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Microplastics in the marine environment

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ABSTRACT

This review discusses the mechanisms of generation and potential impacts of microplastics in the ocean environment. Weathering degradation of plastics on the beaches results in their surface embrittlement and microcracking, yielding microparticles that are carried into water by wind or wave action. Unlike inorganic fines present in sea water, microplastics concentrate persistent organic pollutants (POPs) by partition. The relevant distribution coefficients for common POPs are several orders of magnitude in favour of the plastic medium. Consequently, the microparticles laden with high levels of POPs can be ingested by marine biota. Bioavailability and the efficiency of transfer of the ingested POPs across trophic levels are not known and the potential damage posed by these to the marine ecosystem has yet to be quantified and modelled. Given the increasing levels of plastic pollution of the oceans it is important to better understand the impact of microplastics in the ocean food web.

Contents

1. Introduction

The first reports of plastics litter in the oceans in the early 1970s (Fowler, 1987; Carpenter et al., 1972; Carpenter and Smith, 1972; Coe and Rogers, 1996; Colton and Knapp, 1974) drew minimal attention of the scientific community. In the following decades, with accumulating data on ecological consequences of such debris, the topic received increasing sustained research interest. Most studies have focused on the entanglement of marine mammals (Laist, 1997), cetaceans (Clapham et al., 1999) and other species (Erikson and Burton, 2003) in net fragment litter and on 'ghost fishing' by derelict gear in the benthos (Bullimore et al., 2001; Tschernij and Larsson, 2003). Ingestion of plastics by birds (Mallory, 2008; Cadee, 2002) and turtles (Mascarenhas et al., 2004; Bugoni and Krause, 2001; Tomas and Guitart, 2002) is extensively documented worldwide and at least 44% of marine bird species are known to ingest plastics (Rios and Moore, 2007) with verified accounts of species such as the black-footed albatross feeding plastics granules to its chicks. With recent reports on the unexpectedly high incidence of plastic debris in the North Pacific gyre (Moore et al., 2001, 2001a, 2002; Moore, 2008) this interest has culminated in defining the topic as a high-priority research area in Marine Biology (Derraik, 2002; Page and McKenzie, 2004; Arthur et al., 2009). A particular concern is the occurrence of smaller pieces of plastic debris including those not visible to the naked eye, referred to as microplastics, in the world's oceans. This review attempts to address the fate of plastics in the marine environment, the mechanisms by which microplastics are derived from marine debris and the potential ecological impacts of microplastics.

1.1. Plastics used in the marine environment

The annual global demand for plastics has consistently increased over the recent years and presently stands at about 245 million

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tonnes. Being a versatile, light weight, strong and potentially transparent material, plastics are ideally suited for a variety of applications. Their low cost, excellent oxygen/moisture barrier properties, bio-inertness and light weight make them excellent packaging materials. Conventional materials such as glass, metal and paper are being replaced by cost effective plastic packaging of equivalent or superior design. Nearly a third of the plastic resin production is therefore converted into consumer packaging material that include disposable single-use items commonly encountered in beach debris (Andrady, 2003). How much of the 75–80 million tonnes of packaging plastics used globally each year ends up in the oceans, has not been reliably estimated.

Several broad classes of plastics are used in packaging: Polyethyelene (PE), Polypropylene (PP), Polystyrene (PS), Poly(ethylene terephthalate) (PET); and Poly(vinyl chloride) (PVC). Their high-volume usage is reflected in their production figures given in Table 1 and consequently these in particular have high likelihood of ending up in the ocean environment. Extensive fishing, recreational and maritime uses of the ocean, as well as changing demographics favoring immigration to coastal regions, will increase the future influx of plastics waste into the oceans (Ribic et al., 2010). Land-based sources including beach littler contributes about 80% of the plastic debris. The entire global fishing fleet now uses plastic gear (Watson et al., 2006) and some gear is invariably lost or even discarded carelessly at sea during use. Polyolefins (PE and PP), as well as nylons are primarily used in fishing gear applications (Timmers et al., 2005; Klust, 1982). About 18% of the marine plastic debris found in the ocean environment is attributed to the fishing industry. Aquaculture can also be a significant contributor of plastics debris in the oceans (Hinojosa and Thiel, 2009). The rest is derived largely from land-based sources including beach litter. Virgin resin pellets, a common component of debris, enter the oceans routinely via incidental losses during ocean transport or through run-off from processing facilities (Gregory, 1996; Doyle et al., 2011; Ogata et al., 2009).

Quantifying floating plastic debris (generally using surface-water collection of debris with neuston nets) seriously underestimates the amounts of plastics in the ocean as those in the sediment and mid-water are excluded by the technique. The visibility of debris as flotsam requires plastics to be positively buoyant in sea water (specific gravity of sea water is ∼1.025). However, as seen from Table 1 only a few of the plastics typically used in the marine environment has a specific gravity lower than that of seawater. (The specific gravities given are for the virgin resins; plastics in products are often mixed with fillers and other additives that may alter their specific gravity.) Denser varieties of plastics such as nylons tend to submerge in the water column and even reach the coastal sediment.

1.2. Microplastics in the oceans

A recent significant finding is that minute fragments of plastic debris, termed microplastics, occur in oceans worldwide (Barnes et al., 2009) including even in Antarctica (Zarfl and Matthies, 2010). Microplastics, a form of man-made litter, have been accumulating in the oceans for at least over the last four decades (Thompson et al., 2004, 2005). Sampled from surface waters or from beach sand this fraction of litter includes virgin resin pellets, compounded masterbatch pellets and smaller fragments of plastics derived from the larger plastic debris (Moore, 2008).

The term 'microplastcs' and 'microlitter' has been defined differently by various researchers. Gregory and Andrady (2003) defined microlitter as the barely visible particles that pass through a 500 µm sieve but retained by a 67 µm sieve (∼0.06–0.5 mm in diameter) while particles larger than this were called mesolitter. Others (Fendall and Sewell, 2009; Betts, 2008; Moore, 2008), including a recent workshop on the topic (Arthur et al., 2009) defined the microparticles as being in the size range <5 mm (recognising 333 µm as a practical lower limit when neuston nets are used for sampling.) Particles of plastics that have dimensions ranging from a few µm to 500 µm (5 mm) are commonly present in sea water (Ng and Obbard, 2006; Barnes et al., 2009). For clarity, this size range alone is referred to as 'microplastics' here; the larger particles such as virgin resin pellets are referred to as 'mesoplastics' after Gregory and Andrady (2003). Persistent organic pollutants (POPs) that occur universally in sea water at very low concentrations are picked up by meso-/microplastics via partitioning. It is the hydrophobicity of POPs that facilitate their concentration in the meso-/microplastic litter at a level that is several orders of magnitude higher than that in sea water. These contaminated plastics when ingested by marine species presents a credible route by which the POPs can enter the marine food web. The extent of bioavailability of POPs dissolved in the microplastics to the biota (Moore, 2008) and their potential bio-magnification in the food web (Teuten et al., 2007) has not been studied in detail.

Unlike larger fragments microplastics are not readily visible to the naked eye; even resin-pellets (mesoplastics) mixed with sand are not easily discernible. Net sampling does not of course collect the smaller microplastics and no acceptable standard procedure is presently available for their enumeration in water or sand. The following is only a suggested procedure derived from published reports as well as personal experience of the author.

Water samples are filtered through a coarse filter to remove mesolitter. Sediment or sand samples are slurried in saline water to allow microplastics to float to the surface. A mineral salt may be dissolved in the collected sea water or slurry sample to increase the water density sufficiently to float plastic fragments. Samples of surface water with floating microparticles are carefully removed for study. Concentrating samples of sea water samples by evaporation can also concentrate the microplastic litter at the surface. Microplastics in surface water samples can be visualised under a microscope using a lipophilic dye (such as Nile Red) to stain them (Andrady, 2010). The water samples will also contain microbiota such as plankton of the same size range but these will not be

Table 1
Classes of plastics that are commonly encountered in the marine environment.

Plastic Class		Specific Gravity	Percentage production[#]	Products and typical origin
Low-density polyethylene	LDPE LLDPE	0.91–0.93	21%	Plastic bags, six-pack rings, bottles, netting, drinking straws
High-density polyethylene	HDPE	0.94	17%	Milk and juice jugs
Polypropylene	PP	0.85–0.83	24%	Rope, bottle caps, netting
Polystyrene	PS	1.05	6%	Plastic utensils, food containers
Foamed Polystyrene				Floats, bait boxes, foam cups
Nylon	PA		<3%	Netting and traps
Thermoplastic Polyester	PET	1.37	7%	Plastic beverage bottles
Poly(vinyl chloride)	PVC	1.38	19%	Plastic film, bottles, cups
Cellulose Acetate	CA			Cigarette filters

[#] Fraction of the global plastics production in 2007 after (Brien, 2007).

stained by lipophilic dyes. Digestion of the sample with hot dilute mineral acid can be used to remove the biomass impurities as the treatment will not have any impact on the microplastics fraction. Microplastics suspensions might be identified using optical microscopy, electron microscopy, Raman spectroscopy and FTIR spectroscopy. The Fig. 1 below shows a schematic of this suggested sampling approach designed to isolate microplastics.

As a prelude to discussing the mechanisms responsible for generation of microplastics, understanding the light-induced degradation and biodegradation of plastics in the marine environment is important.

1.3. Plastics degradation under marine conditions

Degradation is a chemical change that drastically reduces the average molecular weight of the polymer. Since the mechanical integrity of plastics invariably depends on their high average molecular-weight, any significant extent of degradation inevitably weakens the material. Extensively degraded plastics become brittle enough to fall apart into powdery fragments on handling. Even these fragments, often not visible to the naked eye, can undergo further degradation (generally via microbial-mediated biodegradation) with the carbon in polymer being converted into CO_2 (and incorporated into marine biomass). When this process goes onto completion and all the organic carbon in the polymer is converted, it is referred to as complete mineralisation (Andrady, 1994, 1998; Eubeler et al., 2009).

Degradation is generally classified according to the agency causing it.

(a) Biodegradation – action of living organisms usually microbes.
(b) Photodegradation – action of light (usually sunlight in outdoor exposure).
(c) Thermooxidative degradation – slow oxidative breakdown at moderate temperatures.
(d) Thermal degradation* – action of high temperatures.
(e) Hydrolysis – reaction with water.
*Not an environmental degradation mechanism.

With common polymers such as LDPE, HDPE, PP and nylons exposed to the marine environment it is primarily the UV-B

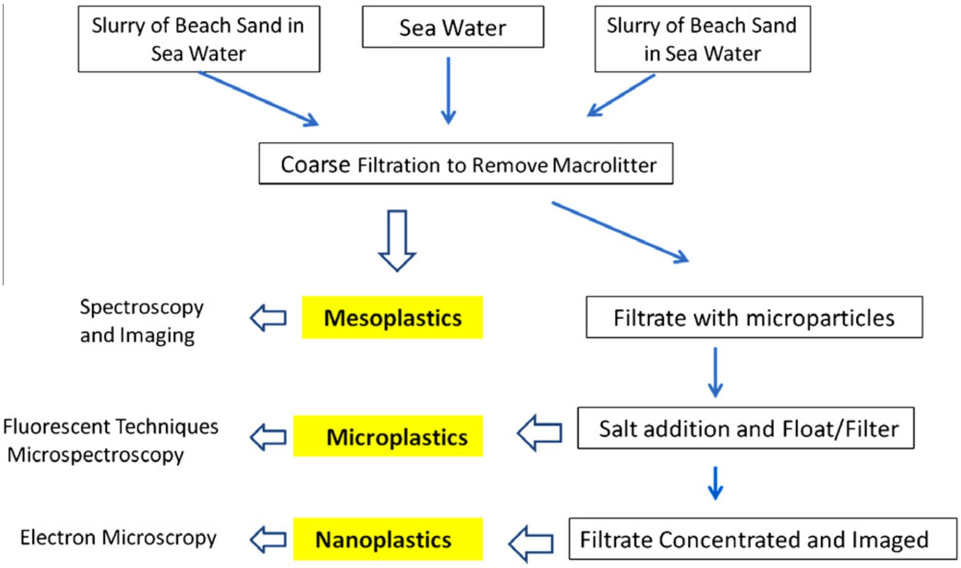

Fig. 1. Proposed scheme for isolation of plastics from samples of water or sand.

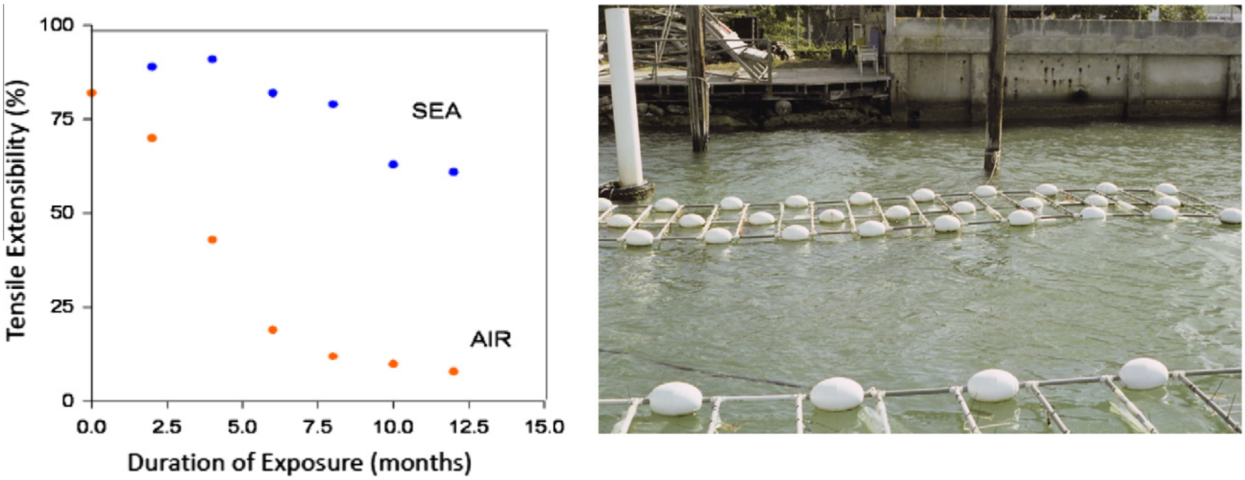

Fig. 2. (Left): Change in percent original tensile extensibility of polypropylene tape exposed in air and floating in sea water in Biscayne Bay, FL. (Right): The floating rig used to expose plastics to surface water environment (Miami Beach, FL).

radiation in sunlight that initiates photo-oxidative degradation. Once initiated, the degradation can also proceed thermooxidatively for some time without the need for further exposure to UV radiation. The autocatalytic degradation reaction sequence can progress as long as oxygen is available to the system. On degradation the molecular weight of the polymer is decreased and oxygen-rich functional groups are generated in the polymer. Other types of degradation processes are orders of magnitude slower compared to light-induced oxidation. Hydrolysis is usually not a significant mechanism in seawater. While all biomaterials, including plastics, will invariably biodegrade in the marine environment, the rate of this process, even in the benthic sediment, is several orders of magnitude slower compared to light-induced oxidative degradation of plastics.

Degradation initiated by solar UV radiation is a very efficient mechanism in plastics exposed in air or lying on a beach surface. But when the same plastic material is exposed to sunlight at the same location but while floating in seawater, degradation is severely retarded. Andrady and Pegram (1990, 1989a,b) and Andrady et al. (1993) compared the loss of mechanical integrity of several common packaging and gear-related plastics exposed while floating in sea water with those exposed in air at the same sites (in Biscayne Bay, FL and Pugeot Sound, WA.) The dramatic reduction in the degradation rate obtained is illustrated in Fig. 2 (left) with the data for polypropylene tape. Tensile extensibility (%) was used as the measure of degradation in the study and near-embrittlement was the end-point of interest as degradation to this extent precluded entanglement of marine mammals on the debris. Other varieties of plastics exposed on beach or in water also undergo similar degradation. For instance, the degradation of fishing gear by sunlight has been studied by Al-Oufi et al. (2004) and Meenakumari and Radhalakshmi (1995, 1988). The weathering of specific gear-related plastics such as polyethylene netting (Meenakumari and Ravindran, 1985a,b), nylon monofilament exposed in air at marine sites (Meenakumari and Radhalakshmi, 1988; Thomas and Hridayanathana, 2006) and twine (Meenakumari and Ravindran, 1985a,b, 1988) has been reported.

The retardation of degradation in plastics exposed to the elements while floating in sea water is primarily the result of the relatively lower temperatures and the lower oxygen concentration in water environments. Unlike samples exposed in air, the sample temperatures are maintained at the lower water temperature, retarding the reaction. The discrepancy in the degradation rates (between air and floating exposures) is further exacerbated by fouling effects. Floating plastics will readily develop extensive surface fouling, rapidly covering the debris surface first with a biofilm followed by an algal mat and then a colony of invertebrates (Muthukumar et al., 2011). Initial rate of biofouling depends on the surface energy S of the plastic; materials with S between 5 and 25 mN/m are minimally fouled (Kerr and Cowling, 2003). The succession of epibionts that develop on the surface colony was reported for exposures in Biscayne Bay, FL (Andrady and Song, 1991); the sequence was bacteria → diatoms → hydroids → ectocarpales → barnacles → bryozoans. The sequence as well as the kinetics of fouling, however, strongly depend on water conditions as well as the season of exposure. The plastic debris gets encrusted with foulants, increasing in density as fouling progresses. Once the density exceeds that of sea water it can sink well below the water surface (Costerton and Cheng, 1987; Andrady and Song, 1991; Railkin, 2003). Subsequent de-fouling in the water column due to foraging of foulants by other organisms or other mechanisms, can decrease its density causing the debris to return back to the surface. A slow cyclic 'bobbing' motion of floating plastic debris attributed to this cyclic change in density on submersion below a certain depth of water, was proposed by Andrady and Song (1991) and later confirmed (Stevens and Gregory, 1996; Stevens, 1992). Fouled debris may increase in density enough to ultimately reach benthic regions; plastics do occur commonly in the benthos (Stefatos and Charalampakis, 1999; Katsanevakis et al., 2007; Backhurst and Cole, 2000).

Even an extensively weathered, embrittled plastic material (that falls apart on handling) still has an average molecular weight in the tens of thousands g/mol. The logarithmic plot of the tensile extensibility (%) versus the number-average molecular weight for LDPE that had undergone weathering shown in Fig. 3 illustrates this. Even for the data points at the very left of the plot (corresponding to extensively degraded or embrittled plastic) the values of $M_n \sim 10^3$–10^4 g/mol. Even at these lower molecular weights plastics do not undergo ready biodegradation. Ready microbial biodegradability has been observed in oligomers of about $M_n \sim 500$ g/mol polyethylenes. Reduction in particle size by light-induced oxidation does is no guarantee of subsequent biodegradability of the meso- or microplastic fragments.

High molecular weight plastics used in common applications do not biodegrade at an appreciable rate as microbial species that can metabololize polymers are rare in nature. This is particularly true of the marine environment, with the exception of biopolymers such as cellulose and chitin. Recent work, however, has identified several strains of microbes capable of biodegrading polyethylene (Sivan, 2011) and PVC (Shah et al., 2008). In concentrated liquid culture in the laboratory, Actinomycetes *Rhodococcus ruber* (strain C208) resulted in a reduction of ca. 8% in the dry weight of the polyolefin within 30 days of incubation (Gilan et al., 2004). Laccases secreted by the species reduced the average molecular weight of polymer as demonstrated by GPC indicating degradation via scission of main chains. However, this process does not occur in soil or marine environments as the candidate microbes are not available in high enough native concentration and competing easily-assimilable nutrient sources are always present.

There is virtually no data on kinetics of mineralisation of plastics in the marine environment. However, biopolymers such as chitins (Poulicek and Jeuniaux, 1991; Seki and Taga, 1963), chitosan (Andrady et al., 1992), and a few synthetic polymers such as aliphatic polyesters do biodegrade rapidly at sea (Mayer and Kaplan, 1996; Doi et al., 1992; Leathers et al., 2004). Starch-filled polyolefins (Gonsalves and Patel, 2003; Breslin and Boen, 1993) are sometimes erroneously referred to as 'biodegradable', but only the starch fraction undergoes ready mineralisation in the marine environment. Ideally, the polymer material disposed in the environment should biodegrade completely releasing the carbon into the carbon cycle. Mineralisation is the complete conversion of carbon that constitutes the plastics into CO_2, water and biomass.

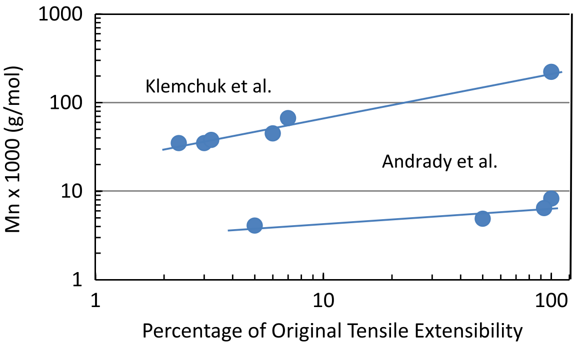

Fig. 3. Two sets of data showing the relationship between number-average molecular weight and the percent retention of extensibility of degraded polyethylene. The upper set is for data is for high-density polyethylene oxidised in oxygen at 100 C (Klemchuk and Horng, 1984). Upper set is for poly(ethylene-co-carbon monoxide (1%)) exposed outdoors at ambient temperature in air (Andrady et al., 1993).

For a polymer such as a nylon that contains C, H, O, N the chemical conversions is as follows:

$$C_aH_bO_cN_d + \left(2a + \frac{3d-b}{2} - c\right)O$$
$$= aCO_2 \frac{3d-b}{2} H_2O + dNH_3 \quad \text{for} \quad (3d > b)$$

$$C_aH_bO_cN_d + \left(2a + \frac{b-3d}{2} - c\right)O$$
$$= aCO_2 \frac{b-3d}{2} H_2O + dNH_3 \quad \text{for} \quad (3d > b)$$

The rate of carbon conversion under simulated marine exposure is measured in the laboratory using respirometry (Eubeler et al., 2009; Shah et al., 2008; Allen and Mayer, 1994). Finely-divided polymer is incubated in a biotic medium such as coastal marine sediment and the carbon dioxide gas evolved during biodegradation is quantified. To accelerate mineralisation, the medium is typically enriched with urea (N)/ Phosphates (P), and seeded with an active microbial culture. The carbon dioxide is estimated titrimetrically and the percent conversion of carbon from polymer to gas-phase is calculated. This forms the basis of the Sturm test widely used with organic compounds. Assessment of Biodegradation of polymers was reviewed (Andrady, 1994; Eubeler et al., 2009; Shah et al., 2008).

Even under optimum laboratory conditions, in soil seeded with activated sewage sludge consortia, the rate of CO_2 evolution from biodegradation of polyolefins is so slow that ^{14}C-labelled polymer was used to monitor the process (Albertsson, 1978; Albertsson and Karlsson, 1988). Recent data show <1.2% carbon conversion over a 3-month period (Abrusci et al., 2011) in agreement with previous rate determinations. Pre-oxidised (extensively degraded) polymers will biodegrade at a faster rate. Rates of 0.2% and 5.7% carbon conversion per 10 years for low-density polyethylene [LDPE] without and with pre-photodegradation were reported, respectively. Guillet et al. reported biodegradation of pre-photooxidized polystyrene in soil with growing plants to proceed at a rate of ~5% over 6 months (Guillet et al., 1988). However, these results are likely to be overestimates as the lower molecular-weight polymer fraction and hydrophilic oxygenated degradation products from extensive pre-degradation (Andrady and Pegram, 1993) are likely to initially biodegrade rapidly. In any event the finding is of little practical consequence. Embrittlement in beach weathering increases the specific surface area of the plastics by several orders of magnitude and this might be expected to increase its rate of biodegradation (Kawai et al., 2004). But, this small increase in the rate of an already very slow process to effect its complete mineralisation in a reasonable timescale of a few years. The laboratory results are generally consistent with the findings from field exposures; HDPE, LDPE and PP coupons immersed in Bay of Bengal (India) observed over a 6-month periods in a recent study. Maximum weight loss was in LDPE (1.5–2.5%), followed by that in HDPE (0.5–0.8%) and PP (0.5–0.6%) (Sudhakar and Doble, 2008).

1.4. Origins of microplastics

How are microplastics in the oceans generated? The origins of the microplastics might be attributed to two main sources: (a) direct introduction with runoff and (b) weathering breakdown of meso- and macroplastics debris. Some microplastics, especially the manufactured micro- and nanoparticles of plastics used in consumer products (Maynard, 2006), are introduced directly into the oceans via runoff. These include the micron-sized plastic particles are typically used as exfoliants in cosmetic formulations (Gregory, 1996; Fendall and Sewell, 2009), those generated in ship-breaking industry (Reddy and Shaik, 2006) and industrial abrasives in synthetic ‘sandblasting’ media (beads of acrylic plastics and polyester). These can easily reach the oceans via runoff.

The likely mechanism for generation of a majority of microplastics, however, is the *in situ* weathering of mesoplastics and larger fragments of plastic litter in the beach environment (Gregory and Andrady, 2003). Plastic litter occurs on beaches, surface water and deep water environments but as already pointed out the rates of weathering in these three sites will be very different. Unlike those floating in water, plastics litter lying on beaches is subjected to very high temperatures. Given the relatively low specific heat of sand (664 J/kg-C), sandy beach surfaces and the plastic litter on it can heat up to temperatures of ~40 °C in Summer. Where the plastic debris is pigmented dark, the heat build-up due to solar infrared absorption can raise its temperature even higher (Shaw and Day, 1994).The light-initiated oxidative degradation is accelerated at higher temperatures by a factor depending on the activation energy E_a of the process. Where the $E_a \sim 50$ kJ/mole for instance, the rate of degradation doubles when the temperature rises by only 10 °C.

Especially with opaque plastics, nearly all the initial oxidative breakdown occurs at the surface layers. This localised degradation is because of the high extinction coefficient of UV-B radiation in plastics, the diffusion-controlled nature of oxidation reaction (Cunliffe and Davis, 1982) and the presence of fillers that impede oxygen diffusion in the material. Degradation occurs faster in virgin pellets that contain no UV stabilizers compared to that in plastics products. Net result of this mode of oxidative degradation is a weak, brittle surface layer that develops numerous microcracks and pits as shown in the micrographs in Fig. 4 (Qayyum and White, 1993; Blaga and Yamasaki, 1976; Blaga, 1980). This degraded fragile surface is susceptible to fracture by stress induced by humidity or temperature changes as well abrasion against sand (George, 1995). Microparticles of plastics are derived from this brittle surface layer. Surface microcracking is commonly observed in UV-exposed plastics including HDPE (Akay et al., 1980), LDPE (Küpper et al., 2004; Tavares et al., 2003), polycarbonate (Blaga and Yamasaki, 1976) and polypropylene (Qayyum and White, 1993; Yakimets et al.,

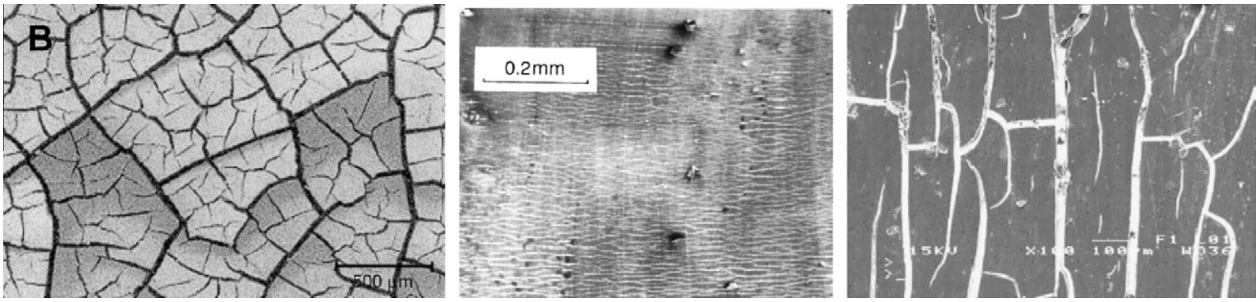

Fig. 4. Right: PP exposed to a 600 watt xenon source for 6 weeks (Yakimets et al. 2004); Middle: PP exposed for 1 week under desert exposure conditions (Qayyum and White, 1993); Left: LDPE weathered in a weatherometer for 800h (Küpper, et al., 2004).

2004). Consistent with these findings, extensive microcracking and pitting is reported on mesoplastic debris collected from beaches as well (Cooper and Corcoran, 2010; Gregory, 1983; Ogata et al., 2009). Polypropylene rope sample that had weathered on a pier for several years (provided courtesy of Capt. Charles Moore, Algalita Marine Foundation) when extracted with distiled water yielded large amounts of plastic microplastics that were visualised by staining with Nile Red (Andrady, 2010).

The same degradation does not occur in plastics exposed while floating in water. As pointed out already, the low water temperature and foulant effects retard the process dramatically. Plastics that are directly discarded into the water (from vessels) or litter washed into the water prior to any significant weathering degradation are also unlikely to yield microplastics via this mechanism. The same is true of plastics debris that sink in the water column. The lack of UV-B (rapidly attenuated in sea water) to initiate the process, the low temperatures and the lower oxygen concentration relative to that in air, makes extensive degradation far less likely than for the floating plastics debris. Thus the most likely site for generation of microplastics in the marine environment is the beach.

Recognition that microparticles (and therefore also nanoplastics) are most likely generated on beaches underlines the importance of beach cleaning as an effective mitigation strategy. The removal of larger pieces of plastic debris from beaches before these are weathered enough to be surface embrittled can have considerable value in reducing the microplastics that end up in the ocean. Beach cleanup therefore can have an ecological benefit far beyond the aesthetic improvements of the beaches, and by reducing microplastics, contributes towards the health of the marine food web.

1.5. Toxicity of ingested microplastics

Sea water already contains numerous natural micro- and nanoparticles ($\sim 10^6$–10^7 particles per ml or 10–500 μg/l) most of them <100 nm in size (Rosse and Loizeau, 2003). Filter feeders in the ocean ranging from the nano-zooplanktons to Balleen Whales, routinely interact with these without any apparent ill effect. As no enzymatic pathways available to break down the synthetic polymers in any of these organisms, ingested of microplastics are also never digested or absorbed and should therefore be bio-inert. Ingestion of microplastics by microbiota, however, presents a very different problem. The concern is their potential for delivery of concentrated POPS, mainly those picked up from sea water, to the organisms (Bowmer and Kershaw, 2010). It is this dissolved POPs that yield the toxic outcomes.

Any toxicity associated with plastics in general, including meso- or microplastics, can be attributed to one or more of the following factors:

(a) Residual monomers from manufacture present in the plastic or toxic additives used in compounding of plastic may leach out of the ingested plastic. {An example of residual monomer is illustrated by the recent issue on residual bis-phenol A (BPA) in polycarbonates products (Vandenberg et al., 2007). The potential toxicity of phthalate plasticizers used in PVC has been widely discussed in the literature (Latini et al., 2004).}

(b) Toxicity of some intermediates from partial degradation of plastics. For instance, burning polystyrene can yield styrene and other aromatics and a partially burnt plastic may contain significant levels of styrene and other aromatics.

(c) The POPs present in sea water are slowly absorbed and concentrated in the microplastic fragments. Plastics debris does 'clean' the sea water of the dissolved pollutant chemicals. On being ingested, however, these can become bioavailable to the organisms (Endo et al., 2005).

The risk posed by the high concentrations of POPs picked up from the sea water is particularly significant. Sea water typically contains low levels of a host of chemical species such as insecticides, pesticides and industrial chemicals that enter the ocean via waste water and runoff (Wurl and Obbard, 2004). POPs such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and perfluorooctanoic acid (PFOA) have a very large water-polymer distribution coefficient, $K_{P/W}$ [L/kg], in favour of the plastic. A linear isotherm model relates the mass of the chemical sorbed per unit mass of solid polymer (q_e) [μg/kg] to the equilibrium solute concentration (C_e) [μg/L] by the following equation:

$$q_e = K_{P/W} \cdot C_e \tag{1}$$

where $K_{P/W}$ (L/kg) is the equilibrium distribution coefficient for the system. This coefficient is approximated sometimes by the lipid–water distribution coefficient. However, this may underestimate the polymer–water distribution coefficient seriously for some POPs (Friedman et al., 2009).

The distribution of organic micropollutants in hydrophobic plastics has been studied in polypropylene pellets (Rice and Gold, 1984) and polyethylene strips (tested as potential passive sampling devices) (Fernandez et al., 2009; Müller et al., 2001; Adams et al., 2007). Karapanagioti and Klontza (2008) estimated the distribution coefficient $K_{P/W}$ for phenanthrene, a model POP, in virgin plastic/sea water system; values of K_d (L/kg) of 13,000 for PE and 380 for PP was reported. A second study by Teuten et al., 2007 reported the uptake of phenanthrene by three types of plastics, concluding the distribution coefficients to be ranked as follows: Polyethylene = Polypropylene > PVC. Values of $K_{P/W}$ [L/kg] of $\sim 10^4$ for polyethylene and $\sim 10^3$ for polypropylene were reported. Importantly, they established that desorption of the contaminant (back into water) was a very slow process and that even the sediment tended to desorb the phenanthrene faster than plastics fragments. Others reported similar high values for $K_{P/W}$ [L/kg] in common polymers; these include Lohmann et al. (2005) who reported 27,000 L/kg for polyethylene, and Mato et al. (2001) who reported even higher values for PCBs in polypropylene. The reported high variability of the experimental $K_{P/W}$ values in literature can be attributed to differences in water temperature, the degree of crystallinity of the plastic and non-equilibrium effects. These values imply that plastic meso- and microparticles in the ocean will at equilibrium yield a highly concentrated source of POPs.

A recent study by Rios and Moore (2007) on plastic mesooparticles on four Hawaiian, one Mexican and five California beaches showed very significant levels of pollutants in the particles. The ranges of values reported were: $\sum$ PAH = 39–1200 ng/g: $\sum$ PCB = 27–980 ng/g: $\sum$ DDT = 22–7100 ng/g. These are cumulative values for 13 PCB congeners and 15 PAHs.The cumulative levels found in plastic pellets collected from locations near industrial sites were understandably much higher. Highest values reported were $\sum$ PAH = 12,000 ng/g and DDT = 7100 ng/g. A 2009 study reported data for 8 US beaches (of which 6 were in CA) as follows (Ogata et al., 2009): $\sum$ PCB = 32–605 ng/g; $\sum$ DDT = 2–106 ng/g; and $\sum$ HCH(4 isomers) = 0–0.94 ng/g. The levels of pollutants in plastic pellets floating in surface layers are comparable to the range observed for sediment concentration of the same compounds. Recent work has suggested that micro- and mesoplastic debris may also concentrate metals (Ashton et al., 2010) in addition to the POPs. This is an unexpected finding as the plastics are hydrophobic but the oxidised surface could carry functionalities that can bind metals.

The situation is reversed in the case of residual monomer and additives compounded into plastics as well as partially degraded plastics carrying degradation products. These plastics debris will slowly leach out a small fraction of the POPs (additives, monomer or products) into the sea water until the appropriate $K_{P/W}$ [L/kg] value is reached. The equilibrium is a dynamic one and the POPs are never irreversibly bound to the polymer but diffuse in an out of the plastic fragment depending on changes in the concentration of the POP in sea water. In contrast to 'cleaning' of sea water by virgin plastics these tend to leach a small amount of the POPs into seawater However, while no good estimates or models are available for the process, the total plastics debris-mediated pollutant load introduced into seawater is likely to be at least several orders of magnitude smaller than that introduced from air and waste water influx into oceans. The critical ecological risk is not due to low-levels of POPs in water but from the bioavailability of highly concentrated pools of POPs in microplastics that can potentially enter the food web via ingestion by marine biota.

Microparticles and nanoparticles fall well within the size range of the staple phytoplankton diet of zooplanktons such as the Pacific Krill. There is little doubt that these can be ingested. Plastic microbeads have been commonly used in zooplankton feeding research. There are numerous references in the literature (Berk et al., 1991; Leys and Eerkes-Medrano, 2006; Powell and Berry, 1990) as well as anecdotal accounts of zooplanktons ingesting plastic particles. The Pacific Krill (*Euphasea Pacifica*), for instance, was observed to ingest its staple algae as well as polyethylene beads ground to about the same size range with no evident foraging bias (Andrady, 2009). However, no studies have been conducted with plastic beads loaded with POPS; also, it is not known if any chemotactic or other warning signals that discourage their ingestion (as opposed to that of 'clean' plastic beads) by at least some of the species at risk, operate in nature. Table 2 Is a selection of some of the marine species shown to be able to ingest plastic beads in laboratory studies.

Table 2
Some marine species reported to ingest plastic microparticles.

Phylum	Species	Size of plastic	Reference
Echinodermata	*Holothuria fieldana, H. grisea, Cucumaria frondosa* and *Thyonella gemmata*	*Mesoplastic*	Graham and Thompson (2009)
Mollusca	*Mytilus edulis*	Microplastics	Browne et al. (2008)
Lug Worms	Arenicola marina		Thompson et al. (2004), Voparil et al. 2004 and Teuten et al., 2007

Information on the bioavailability of sorbed POPS to the organism subsequent to ingestion of tainted microplastics by different species is particularly sparse. In marine lug worms, a deposit feeder, Voparil et al. (2004) demonstrated the bioavailability of PAHs in anthropogenic particles such as tire tread, diesel soot placed in gut fluid. Gut surfactants in benthic deposit feeders possibly enhances the bioavailability of POPs in these species (Voparil and Mayer, 2000; Teuten et al., 2007). Especially with plankton species with a very small body mass, the quantity of POPs delivered via saturated microparticles could have a significant toxicological impact. The dose delivered will depend not only on the volume of microparticle ingested but also on its residence time in the organism and the kinetics of repartition of the POPs between the plastic and tissue medium of zooplanktons. In larger marine species such as the Great Shearwater (*Puffinus gravis*) the amounts of ingested contaminated plastics and polychlorinated biphenyls (PCBs), DDE, DDT, and dieldrin) in adult fat tissue were positively correlated (Ryan et al., 1988). No data is available on the transfer coefficients across marine trophic levels for POPS introduced via ingested microplastics.

1.6. Nanoplastics in the oceans

Engineered plastic nanoparticles derived from post-consumer waste as well as from meso-/microplastics via degradation pose a specific challenge to the ecosystem. Though as yet not quantified, there is little doubt that nanoscale particles are produced during weathering of plastics debris. If these are able to persist as free nanoparticles once introduced into water medium is an important consideration. Nanoparticles in air and water readily agglomerate into larger clusters or lose aggregates with other material. Nanoparticles incorporated in these can still be ingested by filter feeders (Ward and Kach, 2009) but if they will have the same physiological impact of the primary nanoparticles is not known.

Small Eukaryotic protists, Diatoms and Flagellates that measure in the range of 200 nm to a couple of microns are abundant in the oceans. Recent studies based on quantifying the photosynthetic pigments indicate the nano- and picoplankton are not only the predominant group of plankton biomass but are also the predominant contributors to primary production (Uitz et al., 2010). As plastic nanoparticles in the water are of a comparable size scale, understanding their mechanisms of interaction with the nano- or picofauna is particularly important. While some limited data on the interaction of nanoparticles with biota is available, the studies have been for the most part on non-organic, engineered nanoparticles such as oxides, metals, carbon nanotubes and quantum dots (Templeton et al., 2006). Though these have shown different levels of toxicity to algae (Hund-Rinke and Simon, 2006), zooplankton (Lovern and Klaper, 2006: Templeton et al., 2006), *Daphnea* sp. (Roberts et al., 2007), zebra fish embryo (Usenko et al., 2008; Zhu et al., 2007), bivalves (Gagné et al., 2008) fat-head minnow (Zhu et al., 2006), rainbow trout (Smith et al., 2007; Federici et al., 2007), Zebra fish (Griffitt et al., 2008; Asharani et al., 2008), the data cannot be reliably extrapolated to polymer nanoparticles. Inorganic nanoparticles may carry some POPs via surface absorption but plastic particles are expected to have much higher levels of matrix-solubilised POPs. Data on the effects of plastic nanoparticles on marine flora and fauna (Bhattacharya et al., 2010; Brown et al., 2001) are limited.

Pico- and nanoparticles are within the size range where these can enter cells by endocytosis. This route of interaction is effective and the potential of using nanoparticles to deliver drugs intracellularly is being actively explored. Physiological impacts of endocytosed polymer nanoparticles carrying POPS in planktons have not been studied. Interaction of nanoplastic debris with biota can result in their internalisation affecting marine animals systemically. For instance, nanoparticles of Fullerene that deposit on gill epithelium of Bass can be internalised and be directed to the brain via axonic pathway of the olfactory nerve (Oberdörster, 2004), a route also available for biological particles such as virusus. A polymer nanoparticle laden with POPs can also follow the same pathway likely deposit its load into lipophilic neural tissue.

2. Conclusions

Production trends, usage patterns and changing demographics will result in an increase in the incidence of plastics debris and microplastics, in the ocean environment. A primary mechanism for microplastics generation appears to be the weathering-related fracturing and surface embrittlement of plastics in beach environments. Micro- and nanoplastics are recalcitrant materials under marine exposure conditions. While they constitute only a very small fraction of the micro- and nanoparticulates present in sea water, the proven propensity of plastics to absorb and concentrate POPs is a serious concern. As POPs – laden particles are potentially ingestible by marine organisms including micro- and nanoplankton species, the delivery of toxins across trophic levels via this mechanism is very likely. The efficiency of such transfer will depend on the bioavailablity of POPs and the residence time of meso- or microplastics in the organisms. Endocytosis of plastic nanoparticles by micro- or nanofauna can also result in adverse toxic endpoints. As plankton species constitute the very foundation of the marine food web, any threat to these can have serious and far-reaching effects in the world oceans. There is an urgent need to quantify the magnitude of these potential outcomes and assess the future impact of increasing microplastics levels on the world's oceans.

References

Abrusci, C., Pablos, J.L., Corrales, T., López-Marín, J., Marín, I., Catalina, F., 2011. Biodegradation of photo-degraded mulching films based on polyethylenes and stearates of calcium and iron as pro-oxidant additives. Int. Biodeter. Biodegr. 65 (3), 451–459.

Adams, R.G., Lohmann, R., Fernandez, L.A., MacFarlane, J.K., Gschwend, P.M., 2007. Polyethylene devices: passive samplers for measuring dissoled hydrophobic organic compounds in aquatic environments. Environ. Sci. Technol. 41, 1317–1323.

Akay, G., Tinçer, T., Ergöz, H.E., 1980. A study of degradation of low density polyethylene under natural weathering conditions. Eur. Polymer J. 16 (7), 601–605.

Albertsson, A.-C., 1978. Biodegradation of synthetic polymers. 2. Limited microbial conversion of C-14 in polyethylene to (CO-2)-C-14 by some soil fungi. J. Appl. Polym. Sci. 22, 3419.

Albertsson, A.-C., Karlsson, S.J., 1988. The three stages in degradation of polymers – polyethylene as a model substance. J. Appl. Polym. Sci. 35, 1289–1302.

Allen, A.L., Mayer, J., 1994. Simulated marine respirometry of biodegradable polymers. J. Polym. Environ. 2 (4), 237–244.

Al-Oufi, H., McLean, E., Kumar, A.S., Claereboudt, M., Al-Habsi, M., 2004. The effects of solar radiation upon breaking strength and elongation on of fishing nets. Fish. Res. 66 (1), 115–119.

Andrady, A.L., 1994. Assessment of environmental biodegradation of synthetic polymers: a review. J. Macromol. Sci. R. M. C 34 (1), 25–75.

Andrady, A.L., 1998. Biodegradation of plastics. In: Pritchard, G. (Ed.), Plastics Additives. London, Chapman Hall.

Andrady, A.L., 2003. Plastics and the environment. In: Anthony L. Andrady (Ed.), Publisher: John Wiley and Sons, ISBN 0-471-09520-6.

Andrady, A.L., 2009. Proceedings of the International Research Workshop on the Occurrence, Effects and Fate of Micro-plastic Marine Debris, Sept 9-11, 2008. NOAA Technical Memorandum NOS-OR&R-30. Arthur, C., Baker, J., and Bamford, H., (Eds.).

Andrady, A.L., 2010. Measurement and Occurrence of Microplastics in the Environment. Presentation at the 2nd Research Workshop on Microplastic Debris. Tacoma, WA, Nov 5–6, 2010.

Andrady, A.L., Pegram, J.E., 1989a. Outdoor weathering of selected polymeric materials under marine exposure conditions. Polym. Degrad. and Stab. 26, 333.

Andrady, A.L., Pegram, J.E., 1989. Degradable Plastics in the Marine Environment. International Conference on Recent Developments in Petrochemical and Polymer Technologies, Chulalongkorn University, Bangkok, Thailand, Chulalongkorn University, December 1989.

Andrady, A.L., Pegram, J.E., 1990. Weathering of polyethylene (LDPE) and enhanced photodegradable polyethylene in the marine environment. J. Appl. Polym. Sci. 39, 363–370.

Andrady, A.L., Pegram, J.E., 1993. Studies on enhanced degradable plastics: II. Weathering of enhanced photodegradable polyethylenes under marine and freshwater floating exposure. J. Environ. Degrad. 1 (2), 117–126.

Andrady, A.L., Song, Y., 1991. Fouling of floating plastic debris under biscayne bay exposure conditions. Mar. Poll. Bull. 22 (12), 117–122.

Andrady, A.L., Pegram, J.E., Olson, T.M., 1992. Research and Development of Two Marine-Degradable Biopolymers; Technical Report A150452 David Taylor Research Center. US Department of the Navy.

Andrady, A.L., Pegram, J.E., Tropsha, Y., 1993. Changes in carbonyl index and average molecular weight on embrittlement of enhanced-photodegradable polyethylenes. J. Environ. Polym. Degrad. 1 (3), 171–179.

Arthur, C., Baker, J., and Bamford, H., (Eds.), 2009. Proceedings of the International Research Workshop on the Occurrence, Effects and Fate of Micro-plastic Marine Debris, Sept 9-11, 2008. NOAA Technical Memorandum NOS-OR&R-30.

Asharani, P.V., Wu, W.L., Gong, Z., Valiyavetti, 2008. Toxicity of silver nanoparticles in zebrafish models. Nanotechnology 19 (25), 255102.

Ashton, K., Holmes, L., Turner, A., 2010. Association of metals with plastic production pellets in the marine environment. Mar. Pollut. Bull. 60 (11), 2050–2055.

Backhurst, M.K., Cole, R.G., 2000. Subtidal benthic marine litter at Kawau Island, north-eastern New Zealand. J. Environ. Manage. 6, 227–237.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. Philos. Trans. R. Soc. B 364, 1985–1998.

Berk, S.G., Parks, L.S., Tong, R.S., 1991. Photoadaptation alters the ingestion rate of paramecium bursaria, a mixotrophic ciliate. Appl. Environ. Microbiol. 57 (8), 2312–2316.

Betts, K., 2008. Why small plastic particles may pose a big problem in the oceans. Environ. Sci. Technol. 42, 8995.

Bhattacharya, P., Lin, L., Turner, J.P., Ke, P.C., 2010. Physical adsorption of charged plastic nanoparticles affects algal photosynthesis. J. Phys. Chem. C 114 (39), 16556–16561.

Blaga, A., 1980. In: Sereda, P.J., Litvin, G.G., (Eds.), Durability of Building Materials and Compounds. ASTM STP 691. ASTM, Philadelphia, pp. 827–837.

Blaga, A., Yamasaki, R.S., 1976. Surface microcracking induced by weathering of polycarbonate sheet. J. Mater. Sci. 11, 1513–1520.

Bowmer, T., Kershaw, P., 2010. Proceedings of the GESAMP International Workshop on Micro-plastic Particles as a Vector in Transporting Persistent, Bio-accumulating and Toxic Substances in the Oceans June 2010. UNESCO-IOC, Paris.

Breslin, V.T., Boen, L.I., 1993. Weathering of starch-polyethylene composite films in the marine environment. J. Appl. Polym. Sci. 48 (12), 2063–2079.

Brien, S., 2007. Vinyls Industry Update. Presentation at the World Vinyl Forum 2007, Sept. 2007. Retrieved from http://vinyl-institute.com/Publication/WorldVinylForumIII/VinylIndustryUpdate.aspx.

Brown, D.M., Wilson, M.R., MacNee, W., Stone, V., 2001. Donaldson, size-dependent pro-inflammatory effects of ultrafine polystyrene particles: a role for surface area and oxidative stress in the enhanced activity of ultrafines. Toxicol. Appl. Pharmacol. 175, 191–199.

Browne, M.A., Dissanayake, A., Galloway, T.S., Lowe, D.M., 2008. Ingested microscopic plastic translocates to the circulatory system of the mussel, *Mytilus edulis*. Environ. Sci. Technol. 42 (13), 5026–5031.

Bugoni, L., Krause, L., 2001. Marine debris and human impacts on sea turtles in southern Brazil. Mar. Pollut. Bull. 42 (12), 1330–1334.

Bullimore, B.A., Newman, P.B., Kaiser, M.J., Gilbert, S.E., Lock, K.M., 2001. A study of catches in a fleet of 'ghost-fishing' pots. Fish. Bull. 99, 247–253.

Cadee, G.C., 2002. Seabirds and floating plastic debris. Mar. Pollut. Bull. 44 (11), 1294–1295.

Carpenter, E.J., Smith Jr., K.L., 1972. Plastics on the Sargasso Sea surface. Science 175, 1240–1241.

Carpenter, E.J., Anderson, S.J., Harvey, G.R., Miklas, H.P., Peck, B.B., 1972. Polystyrene spherules in coastal water. Science 178, 749–750.

Clapham, P.J., Young, S.B., Brownell, J.R., 1999. Baleen whales: conservation issues and the status of the most endangered populations. Mammal Rev. 29, 35–60.

Coe, J., Rogers, D., 1996. Marine Debris Sources, Impacts, and Solutions. Springer-Verlag, New York.

Colton, J.B., Knapp, F.D., 1974. Plastic particles in surface waters of the northwestern Atlantic. Science 185, 491–497.

Cooper, D.A., Corcoran, P.L., 2010. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. Mar. Pollut. Bull. 60 (5), 650–654.

Costerton, J.W., Cheng, K.J., 1987. Bacterial biofilms in nature and disease. Annu. Rev. Microbiol. 41, 35–464.

Cunliffe, A.V., Davis, A., 1982. Photo-oxidation of thick polymer samples – Part II: The influence of oxygen diffusion on the natural and artificial weathering of polyolefins. Polym. Degrad. Stabil. 4 (1), 17–23.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. 44 (9), 842–852.

Doi, Y., Kanesawa, Y., Tanahashi, N., Kumagai, Y., 1992. Biodegradation of microbial polyesters in the marine environment. Polym. degrad. stabil. 36 (2), 173–177.

Doyle, M.J., Watson, W., Bowlin, N.M., Sheavly, S.B., 2011. Plastic particles in coastal pelagic ecosystems of the Northeast Pacific ocean. Mar. Environ. Res. 71 (1), 41–52.

Endo, S., Takizawa, R., Okuda, K., Takada, H., Chiba, K., Kanehiro, H., Ogi, H., Yamashita, R., Date, T., 2005. Concentration of polychlorinated biphenyls (PCBs) in beached resin pellets: variability among individual particles and regional differences. Mar. Poll. Bull. 50, 1103–1114.

Erikson, C., Burton, H., 2003. Origins and biological accumulation of plastic particles in fur seals from Macquarie Island. Ambio 32, 380–384.

Eubeler, J.P., Zok, S., Bernhard, M., Knepper, T.P., 2009. Environmental biodegradation of synthetic polymers I. Test methodologies and procedures. Trend. Anal. Chem. 28 (9), 1057–1072.

Federici, G., Shaw, B., Handy, R., 2007. Toxicity of titanium dioxide nanoparticles to rainbow trout (*Oncorhynchus mykiss*): Gill injury, oxidative stress, and other physiological effects. Aquat. Toxicol. 84 (4), 415–430.

Fendall, L.S., Sewell, M.A., 2009. Contributing to marine pollution by washing your face. Microplastics in facial cleansers. Mar. Pollut. Bull. 58 (8), 1225–1228.

Fernandez, L.A., MacFarlane, J.K., Tcaciuc, A.P., Gschwend, P.M., 2009. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips. Environ. Sci. Technol. 43 (5), 1430–1436.

Fowler, C.W., 1987. Marine debris and northern fur seals: a case study. Mar. Pollut. Bull. 18 (6), 326–335.

Friedman, C.L., Burgess, R.M., Perron, M.M., Cantwell, M.G., Ho, K.T., Lohmann, K., 2009. Comparing polychaete and polyethylene uptake to assess sediment resuspension effects on PCB bioavailability. Environ. Sci. Technol. 43 (8), 2865–2870.

Gagné, F., Auclair, J., Turcotte, P., Fournier, M., Gagnon, C., Sauvé, S., Blaise, C., 2008. Ecotoxicity of CdTe quantum dots to freshwater mussels: impacts on immune system, oxidative stress and genotoxicity. Aquat. Toxicol. 86, 333–340.

George, G.A., 1995. Weathering of polymers. Metals Forum 19, 145–161.

Gilan, I., Hadar, Y., Sivan, A., 2004. Colonization, biofilmformation and biodegradation of polyethylene by a strain of *R. ruber*. Appl. Microbiol. Biotechnol. 65, 97–104.

Gonsalves, K.E., Patel, S.H., 2003. Development of potentially degradable materials for marine applications. II. Polypropylene-starch blends. J. Appl. Polym. Sci. 43 (2), 405–415.

Graham, E.R., Thompson, J.T., 2009. Deposit- and suspension-feeding sea cucumbers (Echinodermata) ingest plastic fragments. Journal of Experimental Marine Biology and Ecology 368 (1), 22–29.

Gregory, M.R., 1983. Virgin plastic granules on some beaches of eastern Canada and Bermuda. Marine Environmental Research 10, 73–92.

Gregory, M., 1996. Plastic 'Scrubbers' in Hand Cleansers: a further (and minor) source for marine pollution identified. Mar. Poll. Bull. 32 (12), 867–871.

Gregory, M.R., Andrady, A.L., 2003. Plastics in the marine environment. In: Andrady, Anthony.L. (Ed.), Plastics and the Environment. John Wiley and Sons, ISBN 0-471-09520-6, (2003).

Griffitt, R.J., Luo, J., Gao, J., Bonzonga, J.-C., Barber, D.S., 2008. Effects of particle composition and species on toxicity of metallic nanomaterials in aquatic organisms. Environ. Toxicol. Chem. 27, 1972–1978.

Guillet, J.E., Heskins, M., Spencer, L.R., 1988. Studies of the biodegradability of photodegraded plastic Compositions. Polym. Mater. Sci. Eng. 58, 80.

Hinojosa, I., Thiel, M., 2009. Floating marine debris in fjords, gulfs and channels of southern Chile. Mar. Pollut. Bull. 58, 341–350.

Hund-Rinke, K., Simon, M., 2006. Ecotoxic effect of photocatalytic active nanoparticels (TiO2) on algae and daphnids. Environ. Sci. Pollut Res. 13, 225–232.

Karapanagioti, H.K., Klontza, I., 2008. Testing phenanthrene distribution properties of virgin plastic pellets and plastic eroded pellets found on Lesvos island beaches (Greece). Mar. Environ. Res. 65, 283–290.

Katsanevakis, S., Verriopoulos, G., Nicolaidou, A., Thessalou-Legaki, M., 2007. Effect of marine litter on the benthic megafauna of coastal soft bottoms: a manipulative experiment. Mar. Pollut. Bull. 54, 771–778.

Kawai, F., Watanabe, M., Shibata, F., Yokoyama, S., Sudate, S., Hayashi, S., 2004. Comparative study on biodegradability of polyethylene by bacteria an dfungi. Polym. Degrad. Stabil. 86, 105–114.

Kerr, A., Cowling, M.J., 2003. The effects of surface topography on the accumulation of biofouling. Philos. Mag. 83, 2779–2795.

Klemchuk, P.P., Horng, P., 1984. Perspectives on the stabilization of hydrocarbon polymers against thermo-oxidative degradation. Polym. Degrad. Stabil. 7 (3), 131–151.

Klust, G., 1982. Netting Materials for Fishing Gear, second ed. Fraham, Surrey, Fishing News Books Ltd.,, UK.

Küpper, K., Gulmine, J.V., Janissek, P.R., Heise, H.M., 2004. Attenuated total reflection infrared spectroscopy for micro-domain analysis of polyethylene samples after accelerated ageing within weathering chambers. Vib. Spectrosc. 34 (1), 63–72.

Laist, D.W., 1997. Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. In: Coe, J.M., Rogers, D.B. (Eds.), Marine Debris: Sources, Impacts and Solutions. Springer-Verlag, New York.

Latini, G., De Felice, C., Verrotti, A., 2004. Plasticizers, infant nutrition and reproductive health. Reproductive Toxicology 19 (1), 27–33.

Leathers, T.D., Govind, N.S., Greene, R.V., 2004. Biodegradation of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by a Tropical Marine Bacterium, Pseudoalteromonas sp. NRRL B-30083. Journal of Polymers and the Environment 8, 119–124.

Leys, S.P., Eerkes-Medrano, D.I., 2006. Feeding in a Calcareous Sponge: Particle Uptake by Pseudopodia. Biol. Bull. 211, 157–171.

Lohmann, R., MacFarlane, J.K., Gschwend, P.M., 2005. On the importance of black carbon to sorption of PAHs, PCBs and PCDDs in Boston and New York harborsediments. Environ. Sci. Technol. 39, 141–148.

Lovern, S.B., Klaper, R., 2006. *Daphnia magna* mortality when exposed to titanium dioxide and fullerene (C_{60}) nanoparticles. Environ. Toxicol. Chem. 25 (4), 1132–1137.

Mallory, M.L., 2008. Marine plastic debris in northern fulmars from the Canadian high Arctic. Mar. Pollut. Bull. 56, 1501–1504.

Mascarenhas, R., Santos, R., Zeppelini, D., 2004. Plastic debris ingestion by sea turtle in Paraiba, Brazil. Mar. Pollut. Bull. 49 (4), 354–355.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium of toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318–324.

Mayer, J.M., Kaplan, D.L., 1996. Biodegradation of polymer films in marine and soil environments. ACS Symposium Series 627ACS Symposium Series #627. R. M. Ottenbrite, S. J. Huang and K. Park: 159–170.

Maynard A., 2006. Nanotechnology: a research strategy for addressing risk. Woodrow Wilson International Center for Scholars Project on Emerging Nanotechnologies. Available at: http://www.nanotechproject.org/file_download/files/PEN3_Risk.pdf.

Meenakumari, B., Radhalakshmi, K., 1988. Induced photoxidative degradation of nylon 6 fishing net twines. Ind. J. Text. Res. 13, 84–86.

Meenakumari, B., Radhalakshmy, K., 1995. Weathering of PA netting yarns. Fish. Technol. 32, 85–88.

Meenakumari, B., Ravindran, K., 1985a. Tensile strength properties of polyethylene netting twines under exposure to out-door and artificial UV radiation. Fish. Technol. 22, 82–86.

Meenakumari, B., Ravindran, K., 1985b. Effect of sunlight and UV radiation on mechanical strength properties of PA netting twines. Ind. J. Text Res. 10, 15–19.

Moore, C.J., 2008. Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. Environ. Res. 108 (2), 131–139.

Moore, S.L., Gregorio, D., Carreon, M., Weisberg, S.B., 2001. Composition and distribution of beach debris in orange county, California. Mar. Pollut. Bull. 42 (3), 241–245.

Moore, C.J., Moore, S.L., Leecaster, M.K., Weisberg, S.B., 2001a. A comparison of plastic and plankton in the North Pacific Central Gyre. Mar. Pollut. Bull. 42 (12), 1297–1300.

Moore, C.J., Moore, S.L., Weisberg, S.B., Lattin, G.W., Zellers, A.F., 2002. A comparison of neustonic plastic and zooplankton abundance in Southern California's coastal waters. Mar. Pollut. Bull. 44, 1035–1038.

Müller, J.F., Manomanii, K., Mortimer, M.R., McLachlan, M.S., 2001. Partitioning of polycyclic aromatic hydrocarbons in the polyethylene/water system. J. Anal. Chem. 371, 816.

Muthukumar, T., Aravinthan, A., Lakshmi, K., Venkatesan, R., Vedaprakash, L., Doble, M., 2011. Fouling and stability of polymers and composites in marine environment. Int. Biodeter. Biodegrad. 65 (2), 276–284.

Ng, K.L., Obbard, J.P., 2006. Prevalence of microplastics in Singapore's coastal marine environment. Mar. Pollut. Bull. 52 (7), 761–767.

Oberdörster, E., 2004. Manufactured nanomaterials (fullerenes, C60) induce oxidative stress in the brain of juvenile largemouth bass. Environ. Health Perspect. 112, 1058–1062.

Ogata, Y., Takada, H., Mizukawa, K., Hirai, H., Iwasa, S., Endo, S., Mato, Y., Saha, M., Okuda, K., Nakashima, A., Murakami, M., Zurcher, N., Booyatumanondo, R., Zakaria, M.P., Dung, L., Gordon, M., Miguez, C., Suzuki, S., Moore, C., Karapanagioti, H.K., 2009. International pellet watch: global monitoring of persistent organic pollutants (POPs) in coastal waters. Initial phase data on PCBs, DDTs, and HCHs1. Mar. Pollut. Bull. 58 (10), 1437–1446.

Page, B., McKenzie, J., 2004. Entanglement of Australian sea lions and New Zealand fur seals in lost fishing gear and other marine debris before and after Government and industry attempts to reduce the problem. Mar. Pollut. Bull. 49 (1–2), 33–42.

Poulicek, M., Jeuniaux, C., 1991. Chitin biodegradation in marine environments: An experimental approach. Biochem. Syst. Ecol. 19 (5), 385–394.

Powell, M.D., Berry, A.J., 1990. Ingestion and regurgitation of living and inert materials by the estuarine copepod Eurytemora affinis (Poppe) and the influence of salinity. Estuarine Coastal Shelf Sci. 31, 763–773.

Qayyum, M.M., White, J.R., 1993. Effect of stabilizers on failure mechanisms in weathered polypropylene. Polym. Degrad. Stabil. 41, 163–172.

Railkin, A.I., 2003. Marine Biofouling: Colonization Processeses and Defenses, CRC Press.

Reddy, M.S., Shaik, B., 2006. Description of the small plastics fragments in marine sediments along the Alang-Sosiya ship-breaking yard, India. Estuarine. Coastal Shelf Sci. 68 (3–4), 656–660.

Ribic, C.A., Sheavly, S.B., Rugg, D.J., Erdmann, E.S., 2010. Trends and drivers of marine debris on the Atlantic coast of the United States 1997–2007. Mar. Pollut. Bull. 60, 1231–1242.

Rice, M.R., Gold, H.S., 1984. Polypropylene as an adsorbent for trace organics in water. Anal. Chem. 56, 1436–1440.

Rios, L.M., Moore, C., 2007. Persistent organic pollutants carried by synthetic polymers in the ocean environment. Mar. Pollut. Bull. 54 (8), 1230–1237.

Roberts, A.P., Mount, A.S., Seda, B., Souther, J., Qiao, R., Lin, S., Ke, P.C., Rao, A.M., Klaine, S.J., 2007. In vivo biomodification of lipid-coated carbon nanotubes by Daphnia magna. Environ. Sci. Technol. 41, 3025–3029.

Rosse, P., Loizeau, J.-L., 2003. Use of single particle counters for thefor the determination of the number and size distribution of colloids in natural surface waters. Colloids Surf. A 217, 109–120.

Ryan, P.G., Connell, A.D., Gardner, B.D., 1988. Plastic ingestion and PCBs in seabirds: is there a relationship? Mar. Poll. Bull. 19, 174–176.

Seki, H., Taga, N., 1963. Microbiological studies on the decomposition of chitin in marine environment – I. Occurence of Chitinoclastic bacteria in the Neritic region. J. Oceanograph. Soc. Jpn. 19 (2), 101–108.

Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., 2008. Biological degradation of plastics: a comprehensive review. Biotechnol. Adv. 26 (3), 246–265.

Shaw, D.G., Day, R.H., 1994. Colour - and form-dependent loss of plastic micro-debris from the North Pacific Ocean. Mar. Pollut. Bull. 28 (1), 39–43.

Sivan, A., 2011. New perspectives in plastics biodegradation current opinion in biotechnology 22 (3), 422–426.

Smith, C.J., Shaw, B.J., Handy, R.D., 2007. Toxicity of single walled carbon nanotubes to rainbow trout, (*Oncorhynchus mykiss*): respiratory toxicity, organ pathologies, and other physiological effects. Aquat. Toxicol. 82, 94–109.

Stefatos, A., Charalampakis, M., 1999. Marine debris on the seafloor of the Mediterranean sea: examples from two enclosed Gulfs in Western Greece. Mar. Poll. Bull. 38 (9), 389–393.

Stevens, L.M., 1992. Marine Plastic Debris: Fouling and Degradation. Unpublished MSc Thesis, University of Auckland. 110p.

Stevens, L.M., Gregory, M.R., 1996. Fouling Bryozoa on Pelagic and Moored Plastics from Northern New Zealand. Bryozoans in Space and Time. In Proceedings of the 10th International Bryozoology Conference, University of Wellington, Victoria.

Sudhakar, M., Doble, M., 2008. Marine microbe-mediated biodegradation of low- and high-density polyethylenes. Int. Biodeter. Biodegrad. 61 (3), 203–213.

Tavares, A.C., Gulmine, J.V., Lepienski, C.M., Lepienski, A., 2003. The effect of accelerated aging on the surface mechanical properties of polyethylene. Polym. Degrad. Stabil. 81 (2), 367–373.

Templeton, R., Ferguson, P., Washburn, K., Scrivens, W., Chandler, G., 2006. Life-cycle effects of single-walled carbon nanotubes (SWNTs) on an estuarine meiobenthic copepod. Environ. Sci. Technol. 40, 7387–7393.

Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobicm contaminants. Environ. Sci. Technol. 41 (22), 7759–7764.

Thomas, S.N., Hridayanathana, C., 2006. The effect of natural sunlight on the strength of polyamide 6 multifilament and monofilament fishing net materials. Fish. Res. 81 (2–3), 326–330.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science 304, 838.

Thompson, R., Moore, C., Andrady, A., Gregory, M., Takada, H., Weisberg, S., 2005. New directions in plastic debris. Science 310, 1117.

Timmers, M.A., Kistner, C.A., and Donohue, M.J., 2005. Marine Debris of the Northwestern Hawaiian Islands: Ghost Net Identification. Hawaii Sea Grant Publication.

Tomas, J., Guitart, R., 2002. Marine debris ingestion in loggerhead sea turtles, Caretta caretta, from the Western Mediterranean. Mar. Pollut. Bull. 44 (3), 211–216.

Tschernij, V., Larsson, P.O., 2003. Ghost fishing by lost cod gill nets in the Baltic Sea. Fish. Res. 64, 151–162.

Uitz, J., Claustre, H., Gentili, B., Stramski, D., 2010. Phytoplankton class-specific primary production in the world's oceans: Seasonal and inter-annual variability from satellite observations. Glob. Biogeochem. Cycles 24 (19), 3016–3035.

Usenko, C.Y., Harper, S.L., Tanguay, R.L., 2008. Fullerene C_{60} exposure elicits an oxidative stress response in embryonic zebrafish. Toxicol. Appl. Pharmacol. 229, 44–55.

Vandenberg, L.N., Hauser, R., Marcus, M., Olea, N., Welshons, W.V., 2007. Human exposure to bisphenol A (BPA). Reprod. Toxicol. 24 (2), 139–177.

Voparil, I.M., Mayer, 2000. Dissolution of sedimentarypolycyclic aromatic hydrocarbons into the lugworm's (Arenicola marina) digestive fluids. Environ. Sci. Technol. 34, 1221–1228.

Voparil, I.M., Burgess, R.M., Mayer, L.M., Tien, R., Cantwell, M.G., Ryba, S.A., 2004. Digestive bioavailability to a deposit feeder (*Arenicola marina*) of polycyclic aromatic hydrocarbons associated with anthropogenic particles. Environ. Toxicol. Chem. 23, 2618–2626.

Ward, J.E., Kach, D.J., 2009. Marine aggregates facilitate ingestion of nanoparticles by suspension-feeding bivalves. Mar. Environ. Res. 68 (3), 137–142.

Watson, R., Revenga, C., Kura, Y., 2006. Fishing gear associated with global marine catches I. Database development. Fish. Res. 79 (1–2), 97–102.

Wurl, O., Obbard, J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. Mar. Pollut. Bull. 48 (11–12), 1016–1030.

Yakimets, I., Lai, D., Guigon, M., 2004. Effect of photooxidation cracks on behaviour of thick polypropylene samples. Polym. Degrad. Stabil. 86, 59–67.

Zarfl, C., Matthies, M., 2010. Are marine plastic particles transport vectors for organic pollutants to the Arctic? Marine Pollution Bull. 60 (10), 1810–1814.

Zhu, S., Oberdörster, E., Haasch, M.L., 2006. Toxicity of an engineered nanoparticles of in twoaquatic species, *Daphnia* and fathead minnow. Mar. Environ. Res. 62, S5–S9.

Zhu, L., Zhu, Y., Li, Z., Duan, W., Chen, Alvarez, P.J.J., 2007. Developmental toxicity in zebrafish (danio rerio) embryos after exposure to manufactured nanomaterials: buckminsterfullerene aggregates (nC_{60}) and fullerol. Environ. Toxicol. Chem. 26, 976–979.