Wader Beach for Birds not Litter - Tracking the Plastic
Appendix 2

Plastics in the Marine Environment as Carriers of Toxic Chemicals: a Review of Recent Literature

Introduction

Plastic materials in the marine environment are dangerous in several different ways. Addressing the dangers to wildlife is different from expressing concern about unsightly litter in our streets that finds its way into the ocean, or the build-up of material at ocean 'gyres'. Nor is it the same as concerns based on waste and on conservation of material in the 'throw-away society' although all of these matters are interlinked.

A simple classification of plastic in the environment can be based on the size of the plastic items that range from fishing nets to the microbeads present in some cosmetics. The danger of large plastic items in the marine environment is typified by the entanglement of turtles in 'ghost' fishing nets in international waters. Further down the size scale, similar dangers are posed by smaller objects such as plastic bags and six-pack rings that can entangle birds, marine mammals and amphibians, or block metabolism because they mistaken for food and ingested by the animal. Images of incidents of this type are sickening but the extent of the problem can only be guessed at since good statistics are almost impossible to obtain.

Small and very small (micro- and nano-dimensioned) plastic pieces might be expected to pass harmlessly through some digestive systems but to pose hazards to those of other species. Small pieces of plastic can be (a) formed by degradation in the environment of large materials such as beverage containers, packaging or wrappers, (b) present as pellets such as those used in industrial operations such as injection molding and known as 'nurdles', and (c) present as micro-beads that are incorporated in some cosmetics, personal care and cleaning products as mild abrasives. Small particles released during the laundering of clothing and fibres materials made of synthetic fibres have recently been identified as contributing to the load of microplastics in the environment.

Low concentrations of chemical substances of concern are present in the marine environment. They have low solubility in water, bur can be sequestered by plastic materials, in which they are more soluble, thus turning the plastic into vehicles (vectors) for delivery of the chemicals into living organisms where they can re-partition between the plastic and the fatty tissue of the animal. In addition, the plastics themselves may contain chemical substances such as plasticizers, antioxidants, UV-stabilizers and other chemicals of different toxicities. It is the presence of toxic chemical substances, both intrinsic and sequestered, in plastics in the marine environment that is the subject of this review.

At first there were very few scientific studies of this form of marine pollution, but the evidence of possible harm to marine species was picked up by environmental advocates and published in their blogs and newsletters then covered by the popular media. Interest increased and more scientists turned their attention to this emerging research field. After a new research field is identified, there is a time-lag before results appear because researchers usually need to secure grant funding for specified projects, then conduct the research and publish the results in scientific journals. These journals are currently publishing a good deal of such work. In making my review I paid most attention to a fortnightly journal that I read regularly, *Environmental Science and Technology*, published by the American Chemical Society. I followed leads from this and from articles in magazine and newspapers to work published in other journals. The review is thus representative rather than comprehensive but I believe that it gives a correct picture of a year's progress.

Nurdles

Plastic in the form of nurdles can 'flow' like liquid and so be transferred easily in the workplace for uses like injection moulding, but they can be spilled and then transferred to the environment by waste water. Dyes are often incorporated into bulk plastics before nurdles are produced from them. Both dyed and undyed nurdles can be picked up on beaches near cities in Australia and most other industrial countries.

Data for Australia are not available but an estimate is available for nurdles in the UK. Plastic litter is from time to time the subject of coverage by the UK newspaper *The Independent.* On 13 June 2016, it reported that UK factories use 7.3 million tons of plastic each year, most if it at some stage in the form of nurdles weighing 20 mg and approximately 3-5 mm in size. About 0.01% are thought to escape and enter the environment -that is 53 billion of them, according to the paper. My calculation is that the grand total is 3.65×10^{15} and that the escapees therefore number 365 billion!

Concern that plastic pellets could absorb industrial chemicals such as polychlorobiphenyls (PCBs) and lead to their dispersal in the environment led to the formation of International Pellet Watch (IPW) early in the twenty-first century under the leadership of Professor Hideshige Takada of the Tokyo University of Agriculture and Technology. [Y. Mato and 5 others, 'Plastic Resin Pellets as a Transport Medium of Toxic Chemicals in the Marine Environment', *Environmental Science and Technology*, 35 (2001), 316-224. S. Endo and 8 others, 'Concentration of Polychlorinated Biphenyls (PCBs) in Beached Resin Pellets: Variability among the Individual Particles and Regional Differences', *Pollution Bulletin*, 50 (2005), 1103-1114.] Volunteers are encouraged to collect pellets from beaches and mail them to Professor Takada for analysis. Pellet Watch also reports on the content of DDTs (including the parent, DDT as well as degradation products such as DDD and DDE) in plastics submitted to the survey. The results are displayed on the organisation's website www.pelletwatch.org/ accessed November 2016.

General references

Recent research by CSIRO scientists found that about one quarter of the plastic waste in our streets finds its way to the oceans. They also found a strong negative correlation between suburban socio-economic levels and the extent of littering. In their report they noted an oft-reported claim that 9 out of every 10 seabird species have ingested plastics. This 90% figure is an extrapolation from 1962-2012 data and was included in a published review by CSIRO authors.[Chris Wilcox, Erik Van Sebille and Britta Denise Hardesty, 'Threat of plastic pollution to seabirds is global, pervasive and increasing', *Proceedings of the National Academy of Sciences USA*, 112 (2015), 11899-11904. DOI: 10.1073/pnas.1502108112.] They found the figure to be 29% in 2012, with particular reference to seabirds in the Tasman Sea region.

A briefing paper – *Biodegradable Plastics and Marine Litter. Misconceptions, Concerns and Impacts on Marine Environments* – published in early 2016 by the United Nations Environment Programme (UNEP) reported that the most commonly used plastics (polyethylene, polypropylene and polyvinyl chloride) are not biodegradable in marine environments. Even 'biodegradable' plastics are only slowly and incompletely broken down, resulting in the formation of small particles.
[http://web.unep.org/ecosystems/resources/publications/biodegradable-plastics-and-marine-litter
accessed November 2016.]

Another publication from the United Nations Environment Programme, the heavily referenced *UNEP Frontiers 2016 Report*, includes a section on microplastics. [http://web.unep.org/frontiers/content/unep-frontiers accessed November 2016] Sequestration of heavy metals and persistent organic pollutants is covered, as is the incorporation of these substances into the food chain.

The NSW EPA published a bulletin in July 2016 entitled 'Plastic microbeads in products and the environment' that described the presence of microbeads in products such as cosmetics and household cleaning products, and their propensity to sequester toxic substances in the environment and transfer them to marine and aquatic organisms. [http://www.epa.nsw.gov.au/publications/waste/plastic-microbeads-160306.htm, accessed November 2016.] Polyethylene was the most common material collected in a study in South Australia. Proposed and actual voluntary phase-outs in other countries are reported by NSW EPA and the work of governments and the industry body ACCORD to achieve this in Australia is described.

Each kilogram of sea salt purchased by Chinese researchers from supermarkets contained 550-681 microplastic particles, 55% of which were below 200 μm, in size, according to Chinese researchers. [Dongqi Yang and 5 others, 'Microplastic pollution in table salts from China', *Environmental Science & Technology*, 49 (2015), 13622-13627. DOI: 10.1021/acs.est.5b03163.] The most common plastics were polyethylene terephthalate (PET), polyethylene and cellophane.

American researchers reported in late 2016 that floating plastic (polypropylene, high- and low-density polyethylene) is degraded on the side exposed to the sun, but the underside is colonised by algae that produce dimethyl sulphide, a cue to foraging seabirds that then ingest the plastic in what the authors refer to as an 'olfactory trap for susceptible marine wildlife'. [Matthew S. Savoca and 3 others, 'Marine plastic debris emits a keystone infochemical for olfactory foraging seabirds', *Science Advances*, 2, (2016), DOI: e1600395. 9 pp.]

American workers C.M. Rochman and 4 others, 'Polystyrene Plastic: a Source and Sink for Polycyclic Aromatic Hydrocarbons in the Marine Environment', *Environmental Science & Technology*, 47 (2013), 13976-13984. DOI: 10.1021/es403605f.] exposed polystyrene pellets (3 mm long, 2 mm diameter) to the waters of San Diego Bay for 1-12 months. The plastic took up polycyclic aromatic hydrocarbons (PAHs) that are combustion by-products and common air-pollutants and also known carcinogens. Surprisingly, small quantities of these substances were already present in virgin polystyrene. Other plastics - polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) - absorbed less, but high density polyethylene (HDPE) and low density polyethylene (LDPE) behaved similarly to polystyrene. The article includes references to earlier work on passive sampling of PAHs by plastics.

French researchers studied the size distribution of plastics in the North Atlantic subtropical gyre and reported that microplastics make up only approximately 1% of the total. [Alexandra ter Halle and 8 others, 'Understanding the Fragmentation Pattern of Marine Plastic Debris', *Environmental Science & Technology*, 50 (2016), 5668-5675. DOI: 10.1021/acsest.6b00594.] Flat pieces of plastic apparently float so that one side shows degradation from exposure to the sun while the other has more biofilm. Degradation and biofilm were more evenly distributed in solid particles due to tumbling. Of the plastic pieces, 92% were polyethylene, the rest polypropylene, in agreement with findings by other researchers including Australians who found that these two polyolefins made up 98.5% of marine plastics. [J. Reisser and 6 others including Wilcox and Hardesty, 'Marine Plastic Pollution in Water around Australia: Characteristics, Concentrations and Pathways', *PLoS One*, 2013, 8 (11), e8046610.1371/journal.pone.0080466.

Inland waters such as the Great Lakes of North America are also sinks for plastic waste. [Austin K. Baldwin, Steven R. Corsi, and Sherri A. Mason, 'Plastic Debris in 29 Great Lakes Tributaries: Relations to Watershed Attributes and Hydrology', *Environmental Science & Technology*, 50 (2016), 10377-10385. DOI: 10.1021/acs.est.6b02917.] Of sampled particles, 98% were smaller than 4.75 mm and therefore considered microplastics. Fibres from synthetic textiles were the most common particles in the tributaries but the methodology was not appropriate for detecting them in the Lakes and so they are under-represented in that data set.

Personal care products

Personal care products commonly contain additives such as plasticizers, antioxidants and stabilizers that retard degradation by UV light. Some of these additives are hormone mimics and can disrupt endocrine systems in sensitive species. Because the personal care products are removed by washing and find their way into wastewater, they are widespread in the environment, albeit at low concentrations. A literature review of 500 reports of the presence in the environment of chemical substances derived from personal care products identified 95 chemicals in waters (surface water and wastewater) and entered the information in a database. Some chemicals, the authors noted, are readily destroyed in the environment but others are persistent. [Z. Hopkins and L. Blaney, 'An aggregate analysis of personal care products in the environment: identifying the distribution of environmentally-relevant concentrations', *Environment International*, 92-93 (2016), 301-316. DOI: 10.1016/j.envint.2016.04.026.] They recommend continued monitoring, extension of the suite of analyses to new chemicals, and improved wastewater treatment.

Concern has been expressed about the presence of plastic microbeads that are included in some cosmetics and personal care products as mild abrasives (exfoliants). Microbeads can have direct (physical) effects and indirect effects resulting from their ability to act as vectors for toxic chemicals. Because of these concerns, their use in personal care products is being phased out in Australia, Canada, UK and USA under a combination of government bans and voluntary withdrawal by manufacturers. There is evidence that microbeads could concentrate up the food chain and become a threat to human health. Attention has been drawn to this possibility [A. Dick Vethaak and Heather A. Leslie, 'Plastic Debris is a Human Health Issue', *Environmental Science & Technology*, 50 (2016), 6825-2826. DOI: 10.1021/acs.est.6b02569.]

Heavy metals

The Australian Nuclear Science and Technology Organisation (ANSTO) has involved community groups in collecting and classifying plastic litter from beaches and waterways and returning samples to ANSTO for chemical analysis of the heavy metals present in them. Professor Richard Banati, who leads the Plastic project, has also investigated the presence of metals in the feathers of sea birds. Much of the Australian research of this type has been published by eco-toxicologist Dr Jennifer Lavers. Shellfish can be impacted by metals such as lead, copper and zinc marine harbour sediments. Professor Emma Johnston has published extensively on this pollution. [https://research.unsw.edu.au/people/professor-emma-johnston/publications, accessed February 2017.]

The most recent addition to the list of plastic wastes is the non-natural fibres such as nylons and polyesters from clothing that can be released in the washing process and so find their way into the environment. Natural fibres like cotton and wool would probably absorb metals.

Physical effects

The physical impacts of small plastic particles were assessed by allowing crabs collected in southern England to ingest, along with normal food, microfibres (1-5 mm x 500 μm, prepared by fragmentation of commercial polypropylene rope that had contained negligibly small concentrations of chemical additives and contaminants. [Andrew J.R. Watts and 4 others, 'Ingestion of Plastic Microfibers by the Crab *Carcinus maenas* and Its Effect on Food Consumption and Energy Balance', *Environmental Science & Technology*, 49 (2015), 14597-14604. DOI: 10.1021/acsest.5b04026.] Crabs exposed to higher concentrations of plastic ate less food and grew more slowly as a consequence of having less energy for growth. The plastic was excreted in modified form. A further publication from this group [Andrew J. R. Watts and 5 others, ‘Effect of Microplastic on the Gills of the Shore Crab *Carcinus maenas*’, *Environmental Science & Technology*, 49 (2015), 5364-5360. DOI: 10.1021/acs.est.6b01187.] reported that 8 μm polystyrene spheres in the crabs’ gill chambers had only short-term transient effects on oxygen consumption.

In contrast to the results with polypropylene and crabs, the ingestion of polystyrene particles by oysters was shown not to affect their growth. [Matthew Cole and Tamara S. Galloway, ‘Ingestion of Nanoplastics and Microplastics by Pacific Oyster Larvae’, *Environmental Science & Technology*, 49 (2015), 14625-14632. DOI: 10.1021/acsest.5b04099.] Oyster larvae were exposed to, and ingested, polystyrene particles of a range of sizes (70 nm – 20 μm) and shapes, in greater concentrations than would normally be experienced in the marine environment, but there were no measurable effects of development or feeding capacity over the 8 days of the study. The authors refer to earlier work on pelagic zooplankton that exhibited reduced feeding and sublethal health impacts due to ingestion of plastic.

Chinese researchers report evidence that microplastics, in experiments where organic chemical pollutants were not involved, nonetheless upset fish metabolism. After 7 days of exposure, polystyrene microbeads of 5 μm diameter accumulated in fish gills, liver, and gut; while 20 μm diameter microbeads accumulated only in fish gills and gut. Both 5 μm and 70 nm microbeads PS-MPs caused inflammation and lipid accumulation in fish liver and there were disturbances to lipid and energy metabolism. [Yifeng Lu and 7 others, Uptake and Accumulation of Polystyrene Microplastics in Zebrafish (*Danio rerio*) and Toxic Effects in Liver’, *Environmental Science & Technology*, 50 (2016), 4054-4060.]

Some Swedish research has demonstrated that microplastic particles operate both chemically and physically on larval fish performance and development. [Oona M. Lönnstedt and Peter Eklöv, ‘Environmentally relevant concentrations of microplastic particles influence larval fish ecology’, *Science*, 352 (2016), 1213-1216. DOI:10.1126/science.aad8828. **] Polystyrene particles (90 μm) inhibit hatching, decrease growth rates, and alter feeding preferences and innate behaviours of European perch (*Perca fluviatilis*) larvae. Furthermore, individuals exposed to microplastics do not respond to olfactory threat cues and this greatly increases predator-induced mortality rates. If the impacts had chemical causes then we might expect fewer impacts from polyethylene and polypropylene that are also used in the form of microbeads. If, on the other hand, the impacts were caused by the intrusion of these foreign objects in the organisms (physical causes) then microbeads formed from other plastics would be expected to behave similarly.

Fish, other marine animals and whales

An RMIT group explored the uptake of polybrominated diphenyl ethers by amphipods that were exposed to these flame retardant chemicals alone or in the presence of small particles (<5 mm) of plastic (probably polyethylene) that had been extracted from a commercial exfoliating face cream. Low concentrations (5 and 50 ng/ml) of a mixture of flame retardants were used in the study. [E.M. Chua, J. Shimeta, D. Nugegoda, P.D. Morrison and B. O. Clarke, ‘Assimilation of Polybrominated Diphenyl Ethers by the Marine Amphipod, *Allorchestes compressa*’, *Environmental Science & Technology*, 48 (2014), 8127-8134. DOI: 10.1021/es4057172.] Scientists at RMIT University and colleagues in China extracted polyethylene microbeads (10-700 μm, irregular shapes) from a commercial face cleaner and ‘doped’ them with ‘environmentally relevant’ concentrations of the polybromodiphenyl ethers. These substances were once common flame retardants and although they are being phased out under the Stockholm Convention on persistent organic pollutants they can still be found in in-use products such as furniture foams and they are present in the Australian environment. When the doped microbeads were included in feed for Murray River rainbow fish, up to 12.5% of the pollutant was transferred to the tissue of the fish. [Peter Wardrop and 6 others, Chemical Pollutants Sorbed to Ingested Microbeads from Personal Care Products Accumulate in Fish', *Environmental Science & Technology*, 48 (2014), 4037-4044. DOI: 10.1021/acs.est.5b06280.] Small amounts of PBDEs were present in fish before the experiment, reflecting the presence of these substances in the environment.

A large research group [M. Fossi and 15 others, 'Fin whales and microplastics: the Mediterranean Sea and the Sea of Cortez scenarios', *Environmental Pollution*, 209 (2015), 68-78. DOI: 10.1016/j.envpol.2015.11.022] found that whales in the Mediterranean had higher concentrations (13.3 mg/g) of plastic particles and of persistent, bioaccumulative and toxic (PBT) chemicals (such as polychlorobiphenyls (PCBs), organochlorine pesticides (OCPs) and phthalates) than those in the less polluted Sea of Cortez, off the coast of Mexico (8.8 mg/g). Biological indicators of harm were also stronger in the Mediterranean whales.

Birds

Researchers from Norway and the Netherlands [Dorte Herzke and 7 others, 'Negligible Impact of Ingested Microplastics on Tissue Concentrations of Persistent Organic pollutants in Northern Fulmars off Coastal Norway', *Environmental Science & Technology*, 50 (2016), 1924-1933. DOI: 10.1021/acsest.5b04663.] measured the concentrations of persistent organic pollutants (POPs – PCBs, DDTs and flame retardants) in liver and muscle of seabirds and in the plastic fragments found in their guts. There was no correlation between the two concentrations, and they concluded that the plastic acted as a passive sampler rather than a vector for delivery of POPs to the birds, and probably reflected the POPs burden of ingested prey.

Small organisms and shellfish

Impacts on sessile marine species were caused by additives already present in commercial plastics when they were leached out by seawater. [Heng-Xiang Lee and 5 others, 'Effects of Toxic Leachate from Commercial Plastics on Larval Survival and Settlement of the Barnacle *Amphibalanus amphitrite*', *Environmental Science & Technology*, 50 (2016), 924-931. DOI: 10.1021/acsest.5b02781.] The plastics were high- and low-density polyethylene (HDPE and LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polycarbonate (PC). Leachate mixtures included metals, phthalates, and organo-tin species.

Korean researchers investigated the impact of small polystyrene particles – 0.05, 0.5 and 6 μm – on plankton animals 01-0.5 mm in size and found that the smaller particles were most toxic, inhibiting growth and fecundity. [Chang-Bum Jeong and 9 others 'Microplastic Size-Dependent Toxicity, Oxidative Stress Induction, and p-JNK and p-p38 Activation in the Monogonont Rotifer (Brachionus koreanus)', *Environmental Science & Technology*, 50 (2016), 8849-8857. DOI: 10.1021/acs.est.6b01441.]

In work that should qualify for an Ig Nobel Prize, an English group showed that copepods can ingest polystyrene microspheres (20.6 μm) and excrete them in faeces that, as a consequence sink more slowly although they do serve to remove plastic from surface waters. [Matthew Cole and 6 others, 'Microplastics Alter the Properties and Sinking Rates of Zooplankton Faecal Pellets', *Environmental Science & Technology*, 50 (2016), 3239-3246. DOI: 10.1021/acs.est.5b05905.] The faecal pellets, with the microspheres, were ingested by another species.

Microparticles produced by abrasion of commercial polystyrene and polyacrylic plastics were shown to adhere to the surfaces of brown seaweed (*Fucus vesiculosis*) and to be ingested by the common periwinkle (*Littorina littorea*) as it grazed on the algae. [Lars Gutow and 3 others, 'Experimental Evaluation of Seaweeds as a Vector for Microplastics into Marine Foodwebs', *Environmental Science & Technology*, 50 (2016), 913-923. DOI:

10.1021/acsest.5b02431.] The plastic particles were excreted and did not accumulate in the animal.

Another Korean group [Mi Jang and 5 others, 'Styrofoam Debris as a Source of Hazardous Additives for Marine Organisms', *Environmental Science & Technology*, 50 (2016), 4951-4960. DOI: 10.1021/acs.est.5b05485.] found that mussels growing on polystyrene foam in which hexabromocyclododecane (HBCD) was present as a flame retardant, contained up to 5160 ng/g lipid of the brominated compound. Micro-size polystyrene foam particles were also detected in the mussels.

Mechanism of action
Most organisms have mechanisms for ridding themselves of toxic substances that might pose a threat to their well-being. The protein (P-glycoprotein, P-gp) acts in this defensive way but can be inhibited when it binds to persistent organic pollutants including organochlorine pesticides such as DDT, polychlorinated biphenyls, and flame retardants such as polybrominated diphenyl ethers. This has been demonstrated with mouse and human P-pg, thus providing insights into the way that such substances impact on organisms. The levels of typical pollutants in yellowfin tuna in the Gulf of Mexico have also been measured. [Sascha C.T. Nicklisch and 10 others, *Science Advances*, 2016:e1600001. 11 pp.]

Getting it into perspective
There have been conflicting reports about the ability of plastic litter to absorb from the environment hydrophobic organic chemicals (HOC) and to act as a vector to deliver toxic substances to vulnerable organisms. A recent review claimed that the risks had been over-stated. More HOCs are absorbed by other media in the ocean such as organic matter and this conclusion was also reached in other studies. 'We calculate the fraction of total HOC sorbed by plastics to be small compared to that sorbed by other media in the ocean', the authors wrote, and 'we conclude that overall the flux of HOCs bioaccumulated from natural prey overwhelms the flux from ingested microplastic for most habitats, which implies that microplastic ingestion is not likely to increase the exposure to and thus risks of HOCs in the marine environment'. [Albert A. Koelmans and 3 others, 'Microplastic as a Vector for Chemicals in the Aquatic Environment: Critical Review and Model-Supported Reinterpretation of Empirical Studies', *Environmental Science & Technology*, 50 (2016), 3315-3326. DOI: 10.1021/acs.est.5b06069.]

Concluding remarks
There is no doubt that some, possibly all, plastic particles in the marine environment can sequester toxic substances from the water. The extent to which a 'loaded' particle can deliver harmful amounts of toxic chemicals to a host that ingested the particle is unclear but some experiments show that it can happen.

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**** Update 3 May 2017** This report has now been retracted following recommendations from the Central Ethical Review Board in Sweden. For more information refer to Science as published online on 3 May 2017 [10.1126/science.aan5763]