Marine Pollution Bulletin 60 (2010) 2050–2055

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Association of metals with plastic production pellets in the marine environment

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ARTICLE INFO

Keywords:
Plastic production pellets
Metals
Adsorption
Precipitation

ABSTRACT

Plastic production pellets sampled from four beaches along a stretch of coastline (south Devon, SW England) and accompanying, loosely adhered and entrapped material removed ultrasonically have been analysed for major metals (Al, Fe, Mn) and trace metals (Cu, Zn, Pb, Ag, Cd, Co, Cr, Mo, Sb, Sn, U) following acid digestion. In most cases, metal concentrations in composite pellet samples from each site were less than but within an order of magnitude of corresponding concentrations in the pooled extraneous materials. However, normalisation of data with respect to Al revealed enrichment of Cd and Pb in plastic pellets at two sites. These observations are not wholly due to the association of pellets with fine material that is resistant to ultrasonication since new polyethylene pellets suspended in a harbour for 8 weeks accumulated metals from sea water through adsorption and precipitation. The environmental implications and potential applications of these findings are discussed.

1. Introduction

Although plastics have been recognised as an important component of marine litter for several decades, their ecological and biological impacts have only been acknowledged and understood recently (Derraik, 2002; Moore, 2008). Pre-production pellets, or resin pellets, the raw materials from which plastics are moulded, are a common, global form of litter encountered on the strandline of beaches and in suspension in coastal and oceanic waters (Gregory, 1983; Shiber, 1987; Khordagui and Abuhilal, 1994; McDermid and McMullen, 2004). Pellets are lost during loading and transportation, both on land and at sea, and during their handling at plastic moulding factories (Redford et al., 1997). Due to their buoyancy and durability, lost pellets may be transported considerable distances in the oceans before becoming temporarily or permanently stranded (Ivar do Sul et al., 2009).

Descriptions of beached litter commonly report heterogeneous assortments of plastic production pellets (Endo et al., 2005; Rios et al., 2007). They are generally 2–5 mm in diameter and are most commonly polyethylene or polypropylene, are usually disc-, ovoid- or cylindrical-shaped and may be colourless, translucent or coloured (Endo et al., 2005; Rios et al., 2007). Aging of pellets is usually accompanied by discolouration (e.g. yellowing), abrasion, cracking, fouling, tarring and encrustation by precipitates (Endo et al., 2005).

Compared with larger forms of litter, plastic production pellets are more difficult to clear from a beach but are aesthetically less obtrusive. The main ecological risk associated with pellets, however, appears to be their inadvertent (or sometimes selective) ingestion by animals, including birds, fish and invertebrates, resulting in diminished foraging ability and feeding stimulus, loss of nutrition and intestinal blockage (Ryan, 1987; Toda et al., 1994; Provencher et al., 2009; Graham and Thompson, 2009). Pellets are also carriers of organic contaminants, including components of the plastic itself (e.g. plasticisers) and persistent, hydrophobic compounds, such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons, that sorb onto or into the pellets during their transport in the aqueous phase (Mato et al., 2001; Endo et al., 2005; Karapanagioti and Klontza, 2008).

In the present study, we examine the association and interactions of new and beached production pellets with a variety of metals. Although pure polymers are generally acknowledged to be rather inert towards aqueous cations, loss of trace metals to container surfaces during the storage of water samples is a common problem (Giusti et al., 1994; Cobelo-Garcia et al., 2007). Moreover, adsorption of metals to polymers is predicted to be enhanced as the material ages and its polarity, surface area and porosity increase and it becomes fouled with organic matter and hydrous metal oxides. Thus, it is possible that plastics may serve as a means of metal transport in the marine environment, and that metal signatures of plastics may afford a means of tracing the provenance and age of the litter.

2. Materials and methods

2.1. Sample sites

Twelve beaches along a 40 km stretch of coastline between Plymouth and the Kingsbridge estuary (Devon, SW England) were

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0025-326X/$ - see front matter
doi:10.1016/j.marpolbul.2010.07.014

visited between May and October, 2009. Pellets were subsequently sampled from four beaches, shown in Fig. 1 and described below, selected on the basis of contrasting size, geomorphology, orientation, uses, and variety and abundance of pellets. Soar Mill Cove is a small, remote sandy inlet that faces southwest. It is owned (and protected) by the National Trust and is popular with bathers during the summer. Thurlestone is a wide, expansive sandy beach facing southwest that is also owned by the National Trust and is backed by a nature reserve. It is a popular destination for non-motorised water sports. Bovisand is a sheltered, gently-sloping sandy bay facing west towards Plymouth Sound that serves the residents of Plymouth (250 000) throughout the year. Saltram is an intertidal silt-sandflat on the east bank of the Plym estuary. The estuary is urbanised along most of its 5 km tidal axis and receives treated sewage effluent and landfill leachate during ebb flow.

2.2. Sampling

Several hundred pellets were retrieved from the high tide line and berm zone of each beach using plastic tweezers and were stored as composite samples in acid-cleaned 50 ml screw-capped polypropylene centrifuge tubes. In the laboratory, 100 pellets from each site (or 4 × 100 pellets from Soar Mill Cove for replication purposes) were transferred to clean centrifuge tubes before 25 ml of English Channel sea water, collected in bulk and available on tap in the laboratory following on-line filtration through 0.6 μm, was added. The contents were ultrasonicated for 5 min to remove extraneous material (loosely adhered or entrapped debris) before being sieved through a 1 mm nylon mesh. Material passing the sieve was filtered through 0.45 μm using an acid-cleaned polyethylene Buchner filtration unit connected to a vacuum pump. Filters and pellets were then air-dried in Perspex Petri dishes at 45 °C for 48 h.

2.3. Suspension experiment

In order to examine the physical and chemical changes conferred on plastics in sea water, new polyethylene pellets (white, diameter ~ 4 mm, mass ~ 25 mg), sourced from a local moulding factory (Algram Group Ltd, Plymouth), were suspended in a Sutton Harbour, Plymouth (Fig. 1) for a period of 8 weeks (October–December, 2009). This was achieved by tying a nylon-mesh bag (15 cm × 10 cm) containing 100 pellets to a mooring chain just below the water surface. Pellets retrieved from the bag were air-dried as above, and divided into four subsamples.

2.4. Pellet analysis

The polymers of 30 individual beached pellets of various colours and shapes were identified by Fourier transform-infrared (FTIR) spectroscopy using a Bruker IFS 66 spectrometer attached to a Hyperion 1000 IR microscope with a liquid nitrogen cooled mercury–cadmium–telluride detector. Slices of each pellet were cut using a stainless steel scalpel and then compressed between the windows of a Specac diamond compression cell until an appropriate thickness was attained. Transmission spectra were acquired by averaging 100 scans at a resolution of 4 cm^{-1} over the range 4000–400 cm^{-1}. A qualitative evaluation of the age of the pellets was ascertained from the carbonyl index; that is, the height of the carbonyl peak measured at 1717 cm^{-1} relative to the height of a reference peak (unaffected by weathering) measured at 1465 cm^{-1} (Artham et al., 2009).

The surface characteristics of selected pellets were examined by scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS). Pellets were sputter-coated with a thin film in an EMITECH K 450X high vacuum carbon-coating unit before being attached to the SEM with adhesive tape. Samples were photographed using a JEOL JSM-6100 operated at 20 kV and at a working

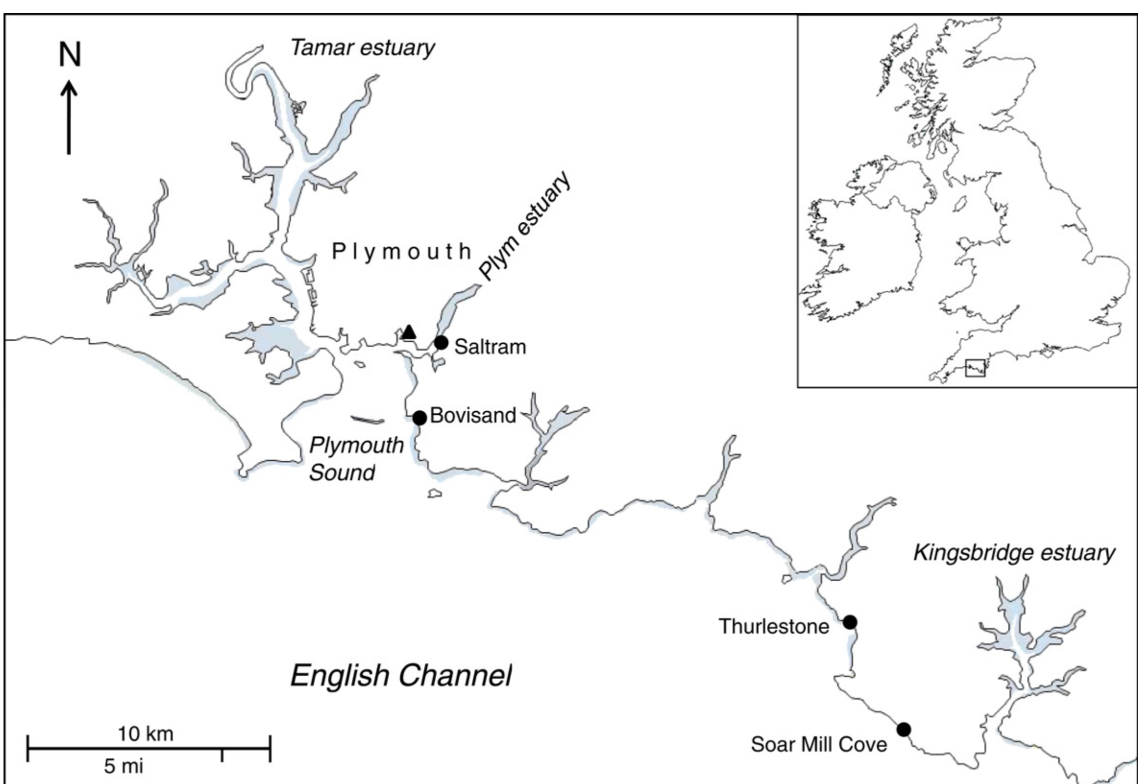

Fig. 1. The beaches and intertidal areas of south Devon, SW England (shaded), and the locations at which pellets were sampled (●) and where the suspension experiment was conducted (▲).