MICROPLASTICS IN IRISH FRESHWATERS: A PRELIMINARY STUDY

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ABSTRACT

Microplastics in the marine environment have been recognized as an issue of concern in recent decades, leading to a significant body of research in this area, as summarised in recent review articles by by Andrady (2011) and Cole *et al.* (2014). Microplastics can be categorised as primary or secondary microplastics. Primary microplastics are manufactured with sub-millimeter dimensions and used in cosmetic products such as facial scrubs, in air-blasting processes for rust or paint removal, and as vectors for drug delivery in medicine. Secondary microplastics arise from the breakdown of larger plastic materials and debris, due to physical, chemical and biological processes in the aquatic or terrestrial environment. Microplastics are of concern due to their potential for ingestion and subsequent bioaccumulation by aquatic organisms from plankton to fish, birds and mammals, as well as their potential to release plasticizers and other additives by leaching and due to further breakdown of the microplastic particles (Wagner *et al.*, 2014).

Until recently however, there has been relatively little focus on microplastics in freshwater systems (Imhof *et al*., 2013; Free *et al*., 2014; Lechner *et al*., 2014) despite their obvious significance as inputs to the marine environment. To date, no data has been published on the prevalence or characteristics of microplastic pollution in Irish freshwaters. In this study we have validated methods for the detection, characterization and quantification of microplastics in water and sediment samples. Samples were collected from lake and riverine locations and the microplastics content was analyzed using physico-chemical tests and FTIR spectroscopy. Samples from wastewater treatment plants were also collected and analyzed in order to assess the contribution of these plants to microplastic inputs to freshwater systems.

Keywords: microplastics, sampling, characterization, freshwater, wastewater

1. Introduction

In recent decades, pollution of the marine environment by microplastic particles has been widely acknowledged as a significant issue, leading to a significant body of research focussing on this topic, as summarised in reviews by Andrady (2011) and Cole *et al.* (2014). Microplastics are of concern due to their potential for ingestion and subsequent bioaccumulation by aquatic organisms from plankton to fish, birds and mammals, as well as their potential to release plasticizers and other additives by leaching and due to further breakdown of the microplastic particles (Wagner *et al.*, 2014).

Polymers such as polyvinylchloride, polystyrene, and polycarbonate have been shown to release toxic monomers which are linked with cancer and reproductive abnormalities in humans, rodents, and invertebrates. In addition, various chemical additives are incorporated into many plastics, including catalysts (organotin), antioxidants (nonylphenol), flame retardants (polybrominated diphenyl ethers), and antimicrobials (triclosan). Lithner *et al.* (2011) have provided a comprehensive hazard ranking of polymers based on monomer classifications. Plastic materials can also adsorb and concentrate hydrophobic contaminants such as polychlorinated biphenyls from the marine environment at concentrations several orders of magnitude higher than those of the surrounding seawater (Mato *et al.* 2001). Therefore, ingested plastics could act as a mechanism facilitating the transport of chemicals to wildlife. A wide range of vertebrates and invertebrates have been shown to ingest and accumulate plastic

debris (Browne *et al*., 2011) and while the biological effects have not been definitively established, microscopic plastic particles have clear potential to cause harmful effects through the combined effect of their intrinsic toxicity and their large surface area.

There has been relatively little attention directed towards microplastics in freshwater systems, despite the obvious significance of rivers as inputs to the marine environment, as well as the potential for lakes to accumulate significant burdens of microplastic contaminants, with possible ecosystem effects. This study focusses on the detection, characterisation and quantification of microplastics in water and sediment samples from Irish freshwaters and wastewaters. Water and sediment samples were collected from a number of rivers and lakes in the Irish midlands and the microplastics content was analysed using a variety of physico-chemical tests and FTIR spectroscopy. Samples from wastewater treatment plants (WWTPs) were also collected and analysed in order to assess the microplastics contribution of wastewater discharges to freshwater systems.

2. Methods

Following separation from freshwater, wastewater and sediment samples by filtration and visual inspection, a number of simple physico-chemical tests were used to qualitatively identify plastic and microplastic materials. These included: (i) gravimetric tests based on flotation in media of different densities (deionized water, isopropyl alcohol, and olive oil), (ii) the copper wire test which identifies polymers containing chlorine, (iii) the acetone solubility test, and (iv) heating test using immersion in boiling water, and (v) wet peroxide oxidation (WPO). WPO was used to eliminate organic matter that was obtained in freshwater, wastewater and sediment samples. 0.05M Fe(II) solution was prepared by dissolving 3.755g of iron sulphate in 250 cm^3 of deionized water. 3 cm^3 of conc. sulphuric acid were added to help dissolve iron sulphate. 20 cm^3 of aqueous 0.05M Fe(II) solution was transferred into a beaker containing sediment/water sample with microplastics. 20 cm^3 of 30% H_2O_2 was added to the beaker and allowed to stand at room temperature for 5 minutes prior to heating. The mixture was then heated to 75^0C until gas bubbles were observed and removed from heat until boiling subsided. The mixture was heated for additional 30 minutes to 75^0C. 7g of NaCl was added to increase the density of the aqueous solution. The mixture was then heated until all the salt dissolved. Visible microplastics were removed and dried in oven for 30 minutes at 40^0C. To validate the method, 0.0988g of polymer sample was added to a reference sediment sample. WPO was performed on the reference sample using the procedure described above. 0.0981g (99.3%) of the polymer was recovered.

Microplastic materials recovered from samples were analyzed using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Spectra were recorded as % transmission using a Perkin Elmer, Spectrum 65 FT-IR Spectrometer.

Analysis of wastewater samples: Samples from three wastewater treatment plants (WWTP) were collected and analyzed; these were at Portlaoise, Co. Laois, Mortarstown, Co. Carlow, and Tullow, Co. Carlow. These plants discharge treated effluent to the Triogue, Barrow, and Slaney Rivers respectively. The samples were obtained in large containers according to WWTP sampling protocol. The treated wastewater sample was passed through a sieve (Fisherbrand Test Sieve BS410-1:2000 180 MIC). The remaining organic particles were introduced to WPO. Microplastics found were dried in the oven, analyzed using ATR-FTIR, and visually inspected under a microscope.

Analysis of freshwater and sediment samples: Four freshwater bodies were sampled: River Barrow (three sampling locations), River Nore (two sampling locations), Lough Lurgan (Cushina, Co. Offaly) and River Liffey (Newbridge, Co. Kildare). Water samples were obtained by *in situ* and *ex situ* methods. *Ex situ* water samples were collected in appropriate containers and transported to the laboratory. The water was then sieved; visible microplastics were examined under the microscope and analyzed using ATR-FTIR. *In situ* sampling was performed by immersing the sieve directly into the river flow for specified periods of time. After sampling, visible MPs were analyzed under the microscope and using ATR-FTIR. Sediment samples were

collected in appropriate containers and transported to the laboratory. Sediment was sieved, after which any visible microplastics were subjected to wet peroxide oxidation. Following this procedure, microplastics were dried and analyzed under microscope and using ATR-FTIR.

3. Results

Figure 1 shows a variety of polymeric materials recovered from wastewater and freshwater samples. Tables 1 and 2 summarize the results of analysis of samples from wastewater and freshwater sources respectively. The polymer most commonly detected in freshwater was polystyrene, found at four locations (R.Barrow, R.Liffey, R.Nore and Lough Lurgan). FTIR spectra for polystyrene samples recovered from freshwater samples (not shown due to space constraints) exhibited some differences from the polystyrene reference spectrum, likely due to degradation of the polymer in the water/sediment body, and/or the presence of additives. Polyethylene was found at R. Liffey, R.Nore (Bennettsbridge) and Derryounce Lake, ranging in size from 7.64mm (R.Nore) to 15.55mm (R. Liffey). FTIR spectra identified polymer in samples from Portlaoise WWTP as polyethylene.

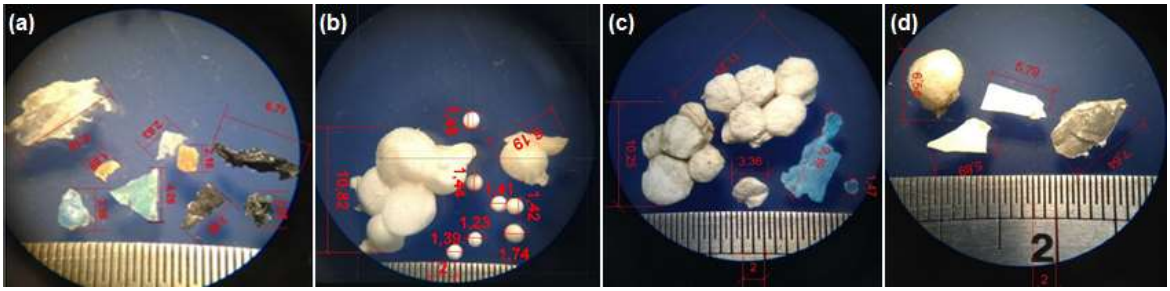

Figure 1: Polymer fragments recovered from samples collected from (a) Portlaoise WWTP, (b) River Barrow, (c) Derryounce Lake, (d) River Nore. Dimensions in mm.

Table 1: Summary of results for freshwater samples (MP = microplastics).

Freshwater	Date and time	Volume sampled	Water /sediment	Comments
R.Barrow	10/02/2015	5.4L	Water	Carlow Town. No MP found.
	11/02/2015	18.5L	Water	Carlow Town. No MP found.
	18/02/2015	125L	Water	Carlow Town. No MP found.
	25/02/2015	600cm^3 water sample 1200cm^3 sediment sample	Water and sediment	Location: by Dolmen Hotel. No plastics found in sediment samples. Polystyrene found in water sample.
	5/03/2015	41.52m^3 in 20 min	Water	Location: Milford. No MP found
	10/03/2015	108m^3 in 1 hour	Water	Location: Milford. No MP found
Lough Lurgan Cushina, Co. Offaly	26/02/2015	1.4L sediment	Sediment	Polystyrene and blue polymers found
R. Bauteogue, Stradbally, Co.Laois	26/02/2015 14/03/2015	62.28m^3 in 30 min 67.5m^3 in 30 mins	Water Water	No MP found No MP found
R.Nore, Abbeyleix, Co.Laois	01/03/2015 07/03/2015	54m^3 in 30 min 202.5m^3 in 1 hr	Water Water	No MP found No MP found
R.Nore, Bennettsbridge, Co. Kilkenny	15/03/2015	31.76m^3 in 1 hr	Water	1 polystyrene, 2 white polymer particles and 1 food wrapper polymer
R.Liffey, Newbridge, Co.Kildare	06/03/2015	63.52m^3 in 1 hour	Water and sediment	1 polystyrene (water sample) 1 blue polymer (visual sorting)

Table 2: Summary of results for wastewater samples.

WWTP	Date	No. of samples	Sampling point and (volume)	No. of MP found	Size range	Particle colour
Portlaoise	29/01/2015	3	AIW (400cm^3) AC(13L) ATF (400cm^3)	AIW (6) AC (22)	<8mm	blue, white black, brown, red
	11/02/2015	3	AIW (15.5L) AC (5L) ATF (4.5L)	AIW (4) AC (5)	<3mm	black, blue
	04/03/2015	3	AIW (4L) AC (4l) ATF (4L)	AC (4)	<3mm	black
	11/03/2015	3	ATF (4L) AIW (4L) AC (15L)	AC (31)	<14.75mm	yellow, red black, blue
Mortarstown	04/02/2015	3	AIW (5L) AAT (3L) AC (13L)	AAT (2)	<3mm	black
Tullow	06/02/2015	3	AIW (5L) AAT (5L) AC (4.5L)	AAT (1)	3.63mm	green

Key: AIW- After Inlet Works; *AC- After Clarifier; *ATF- After Tertiary Filters; *AAT- After Aeration Tank

4. Conclusions

While no microplastics were recovered from the majority of freshwater samples, there is sufficient evidence of microplastics contamination to suggest that sampling over longer periods of time and with wider coverage is justified in order to obtain a more representative picture of microplastics pollution in Irish rivers and lakes. Polystyrene and polyethylene were the predominant polymers detected in freshwater samples. Significant numbers of microplastic particles were detected in samples collected from three wastewater treatment plants. Results of samples taken from different points in the treatment processes indicated that the majority of microplastics were removed during treatment; however there is clear evidence that there is a significant microplastics content in Irish municipal wastewaters. Further investigation of the sources and fate of these materials is required.

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