Contaminants in Marine Plastic Pollution: ‘the new toxic time-bomb’

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This report is intended to be a living document and will be updated as new and important information is released.

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1. **Summary**

The United Nations Environment Program called marine plastics the "*new toxic time-bomb*". Marine plastic is not only entangling and drowning wildlife, it is being mistaken for food and ingested along with its toxic contaminants. Marine plastics and in particular microplastics, provide a global transport medium for the most toxic chemicals into the marine food chain and ultimately, to humans.

Persistent bioaccumulative toxins (PBTs) contaminate all forms of marine plastics (eg resin pellets, microbeads, polystyrene and microplastic debris like tiny threads from ropes and nets. Because microplastics have larger surface area to volume ratio, they accumulate and concentrate PBTs and metals. Once in marine environments plastic polymers undergo some weathering and degradation, aiding the adsorption of PBTs from the seawater, where they exist at very low concentrations. The contaminants concentrate in microplastic fragments at several orders of magnitude higher than background levels in seawater.

By ingesting the minute pieces of plastic, marine species consume persistent organic pollutants (POPs) including pesticides such as DDT, PCBs, lindane, as well as many toxic plastic additives (eg bisphenol A (BPA), phthalate plasticizers, brominated flame retardants (PBDE) and heavy metal stabilisers.) Many of these contaminants are endocrine (hormone) disruptors capable of adverse effects at very low levels. Marine organisms are also exposed to the chemical intermediates from the plastics' partial degradation like carcinogenic styrene and highly toxic, polycyclic aromatic hydrocarbons (PAHs). Perfluorinated compounds (PFCs) used to make fluoropolymers eg, Polytetrafluoroethylene (PTFE) have also been found in microplastics.

PBTs and POPs are highly bioaccumulative in animals and can cause cancer, affect reproduction and development as well as impact on the immune system. Once in the digestive tract, these contaminants can enter the bloodstream, by which they reach other organs resulting in physiologic damage.

Microplastics are found in every marine habitat, including estuaries, the breeding areas for fish. Australian research detected POPs and other contaminants in plastic resin pellets in Australian waters and studies of Shearwaters from Lord Howe showed that their contaminant load was positively correlated the amount of plastic they had ingested.
2. Production and Wastes

In 2001, approximately 250 billion pounds (approx. 113,398 tonnes) of plastic raw material were produced annually worldwide resulting in unintentional releases to the environment during manufacturing and transport. By 2011, the annual global demand for plastics had significantly increased and stood at about 245 million tonnes. Unfortunately waste management practices, including recycling, have not kept up with increased production and use of plastic products. Land-based sources including beach litter contributes around 80% of the plastic debris in the marine environment. Of particular concern are smaller pieces of plastic debris referred to as microplastics. These include resin pellets, microbeads, polystyrene and plastic debris and tiny threads from ropes, nets and synthetic clothing.

An important source of microplastic appears to be through sewage contaminated by synthetic fibres from washing clothes. Wastewater from domestic washing machines has shown that a single garment can produce >1900 fibers per wash. This suggests that a large proportion of microplastic fibres found in the marine environment may be derived from sewage as a consequence of washing of clothes. Polyester, acrylic, polypropylene, polyethylene, and polyamide fibres contaminate shores across the globe, with more being found in densely populated areas that have sewage outfalls.

Engineered plastic nanoparticles released at various stages of the life cycle of products including waterborne paints, adhesives, coatings, electronics and pharmaceuticals, as well as nanoplastics created by the degradation of microplastics, pose a specific challenge to the marine ecosystem. Nanoplastic pollution is the least understood form of pollution but may turn to be the most hazardous due to its increased surface area to volume ratio and toxicity profile.

Balloons are an important part of marine plastic debris representing a serious choking and digestion hazard for marine turtles and many other species. The mass release of helium balloons is illegal in some states of Australia, eg NSW. However, helium balloons are able to reach the ‘jet-stream’ and eventually deflate and find their way into the ocean.

In 2014, there was an attempt to estimate the current load of plastic present in the ocean based upon 3,070 samples collected from around the world. Researchers estimated that the amount of plastic in the open-ocean surface was between 7,000 and 35,000 tonnes and that over a million tonnes of floating plastic had been released into the open ocean since the 1970s.

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3 Browne et al 2011
A recent report by the Ellen MacArthur Foundation concluded:

“In a business-as-usual scenario, the ocean is expected to contain 1 tonne of plastic for every 3 tonnes of fish by 2025, and by 2050, more plastics than fish (by weight).”

2.1 Types of Plastics

Several broad classes of plastics are used in packaging and have found their way into the marine environment. These include polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC). As well, fluoropolymers like polytetrafluoroethylene (PTFE) and perfluoroalkoxy polymer (PFA) are used in many nonstick plastics.

Toxicity associated with plastics can be attributed to one or more of the following factors:

- Residual monomers from manufacture present in the plastic or toxic additives used in the plastic, which can leach out of the ingested plastic, eg, Bisphenol (BPA), phthalate plasticizers, heavy metals.
- Toxicity of some intermediates from partial degradation of plastics, eg styrene from polystyrene, PAHs
- Persistent organic pollutants (POPs) present in seawater, adsorbed and concentrated in the microplastic fragments.

2.2 Toxic Additives in Plastics

There is a wide range of plastic additives, which include:

- Plasticizers to improve flexibility and durability, added at 10-80% w/w eg phthalates
- Flame retardants (10-20%) eg organophosphorus compounds; halogenated esters, heavily brominated or chlorinated organic compounds, eg SCCP-MCCP, Boric acid, Brominated flame retardants, Tris(2-chloroethyl)phosphate
- Stabilisers (0.1-10.09%) eg arsenic / organic tin compounds, Triclosan, bisphenol A (BPA); cadmium and lead compounds, nonylphenol compounds/ octylphenol
- Curing agents eg formaldehyde
- Colourants eg titanium dioxide, cadmium/chromium/lead compounds

2.3 Persistent Organic Pollutants

Many persistent organic pollutants (POPs) are detected in seawater and microplastics and are listed for global elimination on the Stockholm Convention.

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7 The New Plastics Economy Rethinking The Future Of Plastics

8 www.pops.int
They include:

- Polychlorinated biphenyls (PCBs); highly toxic, chlorinated, industrial chemicals; endocrine disruptors and carcinogens;
- Dichlorodiphenyltrichloroethane (DDT) and its breakdown products; an organochlorine insecticide banned due to serious health effects in animals; an endocrine disruptor;
- Hexachlorocyclohexane (HCH); organochlorine insecticide eg lindane; an endocrine disruptor;
- Hexachlorobenzene (HCB); fungicide and industrial chemical; carcinogen and endocrine disruptor;
- Perfluorinated compounds (PFCs); industrial and consumer chemicals; carcinogens and endocrine disruptors; and
- Polybrominated diphenyl ethers (PBDEs); brominated flame retardants; neurotoxins, developmental toxins.

### 2.4 Degradation of Plastic

Once in marine environment, plastic polymers undergo weathering and degradation via UV solar radiation, chemical degradation and microbial action (i.e., biodegradation). This weakens the plastic, allowing it to become brittle and break apart when subjected to sea motion.

The biodegradation of marine plastics is influenced by a range of factors including the chemical and physical properties of plastics. The surface conditions (surface area, hydrophilic, and hydrophobic properties) and the structures (chemical structure, molecular weight and molecular weight distribution) all play important roles in the biodegradation processes. Generally, the adherence of microorganisms on the surface of plastics is the major mechanisms involved in the microbial degradation of plastics. The molecular weight is also very important for the biodegradability because it determines many physical properties of the polymer. Increasing the molecular weight of the polymer decreases its degradability.\(^9\)

Degradable plastics are often suggested as a way of addressing the problem of marine plastics, however they can still reach natural ecosystems and do damage. Some research has shown degradable plastics have very low biodegradation rates while presenting a higher rate of loss of physical integrity, that is, they don't break down, they just break up.\(^10\)

The biodegradation of marine plastics also aids in the adsorption of toxic contaminants from the seawater where they are present at very low concentrations. Plastics are synthesized from petroleum or natural gas and, as such, repel water and in the ocean, attract other chemicals, like persistent organic pollutants (POPs), which also tend not to combine with, or dissolve in water. As microplastics have a larger surface area to volume ratio, they accumulate and concentrate contamination with

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POPs and some metals. POPs and other contaminants concentrate in microplastic fragments at several orders of magnitude higher than in seawater, with different coloured plastics and different types of polymers adsorbing POPs from the environment differently. When ingested by marine species, the contaminated plastics provide a clear route by which POPs can enter the marine food web.11

3. Levels of Pollutants in Plastic Resin Pellets

Plastic resin pellets, or nurdles are a significant part of marine plastics. Some pellets have higher concentrations of PBTs and POPs than others as the different polymers vary in their accumulation of pollutants and some will spend longer in the ocean or spend time circulating in more heavily polluted areas before eventually being beached.

In 2001, researchers12 demonstrated that plastic pellets were widely distributed through the world’s oceans along with other plastic wastes. PCBs and DDE adsorbed to the polypropylene (PP) resin pellets from the seawater, steadily increasing in concentration over time, with concentrations up to 106 times higher than surrounding seawater.

Researchers measured significant amounts of PCBs, DDE, and nonylphenols (NP) in PP resin pellets collected from four Japanese coasts. The concentrations of contaminants varied among the sampling sites eg PCBs (4-117 ng/g13), DDE (0.16-3.1 ng/g), NP (0.13-16 µg/g14). The NP contents in the PP resin pellets were two orders of magnitude higher than those found in Tokyo Bay sediment (0.1-0.6 µg/g).

In 2007, thermoplastic resin pellets, comprising mainly of PP and PE polymers, were collected from the North Pacific Gyre and selected sites in California, Hawaii, and from Guadalupe Island, Mexico. PAHs and DDT and its metabolites were found in all the plastic samples.15 Total concentration of PCBs ranged from 27 to 980 ng/g; DDTs from 22 to 7100 ng/g, PAHs from 39 to 1200 ng/g and aliphatic hydrocarbons from 1.1 to 8600 ug/g.

3.1 Contamination of Pellets in the Australian Marine Environment

In Australia, plastic resin pellets collected at Foul Bay Western Australia returned positive results for persistent organic pollutants (POPs),16 including PCBs, DDT and breakdown products, HCH, polycyclic aromatic hydrocarbons (PAHs); toxic byproducts and hopanes, an indicator of petroleum pollution.

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13 Nanograms per gram or parts per billion
14 Micrograms per gram or parts per million
Based on the International Pellet Watch\textsuperscript{17}, the contaminant levels found in pellets from Foul Bay were much lower than other sites as can be seen in the following table.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Foul Bay Test Results</th>
<th>Range of levels recorded by International Pellet Watch to Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBs</td>
<td>20 ng/g-pellet</td>
<td>7 to 486 ng/g-pellet</td>
</tr>
<tr>
<td>DDT</td>
<td>9 ng/g-pellet</td>
<td>3 to 323 ng/g-pellet</td>
</tr>
<tr>
<td>PAHs</td>
<td>0.4 ng/g-pellet</td>
<td>0.2 to 15 ng/g-pellet</td>
</tr>
<tr>
<td>Hopanes</td>
<td>14 ng/g-pellet</td>
<td>2 to 49 ng/g-pellet</td>
</tr>
<tr>
<td>HCH</td>
<td>&lt;0.2 ng/g-pellet</td>
<td>0.1 to 37 ng/g-pellet</td>
</tr>
</tbody>
</table>

### 3.2 International Pellet Watch

Research published by International Pellet Watch in 2009 demonstrated that chemical concentrations in pellets collected from 30 beaches from 17 different countries reflected past and present usage of particular POPs in that country. For example, PCB concentrations in the pellets were highest on US coasts, followed by western Europe and Japan, but were lower in tropical Asia, southern Africa and Australia.

DDTs showed high concentrations on the US west coast and in Vietnam. High concentrations of pesticide HCH were detected in the pellets from southern Africa, suggesting current usage of the pesticide in southern Africa.\textsuperscript{18} Based on the testing of pellets collected on Portuguese beaches, the colour of the resin pellet affected the concentrations of contaminants.\textsuperscript{19} Black pellets had the highest concentrations of POPs (PCBs, DDT) except for PAHs.

In a 2012 study, plastic resin pellets from remote islands in the Pacific, Atlantic, and Indian Oceans and the Caribbean Sea returned levels of PCBs, DDTs and HCHs one to three orders of magnitude smaller than pellets from industrialised coastal shores, although sporadic high concentrations of POPs in the pellets were observed.\textsuperscript{20}

### 3.3 Perfluorinated Compounds (PFCs)

The presence of PFCs in marine microplastics is of particular concern as these...
compounds are renowned for being extremely persistent with little or no natural degradation pathways. Because of this resistance to degradation under environmental conditions, PFCs accumulate and biomagnify in marine biota. Two PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been assessed by the United Nations expert panel, the POPs Review Committee, and found to be carcinogens and endocrine disruptors.21

In 2014, eighteen PFCs were measured in both plastic pellets and beach sediment around Greek coastal areas. In sediment, the concentrations varied from 8.2 to 146 ng/Kg 22, with PFOA being found at the highest concentrations. PFCs were confirmed in all the pellets analysed with total concentrations from 10 to 180 ng/Kg. The concentrations in plastic pellets were higher than those in the sediments and the researchers propose that the origin of PFCs on the pellet surface was adsorption from surrounding water.23

4. Level of Pollutants in Other Forms of Microplastics

The type of polymer in ocean debris affects the concentrations of contaminants adsorbed. Adsorption occurs more readily onto LDPE (low density polyethylene) and PP plastic debris than for PET and PVC fragments.24 In 2011, researchers 25 analysed plastic fragments (<10 mm) from the open ocean and from remote and urban beaches. They measured PCBs, PAHs, DDT and its metabolites, PBDEs, alkylphenols and bisphenol A at concentrations from 1 to 10,000 ng/g.

The researchers noted concentrations showed large piece-to-piece variability and concluded PCBs were most probably derived from legacy pollution while PAHs showed a petrogenic signature, suggesting the adsorption of PAHs from oil slicks.

Nonylphenol, bisphenol A, and PBDEs were considered to come mainly from additives. These were detected at high concentrations in some fragments both from remote and urban beaches and the open ocean. For PCBs and PAHs, higher concentrations were observed in plastic fragments from urban beaches. Hence, risks associated with these pollutants are higher in urban beaches than remote beaches and the open ocean.

In 2014 the Norwegian Institute for Water Research released a comprehensive review of contaminants measured in marine plastic26 and confirmed the following list of contaminants found in plastic debris collected in the marine environment:

• Pesticides: DDT and related compounds, HCHs, Chlordanes, Cyclodienes, Mirex, Hexachlorobenzene

22 Nanogram per kilogram or parts per trillion
23 Llorca M et al., Levels and fate of perfluoroalkyl substances in beached plastic pellets and sediments collected from Greece Mar Pollut Bull. 2014 Oct 15;87(1-2):286-91
26 Microplastics in marine environments: Occurrence, distribution and effects, REPORT SNO. 6754-2014 Norwegian Institute for Water Research REPORT
• **Industrial chemicals and plastic additives**: PCBs, polybrominated diphenyl ethers, PBDE 209, Nonylphenols, Octylphenols, Bisphenol A, Perfluorinated compounds
• **Byproducts** PAHs, aliphatic hydrocarbons

### 4.1 Polystyrene Foam in the Marine Environment

Expanded polystyrene foam (EPS) is pervasive in the marine environment as it is used extensively in packaging and by the fishing industry. Polystyrene is lightweight and floats but EPS does break down into smaller and smaller pieces. A study of beach debris at 43 sites along the United States Orange County coast found EPS was the second most abundant form of beach debris. The EPS monomer styrene, is an animal carcinogen, a possible human carcinogen and a neurotoxin. EPS may also contain other contaminants including the POP chemical, Hexabromocyclododecane (HBCD or HBCDD) a brominated flame retardant, now listed on the Stockholm Convention for global elimination.

### 5. Chemical Impacts

The high accumulation potential of POPs and other persistent bioaccumulative toxins means that plastic resin pellets serve both as a global transport medium and a source of toxic chemicals in the marine environment. Some of the chemicals found in resin pellets are endocrine disruptors (eg nonylphenol, phthalates). Endocrine disrupting effects can be triggered at very low concentrations and exhibit non-monotonic (non linear) dose responses.

POPs such as PCB, DDT and its related substances, brominated flame retardants (eg pentaBDE, OctaBDE, HBCDD) and PFOS are extremely persistent, bioaccumulative and toxic (eg carcinogens, neurotoxins, reproductive and development toxins, immunotoxins). All have been listed on the POPs Stockholm Convention for global elimination.

Once in the digestive tracts, POPs from the microplastics can enter the bloodstream, reach other organs and possibly result in physiologic damage. Ingestion of pellets with low concentrations of POPs by marine organisms is expected to present a problem for marine organisms, particularly as POPs are highly bioaccumulative, building up in living organisms and bioconcentrating up the food chain. Mortality due to plastic ingestion is now common in seabirds, marine mammals and sea turtles but the extent to which the ingestion of hazardous chemical components attributes to wildlife deaths is not readily available.

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28 Note, one year after implementation of the San Francisco ordinance that prohibits the use of EPS foodware, San Francisco’s litter audit showed a 36% decrease in EPS litter. EPS has a very low recycling rate (California’s 0.8%)
http://www.mindfully.org/Plastic/Pellets-Transport-Medium.htm
5.1 Laboratory Tests

Researchers have examined the effects of chronic dietary exposure to environmentally relevant concentrations of LDPE plastic on the Japanese medaka (Oryzias latipes), a common model fish species. They found that PE ingestion contributes to the bioaccumulation of potentially hazardous substances in fish. The exposed fish tended to experience adverse health effects in the liver. The toxicity appeared to be a consequence of both the absorbed pollutants and plastic material.

The fish showed signs of hepatic stress, more so in fish that were exposed to marine-treated plastic rather than to virgin (pre-production) plastic. Concentrations of total PAHs, PCBs and PBDEs on marine-LDPE were $4 \times$, $15 \times$ and $1.4 \times$ greater than on virgin-LDPE pellets respectively. After two months of dietary exposure, the general patterns showed a greater concentration of PBTs in fish exposed to the marine-plastic treatment.

Adverse effects included glycogen depletion, fatty vacuolation, and cellular necrosis. Researchers concluded that the lesions observed in fish from the virgin- and marine-plastic treatments were likely related to the plastic as no lesions were apparent in fish from controls. The levels of PBDEs observed were also consistent with previous observations showing a correlation between PBDEs and plastic ingestion in wild seabirds.

5.2 Contamination of Australian Seabirds

Researchers from the University of Tasmania examined the toxic effects of seabirds ingesting marine plastic pollution and population decline. They examined the toxic effects of trace metals caused by the ingestion of plastics in Flesh-Footed Shearwaters. The study found that the proportion of the Shearwater population ingesting plastic increased from 79% in 2005 to 2007 to 90% in 2011. The study found body condition was negatively influenced by the amount of ingested plastic, and that the Shearwater contaminant load is positively related to the amount of ingested plastic. The study went on to find that the Flesh-Footed Shearwater had the highest percentage of their total population with ingested plastics, higher than any marine vertebrate.

Large amounts of plastic are being recovered from Shearwaters on the world-heritage listed Lord Howe Island. In the latest survey, one bird’s stomach contained more than 200 pieces and others held more than 50. Mercury, which is toxic to birds at four parts per million (ppm), was found in the shearwaters at up to 30,000 ppm, according to Dr Lavers. Surface-feeding petrels, shearwaters and albatrosses, including their fledgling chicks are most impacted by floating microplastics.

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http://www.nature.com/articles/srep03263

32 Rochman et al, 2013


5.3 **Microplastics and Baleen Whales**

Microplastics are also ingested by baleen whale species through consumption of planktonic prey however, the impacts of microplastics on baleen whales are largely unknown. In a 2012 study,\(^{35}\) 56% of the surface plankton samples contained microplastic particles with high concentrations of phthalates (DEHP and MEHP). Researchers suggested that the concentrations of Mono-(2-ethylhexyl) phthalate (MEHP) found in the blubber of stranded fin whales represent the first warning of the emerging threat of microplastics to baleen whales.

6. **Conclusion**

By 2014, researchers\(^{36}\) concluded that the presence of microplastics in the marine environment had substantially increased with microplastic debris being observed within every marine habitat, including estuaries - the breeding areas for many fish species.\(^ {37}\)

While some marine species eg holothurians (sea cucumbers) ingest microplastics with specific colours and shapes, all marine organism groups, including seabirds are at a great risk of ingestion of microplastics. which has been documented for a wide range of vertebrate and invertebrate marine species.

By ingesting the minute pieces of plastic, marine species consume a broad range of persistent toxic contaminants. While the full impact of this chronic exposure is not clearly understood, research to date paints an extremely concerning picture of the marine environment into the future.

6.1. **Recommendations**

The long history of Government inquiries in Australia into marine plastic pollution and the various voluntary industry schemes introduced over the years have failed to address plastic pollution and its associated toxic chemical pollution in any meaningful way. Meanwhile, the community outcry for effective solutions to be implemented to address marine plastic pollution is growing louder and the evidence of the damage caused by marine plastic pollution is also increasing.

The following recommendations are essential to begin to address the issue of plastic pollution in the marine environment:

- Australian governments at all levels must take coordinated and immediate regulatory action to stop the sources of marine plastic pollution, which is land-based plastic pollution. Measures must include an immediate ban on single use plastic bags (including so-called degradable bags), plastic microbeads in

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\(^{35}\) Fossi et al., Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (Balaenoptera physalus), *Marine Pollution Bulletin* Vol. 64, Issue 11, November 2012, 2374–2379

\(^{36}\) J.A. Ivar do Sul, M.F. Costa The present and future of microplastic pollution in the marine environment *Environmental Pollution* 185 (2014)

\(^{37}\) A. Bakir et al. Transport of persistent organic pollutants by microplastics in estuarine conditions, *Estuarine, Coastal and Shelf Science* 140 (2014)
personal care products and, banning the mass release of balloons\textsuperscript{38} and the recreational use of glow sticks.

- The introduction of nationally consistent container deposit legislation to address plastic beverage litter.

- Regulatory enforcement of existing laws that prohibit the release of resin pellets (‘nurdles’) into the environment and work with the plastics industry to ensure appropriate measures are in place to minimize their impacts in the production of plastics.

- The Government must immediately ratify all new POPs chemicals listed on the \textit{Stockholm Convention on Persistent Organic Pollutants}, which include many associated with marine plastic pollution.

- The Government must address the inadequate regulation of industrial chemicals in products in Australia. There are over 38,000 industrial chemicals listed on the Australian Inventory of Chemical Substances (AICS), of which less than 3,000 have been assessed for their health and environmental impacts. Life-cycle assessments of industrial chemicals, including those contained in products, must be undertaken otherwise the problem will never be addressed. Australia needs an industrial chemical regulator that has the powers to enforce its recommendations for risk reduction as well as the power to ban industrial chemicals where the risks to the environment and human health are too great and cannot be managed.

\textsuperscript{38} NSW prohibits the mass release (>20) of balloons under the \textit{Protection of the Environment Operations Amendment (Balloons) Act 2000}