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Final report - Open

Analysis of microplastics in sediments from the Hywind Scotland wind farm

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CLIENT(S)	CLIENT'S REFERENCE
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Abstract

The aim of the project was to quantify and characterise microplastic (MP) particles in sediments collected under and in the vicinity of an offshore wind farm (Hywind Scotland), with particular focus on assessing the presence of (i) particles derived from wind farm rotor blades and (ii) background microplastic level from other sources.

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1 Background and objectives

There is currently a lack of scientific information about the contribution of the offshore wind energy sector to the total microplastic (MP) emissions to the oceans. It is known that leading edge erosion and subsequent repair work can lead to the emission of particulate materials. Similarly, leading edge protection materials may also act as a source of polymer-based particulate emissions. The client (Equinor ASA) was interested to assess the MP content present in sediment samples collected under and in the vicinity of an offshore wind farm (OWF, Hywind Scotland) with a specific focus on the occurrence and quantification of larger MP (>300 µm) derived from the OWF infrastructure (e.g., coatings from rotor blades and leading-edge protection materials), as well as the background levels of other MP from other sources. Sediment samples were collected from Hywind Scotland as part of a larger cruise that took part in the Norwegian and Barents Sea in May and June 2022 (Møskeland and Fjukmoen, 2023). The survey at Hywind Scotland OWF area was conducted from the vessel "Olympic Electra" in the period 11-12 of May 2022. An overview of the location of the sampling locations and infrastructure at Hywind Scotland is presented in Fig. 1.
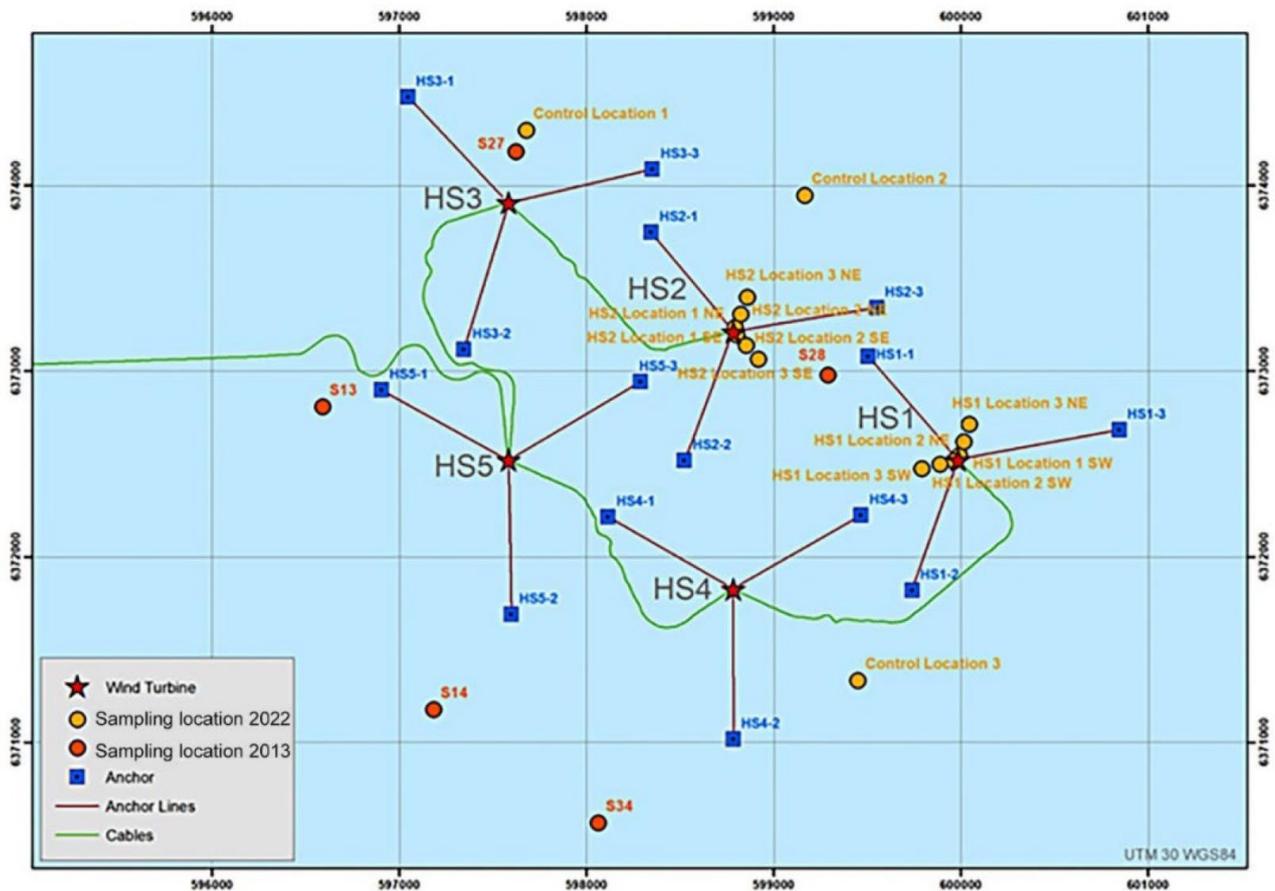
Figure 1: *Overview of the location of the sampling locations and infrastructure at Hywind Scotland (Reproduced from Møskeland and Fjukmoen, 2023).*

Methods for the general extraction, clean up and analysis of MP from sediments are well established (e.g., Lorenz et al., 2019) within the MP field and are validated for many polymers, especially thermoplastics such as polyethylene (PE) polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinylchloride (PVC). However, OWF coating materials may represent a potentially specific type of polymer and to ensure that these particles can be reliably identified and quantified there is a need to have prior knowledge about the polymer composition (for spectral library matching) and verification that the standard extraction and sample clean up techniques to do not damage the particles in any way (dissolution, fragmentation etc).

The aims of the project were (i) to quantify and characterise the MP (>300 µm) content in sediment samples collected from an OWF area and to define the proportion of the MP derived directly from coatings of the rotor blades of the OWF infrastructure, and (ii) determine the background MP levels of conventional thermoplastic polymers (e.g. PE, PP, PS, PET, PVC).

These aims were achieved through the following secondary research objectives:

- Testing the physicochemical effects of the established MP extraction procedure on laboratory-generated particles from coatings used in the Hywind Scotland OWF infrastructure and verification that the extraction procedure has negligible impacts on the pristine reference materials.
- Removal of biogenic material and mineral particles from sediment samples and isolation of MP.
- Quantification (number of particles) and physicochemical characterisation of extracted MP (colour, size, shape, and polymer composition) using a combined approach of microscopy and FTIR analyses and assessment of the presence of coating particles deriving from OWF rotor blades and leading-edge protection material.

2 Material and Methods

2.1 Validation of the extraction procedure and chemical fingerprint of the reference materials

2.1.1 Reference particles

Reference microparticles (RMP) >300 µm from 3 examples of coating materials provided by Equinor were artificially produced in the laboratory. The three materials were:

- Coating A – leading edge protection material
- Coating B – Top (surface) layer of rotor coating
- Coating C – Subsurface layer of rotor material

The different RMPs were prepared by either (i) scraping the coating surface with a scalpel (coatings B and C), or by cutting the bulk material into particles (coating A) (Fig. 2, left column).
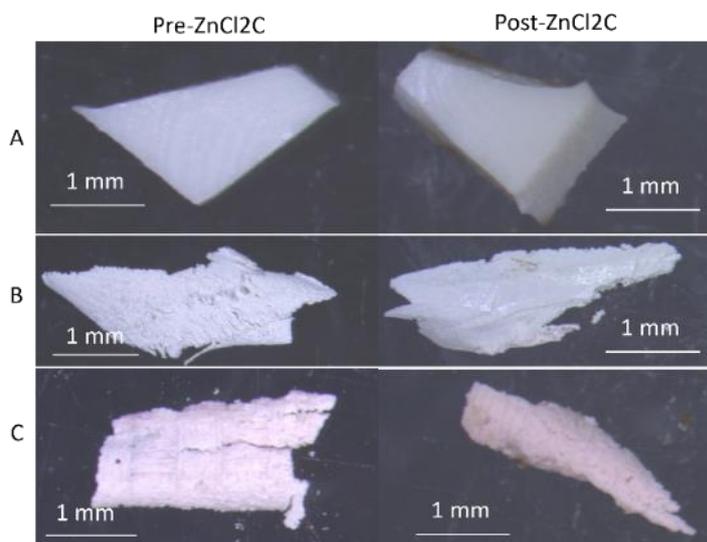
Figure 2: *Photographic examples of the RMP from the 3 coating materials (A, B and C) before (Pre-) and after (After-) 24 hours exposure to high density ZnCl$_2$ solution.*

2.1.2 Chemical 'fingerprint' of reference particles by pyrolysis and thermal desorption GC-MS

Samples (~0.25 mg) were weighed in stainless steel cups and covered with glass wool. Analysis was conducted using a Frontier Multi-Shot Pyrolyzer (PY-3030D) coupled to an Agilent 7890A GC with an Agilent 5975C MS. Two analyses were performed, with the first being a single-shot analysis where the sample was immediately pyrolyzed at 600 °C (1.0 min). For the second analysis, the pyrolyzer was operated in double-shot mode, with initial thermal desorption of the sample at 150-300 °C (initial time 0.10 min, 100 °C/min rate, hold 1 min), followed by pyrolysis at 600 °C (1.0 min). The interface and inlet temperatures were 320 °C, and split ratio 100:1 (pyrograms) or 25:1 (thermal desorption). The carrier gas was helium at a constant flow of 1 mL/min. Separation was achieved using a Frontier Ultra ALLOY+-5 capillary column (30 m length, 0.25 μm film thickness and 0.25 mm internal diameter). The column oven temperature was programmed at 40 °C (2 min), ramped by 20 °C/min until 320 °C (25 min hold). The transfer line temperature was 300 °C, the ion source temperature 230 °C and the quadrupole temperature 150 °C. The ion source was operated in full scan mode (29-600 mz) at 70 eV. High density polyethylene (HDPE) microspheres (90-106 μm, Cospheric LLC) were used as a reference material for verification of instrumental performance.

2.1.3 Validation of the extraction procedure

Twenty-five RPMs from each coating type were individually morphometrically characterised (assessment of the shape, size, and colour) via image analysis with ImageJ software. After this pre-exposure characterisation, the RMPs (n=25) from each coating type were suspended in a high density zinc chloride solution (ZnCl$_2$, ρ = 1.7 g cm^{-3}), which is used to density separate the MP from the rest of the sediment matrix (Imhof et al., 2012). In this pre-test, only RMP and ZnCl$_2$ were used (no sediment). The RMP remained in the ZnCl$_2$ solution for 24 h, which represents the approximate time needed for a complete density separation of real sediment samples (see Section 2.2). After this time, a post-exposure morphometric characterisation of the RMP was performed according to the same pre-exposure procedure described above. Furthermore,

subsamples of each pristine RMP and post-exposure RMP material were also analysed via ATR-FTIR spectroscopy using an Agilent Cary 670 spectrometer (Agilent Technologies, Santa Clara, CA, USA). The instrument parameters for the analyses were: wavenumber range 4000-400 cm^{-1} with a step size of 4 cm^{-1}, and 16 scans per sample.

The physicochemical characterisation and comparison of the pre- and post-$ZnCl_2$ (Fig. 2) exposed RMPs allowed a targeted assessment of any physicochemical effects of the extraction procedures on the coating particles.

2.2 Extraction and characterisation of MP from sediment samples

2.2.1 Density separation

The sediment samples (n=15) were provided by DNV as frozen samples and processed for MP quantification and characterisation by SINTEF Ocean. Three subsamples from each sample, for a total of n=45 subsamples, were subjected to MP extraction and quantification. In addition, processing/laboratory blanks were prepared following the same procedure, but without the use of any sediment, and run alongside the samples (n=1 per each batch of samples that are processed) (see Section 2.2.4).

A density separation step following the approach described by Lorenz et al. (2019) was used to remove natural organic and inorganic matter to facilitate effective MP analysis. Briefly, 100 g of wet weight sediment for each subsample was transferred to an individual 500 mL glass bottle and homogenised with 200 mL of high-density $ZnCl_2$ solution (ρ = 1.7 g cm^{-3}). After homogenisation, each sample solution was transferred into 1 L glass separator funnel after multiple rinsing with extra clean $ZnCl_2$ solution until a total quantity of 800 mL per sample was added. After ca. 24 h to allow the separation process to occur, the bulk of the sediment and heavy detritus had settled to the bottom of the funnel while the lighter material, including MP, remained in suspension are floating at the surface. The density separation was allowed to end only when each sample looked as clear as the procedural blank (Fig. 3).
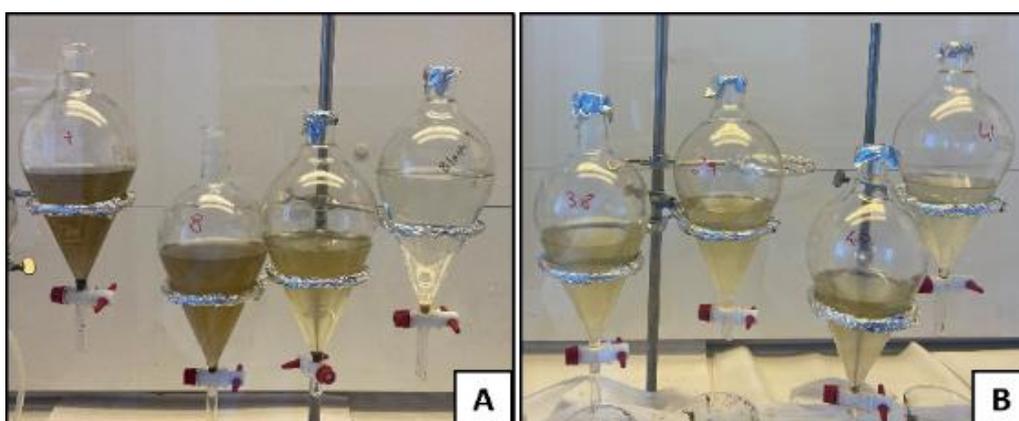
*Figure 3*: Samples before (A) and after (B) 24 hours of density separation in 1 L separator funnels with $ZnCl_2$.

After the density separation, the supernatant was passed through 300 µm Nylon filters (Ø=4.5 cm, PLASTOK®) to remove the $ZnCl_2$ and concentrate any MP particles >300 µm that were present in the sample. No additional sample purification was needed as the filters proved to be sufficiently clean to directly perform the subsequent characterisation and quantification (Fig. 4).
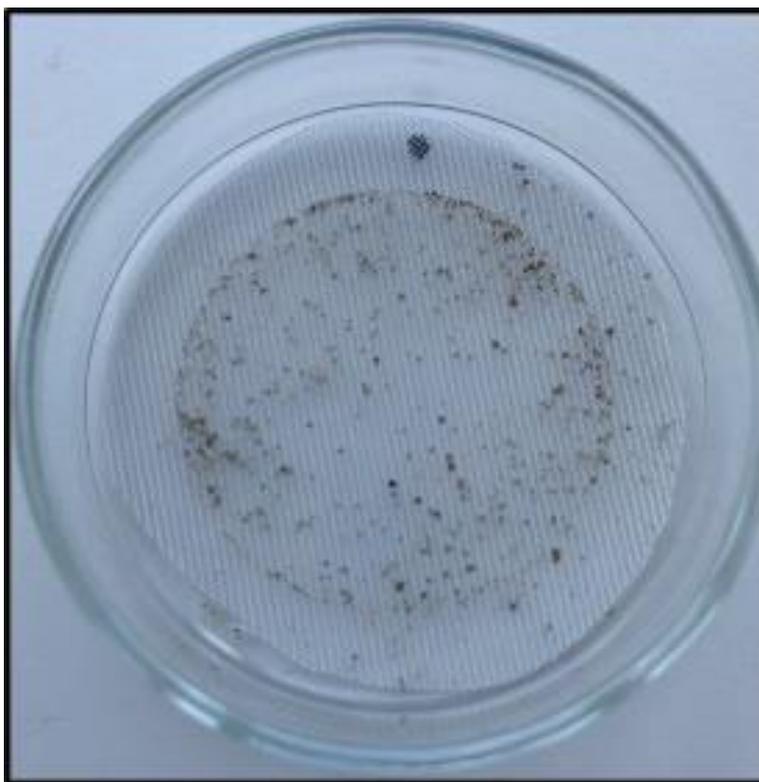
Figure 4: Photographic example of a filtered subsample after the density separation.

2.2.2 Particle selection and physical characterisation

The material retained on each filter was visually inspected under a stereomicroscope (SMZ745T Nikon). Particles were manipulated with stainless steel tweezers during the identification process to exclude non-plastic particles such as glass, sand, mineral and shell. Particles exhibiting an obvious cellular structure were excluded as organic material. Any particle visually identified as being potentially made of plastic was characterised (shape, colour, size at the largest cross section) and photographed (using a stereomicroscope fitted with a DeltaPix camera). Particles were then retained separately for subsequent Fourier-Transform-Infrared (FTIR) analysis. An example of particles selected as potential MP is shown in Fig. 5.
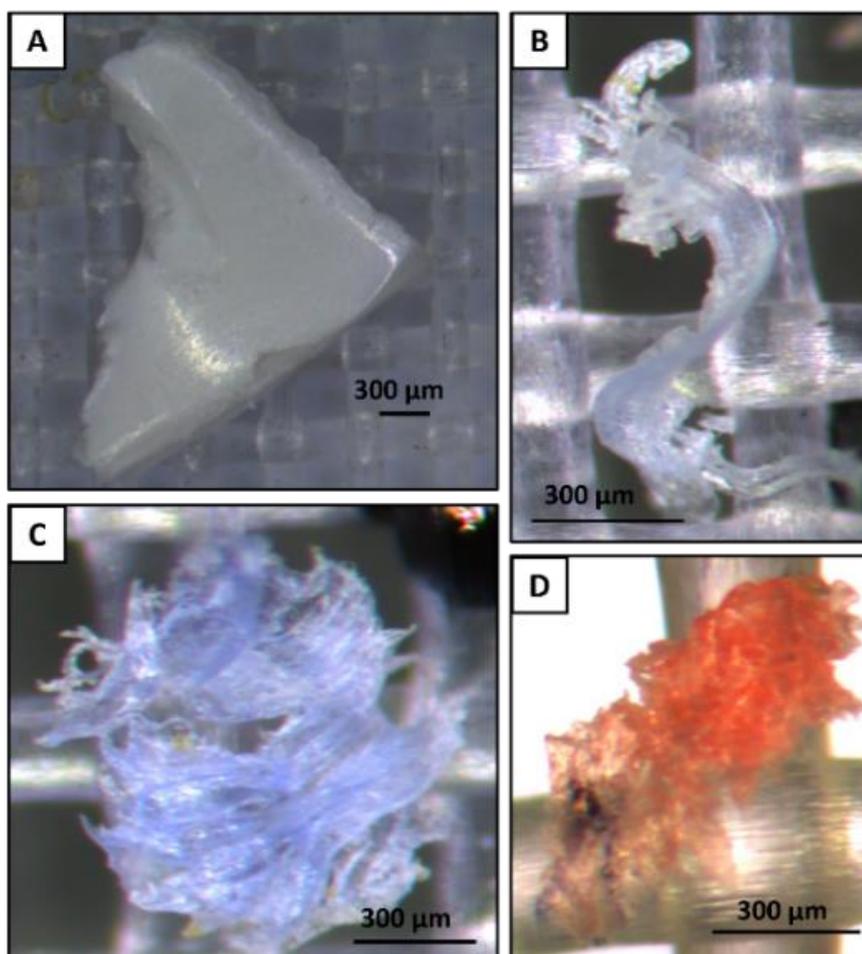
Figure 5: Photographic examples of particles visually selected as potential MP.

2.2.3 Chemical characterisation and polymer validation

A selection of representative particles from each sample that were separated and identified as potentially being plastic (see Section 2.2.2) were analysed by FTIR spectroscopy using an Agilent Cary 620 microscope coupled with an Agilent Cary 670 spectrometer (Agilent Technologies, Santa Clara, CA, USA). The FTIR microscope was equipped with a 128 x 128 focal-plane array (FPA) detector and a 15x IR objective lens (150x final magnification). MP particles were transferred manually from the filters to a BaF_2 slide (25 mm diameter, 1 mm in thickness) using a pair of tweezers under a stereo microscope. Micro-FTIR images were collected in transmission mode in the wavenumber range 3600-900 cm^{-1} with a step size of 4 cm^{-1}, and 16 scans. A background spectrum was collected from an empty area of the BaF_2 slide. To extract FTIR absorption spectra from the micro-FTIR images an inhouse MATLAB (The MathWorks, Inc.) script was used. A dedicated software (KnowItAll Informatics System 2018) was used for spectra interpretation: similarities in wavenumber position and relative intensities of absorption bands were evaluated and compared against a reference library (Bio-Rad Sadtler from Bio-Rad Laboratories) for the assignment of the polymeric composition. The polymer assignment was done for a total of 19 particles with representative physical features being analysed. The same polymeric composition was inferred to non-analysed particles showing

the same physical features. The cumulative polymeric assignments (both analysed and inferred) are shown in the results section.

2.2.4 Anti-contamination procedures

Special attention was given to limiting sample contamination by airborne MP, with precautions implemented at every step of the sample processing by following the anti-contamination protocol described in Piarulli et al. (2019). Briefly, MP extraction was performed in a clean laboratory where all surfaces were pre-cleaned with acidified Milli-Q water prior to processing the samples. Plastic equipment was entirely replaced with metal and glass alternatives wherever possible, which were rinsed with Milli-Q water before use. Contact with air and plastic surfaces during all laboratory procedures was minimised for samples, instruments and reagents by covering them with Milli-Q rinsed aluminium foil before and after use. After filtration, filters were kept covered in glass petri dishes that had previously been rinsed with Milli-Q water. The $ZnCl_2$ solution was prepared using Milli-Q and was pre-filtered on 10 µm glass microfibre filters (Whatman®). The use of cotton clothes and lab coats was mandatory to access the clean laboratory. To validate the effectiveness of the contamination prevention approach one procedural blank (sample-free $ZnCl_2$ solution), treated identically to the sediment samples, was used for each batch of samples processed. Material retained on the procedural blanks was carefully examined following the same procedure as for the sediment samples (see Section 2.2.2) to identify any MP representing external contamination that should be accounted for in the blank correction. No MP were found on the air filters or in the procedural blanks, with only natural cotton microfibres from the laboratory coats that were visually identified. As a result, there was no need to implement any form of blank correction of the MP data for the sediment samples.

3 Results

3.1 Chemical fingerprint of reference materials

3.1.1 Polymer and chemical composition from pyrolysis and thermal desorption GC-MS analysis

The aim of this part of the project was to create an in-house reference 'library' of pyrograms and mass spectra documenting the chemical composition of the reference materials. The approach identifies both the polymer, as well as additive chemicals and other low molecular weight chemicals present in the coatings (including 'non-intentionally added substances (NIAS)', which could be production by-products, degradation products etc), all of which help to generate the chromatographic fingerprint for identifying a specific material. The generated reference material pyrograms were also cross-referenced against existing libraries to help identify the composition of the different materials. These were then used as the basis for making a potential tier 2 identification of any flakes of the same polymer composition found in the sediment samples. Example pyrograms are shown in Table 1.

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Table 1: *Example pyrograms of the three materials analysed by single-shot pyrolysis (SS PY) and double-shot (DS) thermal desorption (DS TD) and pyrolysis (DS PY).*

	Coating A Leading edge protection material	Coating B Top (surface) layer of rotor coating	Coating C Subsurface layer of rotor material
SS PY			
DS TD			
DS PY			

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3.2 Validation of the extraction procedure

After the exposure to the high density $ZnCl_2$ solution for 24 hours, the exposed particles did not show significant alteration in their physical surface properties (Fig. 2). No remarkable physical effects were observed for Coating A RMPs, where only an increase in the total particle mass was observed due to some the presence of some residual $ZnCl_2$ on the extracted RMP. In contrast, a slight reduction in the average particle dimensions and total added particle weight were observed for Coatings B and C (Table 2). Particle fragmentation was observed for Coatings B and C, which led to a significant increase in the total particle numbers of 56% and 44%, respectively. Furthermore, the total particle mass of the Coating C RMPs was reduced by about 63%, suggesting the fragmentation was generating smaller particles that were not retained on the 300 μm filter. These physical changes could have been due to the particular shape of the artificially generated RMPs, which are likely to be more elongated and thinner than real MP emitted from OWF rotor blades. Therefore, these effects were considered negligible in the context of this project, but it should be considered that some fragmentation of certain types of MP present in the sediment samples could occur.

Table 2: *Number, total weight and average size (±SE) of RMP before- and after- the exposure to the high density $ZnCl_2$ solution. Dim1 and Dim2 correspond to the two largest particle cross-sections being analysed.*

Coating material	$ZnCl_2$ exposure	No. particles	Total particle weight (mg)	Dim1 (±SE) (mm)	Dim2 (±SE) (mm)
Coating A	Before	25	38.34	2.25 (±0.1)	2.23 (±0.1)
	After	25	42.35	2.19 (±0.1)	2.06 (±0.1)
Coating B	Before	25	6.95	4.35 (±0.2)	2.1 (±0.2)
	After	39	7.35	2.96 (±0.2)	1.19 (±0.2)
Coating C	Before	25	4.4	3.13 (±0.2)	1.09 (±0.1)
	After	36	1.62	2.01 (±0.1)	0.74 (±0.1)

No substantial changes in the FTIR spectra of the 3 different Coating RMPs were observed when comparing before and after the exposure, suggesting no chemical alteration of the particles occurred as a result of the process (Fig. 6). The broad absorption band at 3000-3600 cm^{-1} in the spectra after exposure is most likely due to moisture still present from the density separation.
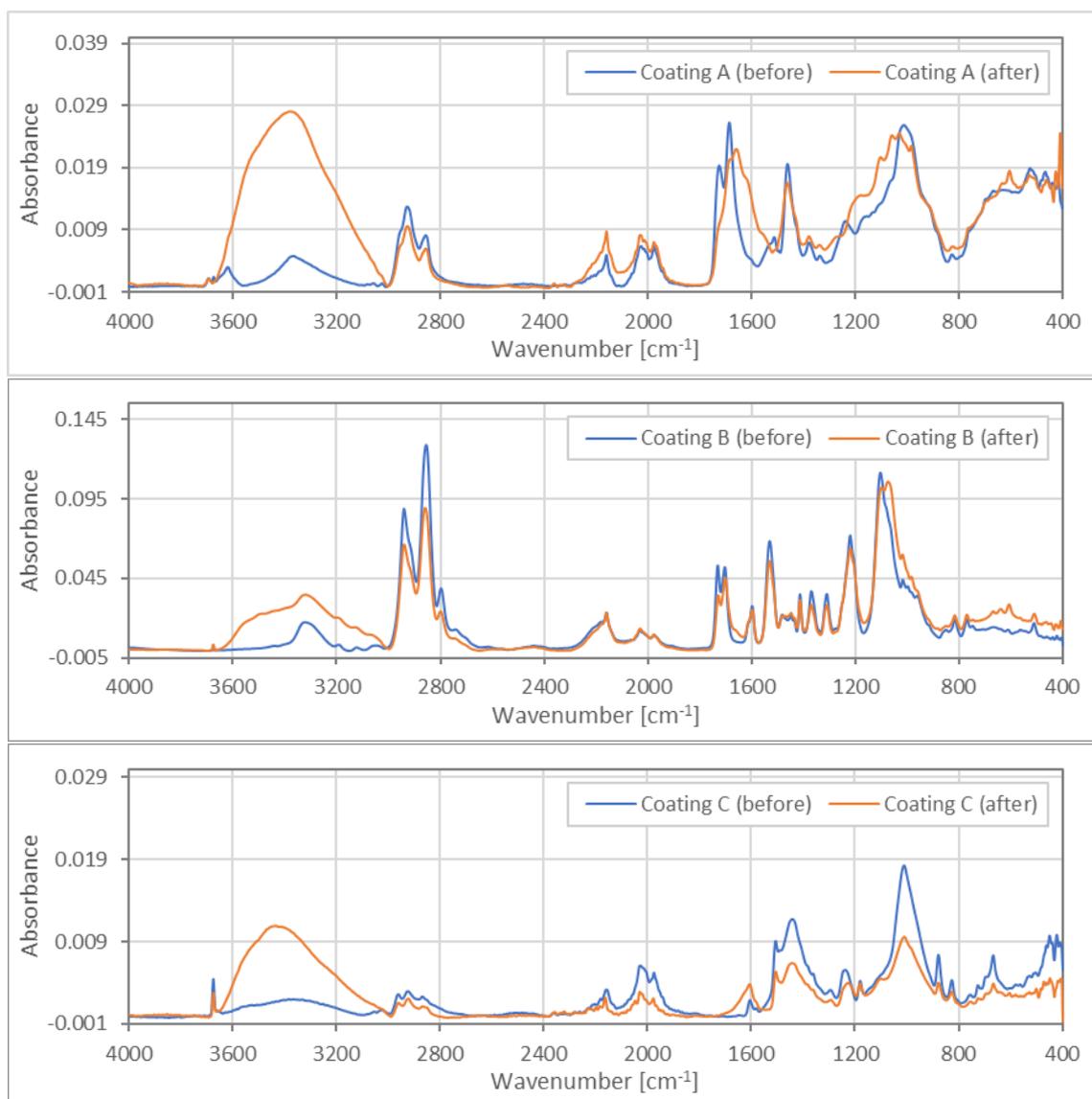
Figure 6: *FTIR spectra of the three coating samples before and after the exposure to ZnCl₂.*

3.3 Extraction and characterisation of MP from sediment samples

A total of 45 subsamples from 15 original sediment samples (n=3 subsample per sediment sample) were analysed in this project. Of the 15 original sediment samples, 60% (n=9) were found to contain MP, although in most cases 1-2 of the subsample replicates did not show any presence of MP (Table 2). A total of 30 particles (*plus two filaments not relevant for the purposes of this project, and therefore not analysed further*) were identified across the 45 subsamples as potentially being MP according to their physical properties, with 20 particles being confirmed as synthetic polymers according to their IR spectra and therefore considered as MP. Overall, none of the confirmed MP exhibited similar physicochemical properties (e.g., colour, texture, polymer composition) to any of the reference coating materials. A full summary of the properties of the confirmed MP and their polymer composition is reported in Table 3.

Table 3: Number of selected potential MP, and number, shape, size and polymeric composition (each analysed particle FTIR spectrum is shown in APPENDIX A) of confirmed MP. PBT=polybutylene terephthalate; PA=polyamide; PS=polystyrene; PE=polyethylene; PP= polypropylene; PS-DVB= polystyrene divinylbenzene.

Original sample ID	Subsample ID	No. Selected particles	No. confirmed MP	Dim1 (mm)	Dim2 (mm)	MP shape	MP polymeric composition
HS1-NE-1	HS1-NE-1-1	1	1	0.40	0.42	Flake	PBT
	HS1-NE-1-2	1	1	0.55	0.67	Flake	PBT
	HS1-NE-1-3	0	0				
HS1-NE-2	HS1-NE-2-1	1	1	0.50	0.85	Flake	PBT
	HS1-NE-2-2	1	1	0.52	0.53	Fragment	PBT
	HS1-NE-2-3	0	0				
HS1-NE-3	HS1-NE-3-1	0	0				
	HS1-NE-3-2	0	0				
	HS1-NE-3-3	0	0				
HS1-SW-1	HS1-SW-1-1	1	1	0.82	0.84	Flake	PA
	HS1-SW-1-2	0	0				
	HS1-SW-1-3	0	0				
HS1-SW-2	HS1-SW-2-1	0	0				
	HS1-SW-2-2	0	0				
	HS1-SW-2-3	0	0				
HS2-SE-1	HS2-SE-1-1	0	0				
	HS2-SE-1-2	0	0				
	HS2-SE-1-3	0	0				
HS2-SE-2	HS2-SE-2-1	0	0				
	HS2-SE-2-2	1	1	0.08	2.01	Thick filament	PS
	HS2-SE-2-3	1	1	0.22	1.90	Thick filament	PE-PP
HS2-SE-3	HS2-SE-3-1	1	1	0.70	0.95		PE-PP
	HS2-SE-3-2	4	4	0.42	0.73	Film; flake	PA, PE-PP
	HS2-SE-3-3	1	0				
HS2-NE1	HS2-NE1-1	1	1	0.18	1.37	Flake	PE
	HS2-NE1-2	0	0				
	HS2-NE1-3	1	1	0.94	1.06	Flake	PE
HS2-NE-2	HS2-NE-2-1	0	0				
	HS2-NE-2-2	0	0				
	HS2-NE-2-3	3	0				
HS2-NE-3	HS2-NE-3-1	1	1	2.75	2.20	Fragment	PS-DVB
	HS2-NE-3-2	1	0				
	HS2-NE-3-3	4	3	0.52	1.68	Film	PE
HS-2022-ref-1	HS-2022-ref-1-1	1	1	0.46	0.36	Flake	PE-PP
	HS-2022-ref-1-2	0	0				
	HS-2022-ref-1-3	3	0				
HS-2022-ref-2	HS-2022-ref-2-1	0	0				
	HS-2022-ref-2-2	2	1	0.35	4.12	Thick filament	PE-PP
	HS-2022-ref-2-3						
Hyw-ref-3	HS-2022-ref-3-1	0	0				
	HS-2022-ref-3-2	0	0				
	HS-2022-ref-3-3	0	0				
Hyw-SW-extra	Hyw-SW-extra-1	0	0				
	Hyw-SW-extra-2	0	0				
	Hyw-SW-extra-3	0	0				

4 General conclusion

The current project aimed to (i) quantify and characterise all MP >300 µm present in sediment samples collected from an OWF (Hywind, Scotland) and define the proportion of the MP derived directly from coating materials used for the rotor blades of the OWF infrastructure, and (ii) determine the background MP levels of conventional thermoplastic polymers. When considering the physicochemical features of the MP found in the analysed fraction of the sediment samples, there was no detectable presence of MP contamination from coating materials used for the rotor blades or from the leading-edge protection materials from the Hywind OWF. However, background MP contamination was detected from other sources. The identified thermoplastic polymers were PBT, PA, PS, PE or PP and PS-DVB, which are among the most common polymers found in marine sediment samples, potentially being released from multiple anthropogenic sources and products (see as examples Carbery et al., 2018 and Lorenz et al., 2019). Although turbine-derived particles were not identified in the current project, the methodological method developed is considered robust for the purpose, especially the use of pristine reference materials as the basis for generating reference pyGC-MS and FTIR spectra for identification of such particles in environmental samples.

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APPENDIX A

FTIR absorption spectra of all analyzed particles. Samples with similar spectra are shown in the same graph.

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