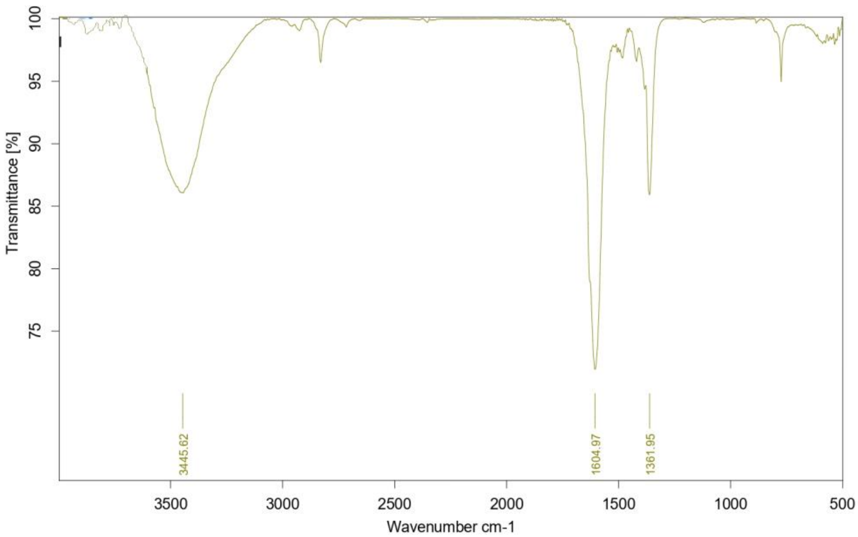

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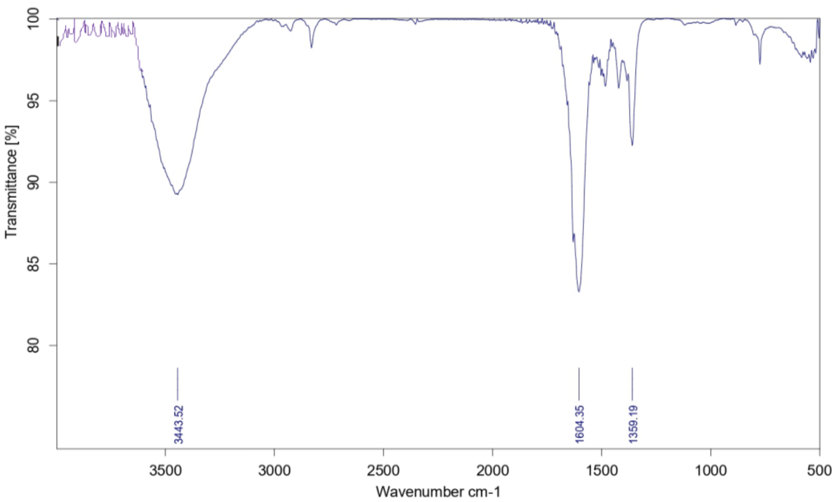

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Fig. 5: FTIR Spectra of Particles of post-monsoon season

Table 4
Polymer identification of Plastic Particles by using Py-GC/MS

Season	Study area	Polymer	Pyrolysis product	Retention time (min)	Initiation time (min)	Area %
Winter season	Site-1 (Jurala)	PS	1-Hexane	2.377	2.350	2.95
		PET	Benzene	2.759	2.725	1.27
		PVC	Toluene	3.537	3.495	0.20
	Site-2 (Koilsager)	PS	1-Hexane	2.410	2.380	4.53
		PET	Benzene	2.786	2.750	2.01
		PVC	Toluene	3.549	3.515	0.72
	Site-3 (Beechupally)	PS	1-Hexane,	2.416	2.380	1.48
		PET	Benzene	2.787	2.750	0.35
		PVC	Toluene	3.547	3.510	0.13
Summer season	Site-1 (Jurala)	PS	Butane 4-Hexene	2.169 2.715	2.120 2.695	8.34 0.47
		PET	Benzene, Benzene, (1-proplyctyl), Benzene, (1-ethynonlyn), Benzene, (1-methyldecyl)	2.790 12.321 12.576 13.026	2.745 12.285 12.540 12.990	2.69 0.12 0.15 0.14
		PVC	Toluene	3.550	3.510	1.26
	Site-2 (Koilsager)	PS	1-Hexene	2.405	2.375	2.29
		PET	Benzene, Benzene propanoic acid Benzene, (1-ethynonlyn)	2.784 4.783 12.569	2.740 4.740 12.530	1.05 0.21 0.11
		PVC	Toluene	3.546	3.505	0.60
	Site-3 (Beechupally)	PS	Butane1-chloro-3-methyl 1-Hexene	2.164 2.405	2.120 2.375	7.84 3.98
		PET	Benzene, Ethylbenzene Benzene, (1-butylheptyl)	2.783 4.440 12.867	2.745 4.410 12.160	1.95 0.24 0.08
		PVC	Toluene o-Xylene	3.540 4.520	3.505 4.520	1.06 0.24
Monsoon season	Site-1 (Jurala)	PS	1-Hexene	2.400	2.375	1.65
		PET	Benzene	2.773	2.740	0.60
		PVC	Toluene	3.547	3.510	0.37
	Site-2 (Koilsager)	PS	1-Hexene	2.409	2.380	7.55

			Hexene,3,3-dimethyl	2.985	2.975	0.94
		PET	Benzene,1,2,3,4-tetraflouro	2.720	2.700	0.93
			Benzene	2.790	2.750	3.21
			Benzene propanoic acid	4.788	4.745	0.49
		PVC	Toluene	3.551	3.510	0.86
	Site-3 (Beechupally)	PS	1-Hexene	2.438	2.400	3.24
			Hexene,2,3-dimethyl	3.792	3.765	0.22
		PE	Dodecane	7.920	7.880	0.17
			Hexadecane	8.880	8.865	0.23
		PET	Benzene	2.802	2.765	0.92
			Benzene(1-propyloctyl)	12.317	12.280	0.16
			Benzene(1-methyldecyl)	13.019	12.915	0.23
		PVC	Toluene	3.550	3.520	0.29
		N-66	Cyclopentane, 2,3-dimethyl	2.936	2.895	1.00
Post-monsoon season	Site-1 (Jurala)	PS	1-Hexene	2.403	2.370	9.91
		PE	Dodecane	7.933	7.915	0.07
			Hexadecane	10.743	10.720	0.08
		PET	Benzene	2.784	2.745	2.50
			Benzene, (1-pentylheptyl)	13.316	13.280	0.07
		PVC	Toluene	3.553	3.515	0.26
		N-66	Cyclopentane, 1,2-dimethyl	2.917	2.865	1.75
	Site-2 (Koilsager)	PS	1-Hexene	2.422	2.370	3.22
		PE	Dodecane	6.916	6.890	0.13
		PET	Benzene	2.796	2.755	0.76
			Benzene(1-methyldecyl)	13.025	12.985	0.12
		PVC	Toluene	3.556	3.520	0.29
	Site-3 (Beechupally)	PS	1-Hexene	2.376	2.350	2.37
			Hexene(2,3,4-trymethyl)	3.781	3.750	0.12
		PET	Benzene	2.755	2.720	0.51
		PVC	Toluene	3.536	3.500	0.20

Py-GC/MS analysis: The use of Py-GC/MS showing the polymer composition of microplastics is now well-described Pyrolysis products have been described for polymers of the "five" i.e. polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS) nylon 66 (N- 66) and polyethylene (PE). The pyrolysis of PS has generated specific peaks composed of1-hexene, butane, 4-hexene, butane1-chloro-3-methyl, hexene 3,3-dimethyl (Table 4).

The compounds found in all four seasons are benzene, benzene (1-proplyctyl), benzene ethynonlyn, benzene methyldecyl, benzene propanoic acid, benzene ethylbenzene, benzene (1-butylheptyl), benzene 1,2,3,4-tetraflouro, benzene pentylhoptyl (Table 4). Analysis of PVC generates only toluene and o-xylene (Table 4). The pyrolysis of PE is composed of dodecane and hexadecane whereas pyrolysis of N-66 has generated only cyclopentane 1,2-dimethyl (Table 4).

Conclusion

The water sample was collected from the three sites and treated with hydrogen peroxide, which precipitates any remaining residues in the water. The sample was then filtered using Whatmann filter paper with varying mesh sizes (40µm, 100µm and 250µm) and Py-GCMS analyses were conducted during the winter, summer, monsoon and post-monsoon seasons[28]. Thus, it may be said that microplastics of the types nylon 6 (N-6), Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) are present in the Krishna River. Every microplastic recovered from the Krishna River's surface water may serve as a possible multiple stressor since additional contaminants may cling to the microplastic.

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