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Degradation of Common Polymer Ropes in a Sublittoral Marine Environment

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ABSTRACT

Contamination by microplastic particles and fibres has been observed in sediment and animals sampled from the Firth of Clyde, West Scotland. In addition to microplastics released during clothes washing, a probable source is polymer ropes in abandoned, lost and discarded fishing and recreational sailing gear. The fragmentation of polypropylene, polyethylene, and nylon exposed to benthic conditions at 10 m depth over 12 months was monitored using changes in weight and tensile properties. Water temperature and light levels were continuously monitored. The degree of biofouling was measured using chlorophyll a, the weight of attached macroalgae, and colonizing fauna. Results indicate microplastic fibres and particles may be formed in benthic environments despite reduced photodegradation. Polypropylene, Nylon, and polyethylene lost an average of 0.39%, 1.02%, and 0.45% of their mass per month respectively. Microscope images of the rope surface revealed notable surface roughening believed to be caused by abrasion by substrate and the action of fouling organisms.
Capsule: By exposing polymer ropes to benthic conditions over a year we calculated that the initial production of microplastic fibres would average 0.427 grams per meter per month.

Highlights:

- Polymer ropes lost between 0.39 and 1.02% or their mass per month
- Average production of microplastics was 0.427 grams per meter per month
- Of the polymers, polyethylene showed the largest reduction in mechanical properties
- Light intensity and temperature were linked to reduction in mechanical properties

Keywords: microplastic; microfibre; marine pollution; biofouling; tensile strength; fragmentation

INTRODUCTION

Plastic pollution, once regarded as a primarily aesthetic issue, is now recognised as physically damaging to both marine organisms and habitats (Barnes et al., 2009; Browne et al., 2011). One of the major concerns regarding plastic debris is its high durability, referred to as recalcitrance (Alexander, 1999). This durability is caused by strong bonds within the polymer and its high molecular weight, which confer resistance to degradation (Palmisano and Pettigrew, 1992; Zheng et al., 2005). As a result plastics persist in the environment for long periods, causing them to build up to high levels in both terrestrial and marine habitats (Barnes et al., 2009). While the structure of polymers is highly durable, plastics are susceptible to embrittlement, cracking, and reduction in mechanical properties (Massey, 2006). This weathering leads to fragmentation and the formation of secondary microplastics (Arthur, 2009). Secondary microplastic particles – less than 5 mm in size – have been seen to negatively impact the marine environment as they are more difficult to remove from the environment and available for uptake by a wider range of organisms. Microplastic ingestion has been observed in cetaceans (Lusher et al., 2015a), wading and pelagic bird species (Connors and Smith, 1982; Ryan, 2008), benthic and mid-water fish (Lusher et al., 2013; Lusher et al., 2015b), and benthic, pelagic and intertidal crustaceans (Devriese et al., 2015; Murray and Cowie, 2011; Ugolini et al., 2013; Welden and Cowie, 2016).

Fragmentation of plastic debris can occur as a result of direct damage to the plastic product (Reddy et al., 2006), or by weakening of the polymer structure (Alexander, 1999; Andrady, 2011). Physical
damage to plastic debris may occur via weathering action of waves and abrasion by either sediment
or other rough benthic substrates. This abrasive action may directly cause the formation of
microplastic, or enable settlement of colonising organisms by changing the surface texture of the
polymer (ter Halle, 2016). Physical degradation may also affect plastics in use in the marine
environment that may not otherwise be considered debris, for example the abrasion of trawl nets,
plastic pontoon components or ropes.

Weakening of a polymer is the result of breaking bonds in the molecule’s backbone (Massey, 2006).
This may occur via a number of reactions, for example hydrolysis (Andrady, 2011; Kinmonth 1964).
For hydrolysis to occur a polymer must contain labile functional groups, for example esters which form
ionized acids. The first stage of the degradation process involves non-enzymatic, random hydrolytic
ester cleavage and its duration is determined by the initial molecular weight of the polymer as well as
its chemical structure (Pitt et al., 1981). Hydrolysis is especially important in the design of degradable
polymers and many have increased numbers of hydrolysable bonds and a more hydrophilic structure,
which increases the rate of polymer breakdown (Göpferich, 1996). Polymer backbones may also be
shortened by the production of highly reactive free radicals, units containing unpaired electrons or an
open electron shell. This breakdown is a three stage process. The first stage, initiation, is characterised
by the scission of the polymer chain either at the chain-end or randomly throughout its length,
resulting in the formation of two free radicals. Free radicals are units containing unpaired electrons or
an open electron shell; this makes the resulting molecules highly reactive. During the second reaction
phase, propagation, radical groups act upon the hydrocarbon chain to cause further breakdown of the
polymer (Leonas and Gorden, 1993; Muasher and Sain, 2006). The initial scission of a polymer chain
may be caused by a number of factors, the most common of which are ultra violet light (UV) and
temperature (Albertsson and Karlsson, 1988; Singh and Sharma, 2008).

The rate of weathering depends on the availability of these factors; as a result polymer degradation is
highly dependent on location and environmental conditions. This can be seen in the different rates of
degradation observed at different latitudes, linked to the level of UV radiation (Statz and Doris, 1987).
This scission of the bond causes the formation of free radicals, which may affect adjacent polymers
causing a secondary breakdown in the polymer structure. The final step in the process is the
stabilisation of the remaining radicals, which either join to form a new product, or form two separate
stable species (Albertsson and Karlsson, 1988; Geuskens and David, 1979). This process reduces a
polymers molecular weight and increases its susceptibility to degradation by biota. Fouled plastic
materials are then susceptible to fragmentation by biodegradation, or biodeterioration. Colonising
organisms and their by-products may cause direct damage to plastics (Andrady, 2011), for example,
through the mechanical action of borers (Davidson, 2012). Fouled debris may also be subject to increased solubility and hydrolysis (Göpferich, 1996; Singh and Sharma, 2008).

The Clyde Sea Area receives plastic inputs from the highly populated and industrialized catchment area and numerous marine activities. This plastic may enter the environment by numerous routes including local littering, transport via wind and currents, landfill run-off, overboard disposal, and the accidental loss of fishing gear (Lattin et al., 2004). Estimates of the relative importance of plastic sources suggest that approximately 80% of marine litter originates from terrestrial sources (Teuten et al., 2009) Of the remaining 20% of plastic litter believed to originate at sea, industrial maritime activities are one of the main sources (Brown and Macfadyen, 2007; Kaiser et al., 1996; Kiessling, 2003; Macfadyen, 2009; Otley and Ingham, 2003). Modern rigging and gear is almost solely of polymer construction, and gear can be accidentally lost even with carefully handling. Fragmentation of abandoned, lost and discarded fishing gear (ALDFG) in the marine environment will result in the release of large quantities of microplastic particles and fibres; in this study the degradation of commonly used polymer ropes is monitored to establish a rate of microfiber formation in benthic environments.

MATERIALS AND METHODS

Nylon, polypropylene and polyethylene ropes were chosen due to their common use in both recreational and industrial maritime activities around the Firth of Clyde. Sisal rope was selected as a natural comparison, historically used in maritime activities. Construction varied between the three rope types; polypropylene was a four strand twisted film, whilst polyethylene and nylon were four strand braided ropes. All samples were 10mm in diameter, to ensure that the same surface area was available. The initial mechanical properties of the samples were determined by tensile testing, carried out using an Zwick-Roell Z250 tensile testing machine with a capacity of 100kN (Breslin and Li, 1993; McKeen, 2008). Tensile strength was calculated by determining the force per unit area required to fracture the sample. Elongation was recorded as both the total increase in length and the ratio between the change in length and the original length. Sample ropes were cut to 50mm lengths and randomly assigned spaces on acrylonitrile butadiene styrene (ABS) frames. Frames were then fixed on the seabed from an existing pier, at 10 meters depth on silty sediment. The deployment site was situated in a tidal eddy off an existing pier, however tidal currents in the Clyde Sea are predominantly weak. Water movement is modulated by wind-driven surface currents, and the site was chose due to its south easterly aspect, facing into the prevailing winds (Wilding et al., 2005).
Abiotic Causes of Degradation

Over the sample period water temperature and light levels were measured using HOBO UA-002-64 loggers. Frames were lifted every two months and three samples of each rope type removed. Where rope samples were to be weighed, biofouling organisms were removed using forceps and a scalpel and gentle rinsing with a wash-bottle. Where removal of attached biota would result in damage to the rope surface care was employed to cut away as much of the attached biomass as possible. Once dried, samples were weighed and the new buoyancy determined. Ropes to be subjected to tensile testing were rinsed with deionised water, air dried, and stored in foil at 20°C until analysis. The tensile strength and elongation at break of each was determined.

Biotic Causes of Degradation

Samples were examined for evidence of colonisation by biofouling organisms. Levels of chlorophyll a, the weight of attached algae, and the number and diversity of invertebrates and attached diatoms were examined for each sample. Chlorophyll a was determined by refrigerating 10mm lengths of rope with 10ml of 90% acetone for 24 hours, after extraction each sample was centrifuged for 10 minutes, and the resulting supernatant transferred to a 1 ml cuvette. The chlorophyll concentration was determined by using a Thermospectronic HeliosY spectrophotometer, with readings taken at 750, 664, 647, and 630 μm, using a 90% acetone blank.

The abundance and type of fouling organisms were determined by enumerating the number of colonising animals and the weight of attached biomass. Biofouling by macro-organisms was determined examining 50mm sections of rope under a binocular microscope. Algae and organisms were removed for identification. Attached macro-algae were removed and oven dried at 40°C overnight to determine the dry weight.

Statistical Analysis

Monthly changes in the weight of the sample, its tensile strength and elongation at break were compared using Kruskall-Wallis analysis, carried out in Minitab 15. The measured factors responsible for variation in tensile strength and elongation at break were subjected to GLM analysis in R (version 3.0.2). Prior examination of the data revealed that a number of variables were found to inter-correlate; these variables were included in sequential models to determine which had the greatest impact on model fit. After running a GLM using all environmental variables, the model was reduced using in a stepwise process in order to improve of the resulting model, this was determined by the relative size of the Akaike information criterion (AIC).
RESULTS

Abiotic Causes of Degradation

Over the exposure period the average sea temperature was 9.73 °C. The recorded temperature range was between 5.7 °C, recorded in March, and 17.9 °C, recorded in July. Average light intensity over the exposure period was 122 Lux, reaching a maximum of 17222 Lux in June. The highest monthly light intensity took place throughout June and July.

Biotic Causes of Degradation

Sisal samples recovered two, four, and six months into the sample period had low chlorophyll a readings and less than 0.01g dry weight of macroalgae – which was first observed after four months. Higher levels of chlorophyll a were observed on polymer ropes (Table 1). All rope samples also exhibited macroalgal growth, which greatly increased over the course of the year. The two most commonly identified macroalgal species were *Alaria esculenta* and *Palmaria palmata*. *P. palmata* was observed on all rope types, occurring after eight months on polymer ropes. *A. esculenta* was only observed on polypropylene and polyethylene ropes, first recorded on polyethylene at six months, followed by polypropylene at eight months. The high algal dry weights observed on these two polymers were the result of large *A. esculenta* fronds.

Table 1. Colonisation of samples by macroalgae over the experimental period

<table>
<thead>
<tr>
<th>Macroalgal Species observed</th>
<th>Max Chlorophyll a</th>
<th>Max Dry Algal Biomass (g per 50 cm)</th>
<th>First macroalga observed</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>P. palmata</em></td>
<td>1.98</td>
<td>2.1</td>
<td>Eight months</td>
<td>Nylon</td>
</tr>
<tr>
<td><em>P. palmata, A. esculenta</em></td>
<td>1.84</td>
<td>10.7</td>
<td>Four months</td>
<td>Polypropylene</td>
</tr>
<tr>
<td><em>P. palmata, A. esculenta</em></td>
<td>0.76</td>
<td>9.3</td>
<td>Six months</td>
<td>Polyethylene</td>
</tr>
<tr>
<td><em>P. palmata</em></td>
<td>0.20</td>
<td>&lt;0.01</td>
<td>Four months</td>
<td>Sisal</td>
</tr>
</tbody>
</table>

Table 2. Colonisation of samples over the experimental period. Values indicate number of months after which the species was observed.
The number and type of invertebrate organisms observed varied over the course of the study period (Table 2). After two months all polymer ropes were colonised by Corophium sp., which formed tubes on the rope surface. Between six and eight months the number of grazers was observed to increase, with the appearance of the periwinkle, Littorina littorea. A late coloniser of polyethylene was Stenula, an amphipod commonly found in sublittoral algae, possibly attracted by increasing macroalgal cover. Prolonged exposure to benthic conditions resulted in fouling by larger encrusting organisms. The barnacle, Eliminus modestus, was found on samples of polypropylene exposed for over eight months, and the blue mussel, Mytilus edulis, was found on all polymers between six and eight months exposure. After 12 months polypropylene had the most recorded species with five per sample, while Nylon had only four species recorded per sample.

### Mechanical Properties

Analysis of the change in the mechanical properties of sisal revealed significant reductions in both elongation and breaking strain. Of the three polymer ropes, polyethylene showed the highest average change in elongation at break, followed by polypropylene and Nylon (Table 2). The mean change in tensile strength was highest in polypropylene, followed by Nylon and polyethylene. For all rope types,
the rate of degradation was greatest in the first months, slowing during the 12 month experimental period. Statistical analysis of the factors related to both elongation at break and tensile strength exhibited different responses, however, a number of factors were common between the three polymers. The most commonly observed significant factors were maximum temperature, average temperature, average light intensity and the weight of macro algae.

**Fragmentation**

All ropes demonstrated a reduction in mass over the twelve month exposure period (Table 2); however, the scale of this loss was highly variable. Statistical analysis of the monthly reduction in sample weight indicated significant differences in the rate of microplastic formation by each rope type (H = 18.23, df = 3, P < 0.001). The natural sisal rope had degraded completely by month eight but even the fastest degrading polymer had not yet lost 13% of their mass.

The polymer ropes displayed differing levels of wear when examined under SEM. Fibrous Nylon line showed indications of there was obvious increasing fraying over the twelve month period; fibres did not lay as flat to the rope surface, and there were notable breakages of individual strands. Extruded polyethylene filament rope revealed increased surface scratching and roughening, and polypropylene twisted film rope developed many visible cracks and fissures, as well as the formation of fine surface fibres - particularly apparent in areas of animal attachment.

GLM analysis was used to compare the average mass lost per month with the observed changes in the tensile properties of the sample and the colonising organisms. The fragmentation of both Nylon and polyethylene was linked to elongation at break. The fragmentation of polypropylene rope samples was not significantly related to any of the measured variables, although a number of weak relationships were apparent.

<table>
<thead>
<tr>
<th></th>
<th>Average Mass lost per Month</th>
<th>Percentage Mass lost per Month</th>
<th>Percentage Mass lost</th>
<th>Max reduction in Elongation (mm)</th>
<th>Max reduction in Tensile Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon</td>
<td>0.422 g</td>
<td>1.02%</td>
<td>12.24%</td>
<td>- 15.265</td>
<td>- 339.60</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.086 g</td>
<td>0.39%</td>
<td>4.68%</td>
<td>- 11.850</td>
<td>- 544.06</td>
</tr>
</tbody>
</table>
**DISCUSSION**

The results of this study indicate that large masses of microplastic can be formed quickly, even in the low energy benthic habitat in the Firth of Clyde. When the numerous sources of rope debris are considered, this indicates that an alarming volume of microplastic is formed annually by ropes alone. The reduction in mechanical properties and the fragmentation rates of the polymer ropes varied over the 12 month experimental period. Nylon rope was observed to fragment the fastest, whilst polypropylene rope fragmented the slowest. The rate of fragmentation may have been partially influenced by differences between the ropes constructions; however, whilst there was an apparent difference in the monthly rate of mass lost, a number of common factors were identified as significantly affecting degradation and fragmentation.

**Abiotic Causes of Degradation**

Of the environmental factors included in the GLM analysis, only maximum and average temperature and average light were identified as significant in analyses. Light is often identified as a driving factor of polymer degradation. Samples of LDPE exposed to UV irradiation showed three stages of degradation. These are believed to represent a rapid change within the material followed by a reduced rate of degradation, and finally a collapse of the polymer structure (Albertsson and Karlsson, 1988). In a study of the degradation of polymer films in the marine environment, reduced UV transmission was found to result in lower rates of degradation over time (O’Brine and Thompson, 2010). Because of the low penetration of light, most photochemical reactions take place on the surface of the plastic; even so, photodegradation is considered to be the primary cause of plastic break down (Singh and Sharma, 2008).

Previous observations of the degradation rates of polyethylene films has demonstrated that exposure to increased temperature significantly reduces a plastic’s tensile properties (Whitney et al., 1993). Temperature influences the degradation of plastics by exciting electrons within the polymer structure causing bond scission and the shortening of the polymer chain (Singh and Sharma, 2008). Increased temperature also affects other forms of degradation. If the temperature is increased this reduces the energy required to break vulnerable bonds in the polymer backbone (Singh and Sharma, 2008).
One abiotic factor that could not be controlled within this study was the impact of abrasion by sediment. The exposure trial was carried out using fixed ropes in a comparatively low energy environment. Abrasion against rocks, encrusting organisms and sediment would increase the rate of fragmentation and, therefore, microplastic formation.

**Biotic Causes of Degradation**

Weak relationships were observed between the number of fouling organisms and the reduction in mechanical properties/sample mass. This may be the result of the constitutive enzymes of sessile invertebrate colonisers on the surface of the polymer. These chemicals act on the bonds in the polymer to weaken them (Flemming, 1998; Göpferich, 1996; Gu and Gu, 2005). Damage to the bonds in the polymer backbone enables biodegradation by other organisms (Bonhomme et al., 2003), as well as an increasing in the surface solubility of the polymer, enabling attachment by other organisms.

The action of grazing colonisers may also influence rope fragmentation. Numerous grazing crustaceans have been seen to consume plastic. Mesocosom experiments have shown that *Gammarus fossarum* ingest both microspheres and fibres (Blarer and Burkhardt-Holm, 2016). More notably, wild caught gammarids from the Dutch marine environment have shown microplastic uptake at approximately 11 per g (dry weight) (Leslie et al., 2013). One of the most common invertebrate colonisers of all rope types were *Corophium*. These grazing invertebrates may rasp the rope surface whilst feeding on algae and, in the process, may take in microplastic particles and fibres, establishing a primary route for microplastics entering the food chain.

The colonisers observed here exist within a defined area of intertidal and shallow subtidal waters, to which they are adapted; outside this niche, the impact of increased polymer biodegradation by fouling organisms may be highly variable. Changing abiotic variables will also influence biotic degradation. One example of such an impact would be that of increasing depth. With increased depth there is a reduction in light penetration which will limit photosynthesis, and therefore, algal biomass as well as the number of grazers.

**Variation in Degradation**

Over the experimental period the average monthly air temperature was between 4.9 – 11.4 °C, and 1271.3 sunshine hours were recorded. These conditions are consistent with local monthly averages recorded in the Firth of Clyde between 1981 and 2010 (between 2.6 – 19.6 °C, and 1320.0 hours of sunshine). The average water temperature at the experimental site was found to be 9.81°C, and
ranged from 5.6 to 17.5 °C; this range is similar to that previously reported by Slesser and Turrell (2005). This suggests that levels of plastic degradation in the CSA will be similar between years.

Globally, the factors linked to plastic degradation in the marine environment are subject to high variability. The rate of microplastic formation from ropes, nets etc. may be expected to vary over the course of the year due to the changing influence of light on both degradation and fragmentation rates. This study indicates that there will be increased microplastic formation during summer months, when light levels are at their highest. This proposed seasonality in microplastic generation does not account for the influence of winter storm events, during which there would be increased mechanical abrasion. Similarly, different latitudes receive light at different intensities over the course of the year. Areas at lower latitudes may be expected to experience higher rates of degradation due to their comparatively high light levels.

The action of organisms on the plastic may increase the rate of degradation; however, encrusting animals may reduce the amount of light reaching the polymer - either by covering the surface and preventing light penetrating the polymer or by causing the plastic to sit lower in the water column. At increasing depth plastic in would experience lower light levels and fewer extremes of temperature, reducing the overall rate of degradation.

The dimensions of the plastic litter will also greatly influence degradation rate. The surface area to volume ratio of rope samples is small when compared to that of films; as a result, much of the mass of the sample would be protected from environmental conditions. Observations of the fragmentation rates of polyethylene films were faster than those observed here (Whitney et al., 1993). The average rate of degradation observed over the twelve month experiment may increase as the rope fragments and the surface area to volume ratio increases the rate of degradation would be expected to increase accordingly (Andrady, 2011).

**Impact on Microplastic Formation**

The mass of microplastic particles and fibres in the marine environment is a combination of that from existing marine debris and those produced from other sources including clothes washing, seen to produce around 1900 fibres in a single wash (Browne et al., 2011). A single washing of a polyester garment has been seen to produce up to 2 g of microfibers, approximately 0.3% of the total garment weight (Hartline et al., 2016). Understanding the rate of rope degradation sheds more light on the pool of secondary microplastics. Previous analysis of non-degradable plastic films in the marine environment revealed that only 2% of the material was lost over 40 weeks (O’Brine and Thompson, 2010). Over the time span, the polymer ropes in during this study demonstrated a reduction in mass
of 5.72%. Whilst the conditions influencing microplastic generation are highly variable, the ability to
categorise areas in which the abiotic conditions favour plastic degradation will enable the
identification of habitats at risk from locally formed secondary microplastics.

The conservative estimates of plastic fragmentation in a temperate environment which are presented
here indicate that there will be vast amounts of microplastic formed from the degradation of global
abandoned lost and discarded fishing gear. The FAO estimate that 640,000 tonnes of fishing gear are
lost to the marine environment every year. Assuming an equal mix of the three polymers observed in
this study the degradation rate of this plastic would be 0.62% per month. Using this conservative
estimate, the monthly mass of microplastic generated would be 3,968 tonnes, totalling 47,616 tonnes
in the first year. This calculation only refers to annual gear losses, and not to the mass of plastic already
in the environment. In addition to ALDFG lost at sea, trawl nets and other ropes used in both
commercial and recreational boating will also release both thick strands and finer fibres to the
environment, greatly increasing this figure. In order to reduce ongoing microplastic production, there
must be an active effort to reduce the volume of parent material in the marine environment. Increased
incentives must be made to “fish of litter” and to recover and recycle plastic at port facilities. Costs
currently levied on the correct disposal of wastes from industrial maritime activities need to be
reassessed to make the reduction of marine litter a priority for maritime industry.

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