

# **A Brief Analysis of Organic Pollutants Sorbed to Pre and Post-Production Plastic Particles from the Los Angeles and San Gabriel River Watersheds**

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## **Abstract**

Plastics as a means to transport pollutants in aquatic and marine ecosystems have become the focus of scientific research as levels of macro and micro plastics in these environments increase.<sup>1,2,3,4</sup> Hideshige Takada and colleagues at the Tokyo University of Agriculture and Technology have studied how polypropylene (PP) pellets in the marine environment adsorb, (with adsorption coefficients of  $10^5$ - $10^6$  from ambient seawater), and transport PCBs, DDE and nonylphenols (NP).<sup>5</sup> Trawls conducted in 1999 by Algalita Marine Research Foundation (AMRF) in the eastern North Pacific found that plastic pellets made up 0.17% of neuston micro plastics 1-5mm in diameter.<sup>6</sup> Polypropylene pellets, therefore, may make up less than two tenths of one percent of marine micro plastic abundance in the 1-5 mm size class. This size class of plastic debris, not regulated under current Total Maximum Daily Loads (TMDLs) for trash, was the focus of a recent AMRF study funded by the State of California Water Resources Control Board.<sup>15</sup> In the study, plastic particles of that size class were found to be the major component of the debris stream in the Los Angeles and San Gabriel Rivers. The particles consisted of both pre-production plastic pellets and post-production plastic fragments of unknown origin.

To begin to assess the role of micro plastic debris in the transport of aquatic and marine environmental pollutants, pellets and fragments between one and five millimeters in diameter were sampled from river banks and beaches in the Los Angeles and San Gabriel Rivers' Watersheds, and subjected to Gas Chromatography-Mass Spectrometry (GCMS) analysis. It was not feasible to trawl up enough pellets and particles from rivers and bays for analysis due to time and equipment constraints. Two samples were also collected from the driveway of a pellet transporter during a rain event. No PCBs or DDE were detected in any of our field samples, but all samples contained Polycyclic Aromatic Hydrocarbons (PAHs) and Phthalates. Nonylphenols were not analyzed, but three chlorinated pesticides (chlordanes), and four base neutral compounds, two Chlorophenyl Phenylethers, Hexachlorobenzene, and n.Nitrosodimethylamine were found in some samples. Field samples were compared to virgin plastic pellets from a plastic bag processor that had never entered the production stream. Analysis of the virgin pellets found that the only compounds present from the list of analytes (see appendix) were phthalates.

## Introduction

Many studies have documented the role of air, water and sediments in the transport of Persistent Organic Pollutants (POPs), but few have looked at the role of a relatively new component of these systems, plastics. Mato et al. analyzed pellets from beaches in Japan and floated virgin pellets in laboratory preparations of seawater to determine sorption coefficients<sup>5</sup>. “Field adsorption experiments using PP virgin pellets demonstrated ... increase in PCBs and DDE...indicating that the source...is ambient seawater and that adsorption to pellet surfaces is the mechanism of enrichment. Comparison of PCBs and DDE concentrations in PP resin pellets with those in seawater suggests their high degree of accumulation (apparent adsorption coefficient:  $10^5 - 10^6$ ). The high accumulation potential suggests...pellets serve as both a transport medium and a potential source of toxic chemicals in the marine environment.” It is unclear whether similar results can be obtained from post consumer plastic fragments. In this paper, we analyze pre-production plastic pellets and broken fragments of post-production plastic products, collected from Southern California rivers and beaches in Los Angeles and Orange Counties for sorbed POPs. Quantities of these target plastics taken in trawl nets from the rivers and their forebays are normally insufficient for laboratory analysis. Samples were collected from river banks and beaches shortly after rain events to maximize the probability that these plastics had spent time afloat. Pellets were also collected from a catch basin insert located in the driveway of a pellet transporter during a rain event. These field samples are compared to virgin pellets from a bag manufacturer.

## Methods

Samples of plastic pellets and plastic fragments from rivers and beaches were collected separately by hand using sterile forceps and sterile glass jars with Teflon lids and stored on ice at 4 C, then delivered to an EPA certified analytical lab for analysis within 48 hours of collection. Because of solvent and equipment limitations, expanded polystyrene (Styrofoam) was eliminated from the samples. Two sets of wet weather samples were collected. The dates of collection were March 4, 2004 and October 18-23, 2004.

- 1) River Samples: River samples were collected along the wrack (strand) line of the river within 48 hours of cresting after a greater than 0.25” rain event. Note: River samples were collected from October 18-23 only.
- 2) River Mouth Samples: River mouth samples were collected along the high tide/strand line within 8 hours of high tide. One site near each river mouth was sampled within 48 hours of a 0.25” rain event.
- 3) Beach Samples: Beach samples were collected at a distance of 500 to 1500 meters downcurrent from the river mouth. Pellets and pieces/fragments of plastics were collected at the high tide/strand line within 8 hours after a high tide and within 48 hours of a 0.25” rain event.

On January 7, 2005, heavy rains in the early AM flooded the loading area and driveway of a transporter of pre-production plastic pellets voluntarily taking part in this study. Per agreement with management, project personnel arrived to take two samples from the 1mm mesh storm drain insert placed by the project and remove it to alleviate the flooding. Pellets were scooped from the insert with a glass jar, covered and placed on ice for delivery to the lab. Virgin polyethylene plastic pellets were obtained from a manufacturer of plastic bags for comparison with field samples. These virgin pellets were delivered in bulk by rail to the bag manufacturing facility and transferred directly from the rail car to the premises by a vacuum hose system. The pellets were held at room temperature in a polyethylene zip lock bag until delivered to the lab for analysis. Sample sizes varied from 1-13 grams of plastic particles. Each sample was extracted for 18 hours by Soxhlet using n-Hexane. The extracts were concentrated using a Buchi Roto-evaporator and transferred into autosampler vials to a final volume of ca. 500  $\mu$ L. A 2.5  $\mu$ L aliquot injected into Shimadzu GCMS temp. programmed from 125° to 295°C at 2.5°C/min was held for 15 min. A list on analytes and their values for each sample can be found in the appendix (on floppy disk).

## Results

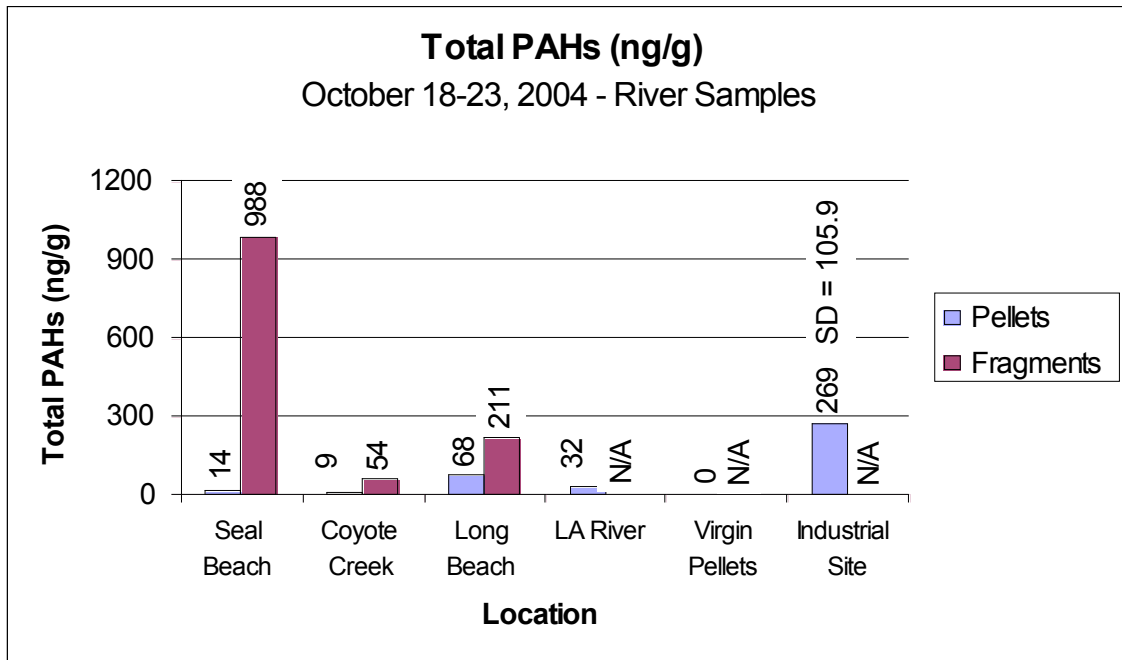
The samples from the transport facility were determined to be 90% (PE) and 10% polyurethane (PU) by use of a "Plastics Identification Chart" provided by Performance Engineered Products of Pomona, CA. Using the same chart, the river and beach samples of pellets and fragments were found to be varying mixtures of (PP) and (PE). In some samples PP predominated, while others were mostly PE. Only one sample had 10% ABS plastic, which is slightly heavier than water. Both PE and PP float. No attempt was made to determine the molecular weight of the individual plastics making up the samples. In general, the higher the molecular weight of the plastic polymer, the slower the uptake of hydrocarbons.<sup>10</sup> The same polymer may have different molecular weights, e.g. Low Density Polyethylene (LDPE), and High Density Polyethylene (HDPE).

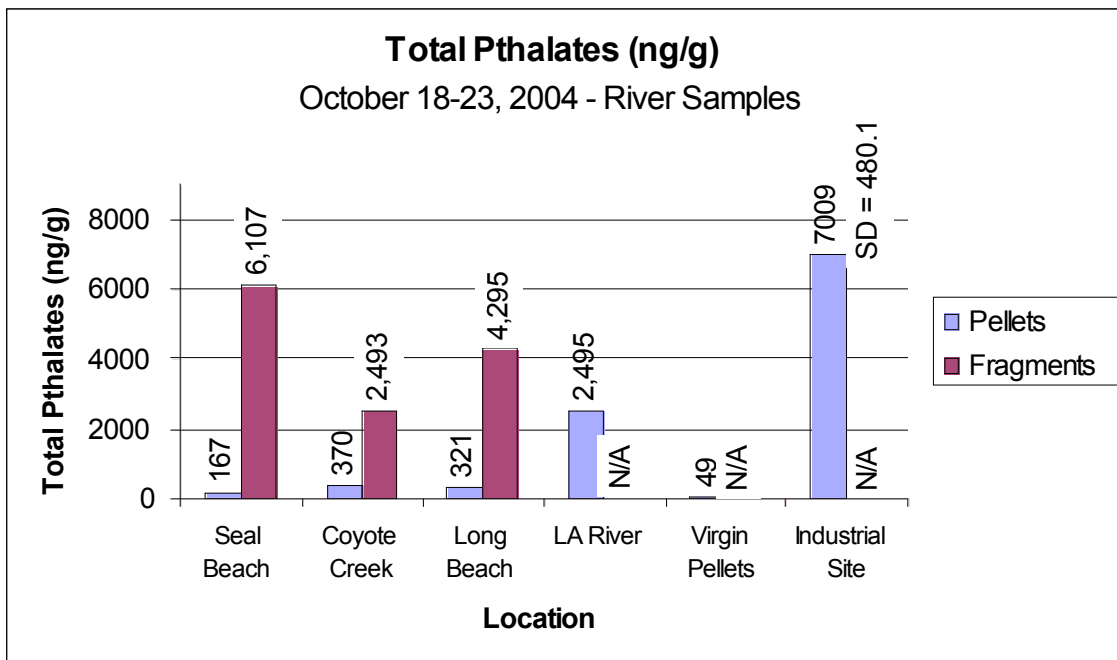
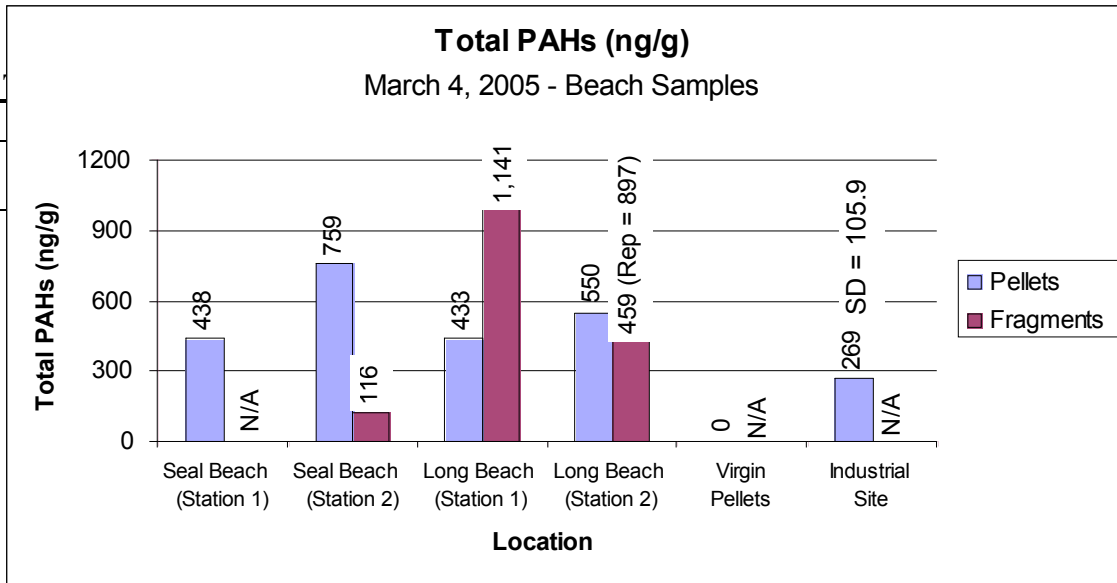
No PCBs or DDE were detected in any of the samples, but all contained Polycyclic Aromatic Hydrocarbons (PAHs) and Phthalates. Nonylphenols were not analyzed, three chlorinated pesticides (chlordanes), and four base neutral compounds (two Chlorophenyl Phenylethers, Hexachlorobenzene, and n.Nitrosodimethylamine), were found in some samples. Thirteen grams of virgin PE pellets from a plastic bag manufacturer were analyzed and found to have no detectable PAHs or any other analytes except for phthalates, which are plastic conditioners probably added at the time of manufacture. The following three phthalates were present in the virgin PE pellets: 1) Bis(2-Ethylhexyl) Phthalate or DEHP at 33.8 ng/g, 2) Diethyl Phthalate estimated at 9.9 ng/g, and 3) Di-n-butyl Phthalate estimated at 5.4 ng/g.

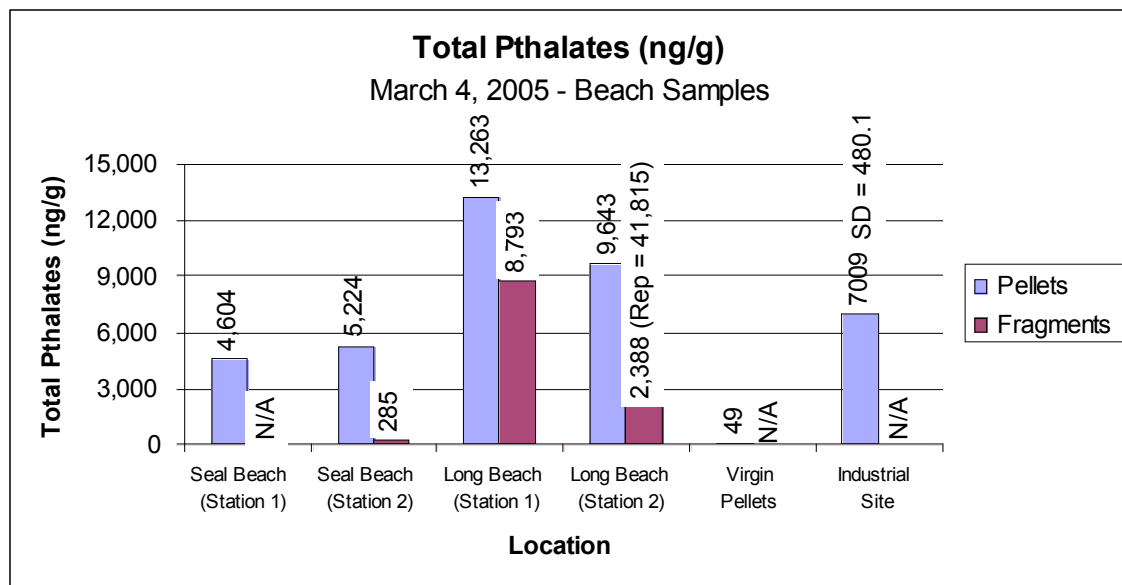
Plastic resin pellets (90% PE, 10% PU), which landed on a transporter's asphalt loading area and were washed into a catch basin had phthalate levels much higher than the virgin PE pellet phthalate levels cited in the preceding paragraph. The levels were from 7100

ng/g for Bis-2 to 33 ng/g for di-n-butyl. It is doubtful that these higher levels were from environmental sorption. The particular additive profile designed for the plastic processor who was to receive the shipment likely called for these phthalate levels in the virgin pellets.

Total PAH levels in the transporter's catch basin pellets were: Sample 31-1, 344.2 ng/g; Sample 31-2, 194.4 ng/g, for an average of 269 ng/g +/- SD 105.9. The following graphs summarize the results for all samples.







## Discussion

**PAHs** have both petrogenic (lower molecular weights from petroleum) and pyrogenic (higher molecular weights from burning and incomplete combustion) sources and can enter the marine and aquatic environments via air-water exchange or storm system runoff. Both of these routes facilitate their global distribution.<sup>7</sup> “Most PAHs do not dissolve easily in water. They stick to solid particles and settle to the bottoms of lakes or rivers...Some PAH particles can readily evaporate into the air from soil or surface waters.”<sup>8</sup>

Plastic resin pellets from the industry sites surveyed in this study would generally reach the storm drain system after traveling less than 100 meters. Many broken pieces of consumer plastics would have traveled further than 100 meters over urban streets, increasing their exposure to PAHs, before reaching a delivery conduit as runoff or blowing into the storm drain system. This may account for, with one exception, the higher PAH loads in fragments compared to pellets in our study. It is interesting to note that all three types of PAHs; volatile, low molecular weight and high molecular weight were present in all samples, and that pellets from the transporter’s facility had higher PAH totals than some pellets from rivers and beaches. It is not known how much of this variability is due to loss of PAHs to the water column and atmosphere during transport by storm drains and rivers, or how much is due to the fact that different pellets from different sources are of differing composition.

**Chlordanes** are non-polar organic molecules, which were used as pesticides until banned for all uses in 1988.<sup>8</sup> They were found in several of our samples at levels not exceeding 37 ng/g.

**4-Chlorophenyl Phenylether** and **Hexachlorobenzene** are semi-volatile target compounds in EPA Superfund lists. They were found in several of our samples at levels not exceeding 233 and 24 ng/g respectively.

(<http://www.epa.gov/superfund/programs/clp/svtarget.htm>)

**“Phthalates**, also known as phthalate esters, are the dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid. The name phthalate is derived from phthalic acid + -ate. When added to plastics, they allow the long polyvinyl molecules to slide against one another. The phthalates show low water solubility, high oil solubility, and low volatility.”

(<http://www.answers.com/topic/phthalates>) The highest levels of phthalates in our study were found in broken pieces of consumer plastics on beaches near river mouths, but high levels existed in pellets as well. In spite of their low solubility in water, it is possible that plastic particulates accumulate phthalates from within the water column. ... [non-polar organic]...”compounds tend to be concentrated in the seasurface microlayer and in the bottom sediments and since plastics are usually less dense than water, they most likely are adsorbing compounds from the surface microlayer.”<sup>9</sup> Another possibility is that the mix of consumer plastic bits is more diverse in the beach samples than in the riverbank samples, and reflects increased use of phthalates in some of those products. The levels of PAHs found in this study sorbed to plastics is less than the levels found in stormwater in the rivers sampled in our study: 9 - 988 ng/g vs 1000 -3000 ng/g in stormwater.<sup>10</sup>

## **Conclusions and Areas for Further Study**

Plastic resin pellets and broken bits of consumer plastics carry certain classes of Persistent Organic Pollutants (POPs) in greater concentrations than virgin polyethylene pellets. Further studies are needed to determine the extent to which these plastic particles transport the sorbed pollutants from urban centers, down rivers to the ocean, and onto adjacent beaches. With continued quantitation of river borne micro plastics and their PAH loads, it should be possible to determine if plastics sorb PAHs more or less than other sediments in the water column, and what percentage of total PAHs transported by the Los Angeles and San Gabriel rivers is transported by plastics. Further research could target other compounds sorbed by these plastic particles. In general, concentrations on the pellets are comparable to those found in stormwater in the same locations (around 2.5 ppb)<sup>10</sup> This is consistent with the conclusions of Mato et al., who found that resin pellets from industrialized areas contained larger amounts of PCBs than those from a remote site, suggesting that contaminant concentrations in resin pellets are determined by their levels in the surrounding environment<sup>5</sup>.

Many plastic resin pellets resemble fish eggs in size, shape and color and have been eaten by at least eight species of fish.<sup>11</sup> Broken and weathered plastic fragments have been found in shapes, sizes and colors resembling various species of zooplankton during separation of trawl samples by AMRF marine biologists, who have also found zooplankton with ingested plastic, and plastic embedded in zooplankton tissue.<sup>6</sup>

Richard Thompson and colleagues ... “kept amphipods (detritivores), lugworms (deposit feeders), and barnacles (filter feeders) in aquaria with small quantities of microscopic plastics. All three species ingested plastics within a few days.”<sup>1</sup> Bioaccumulation of POPs in fatty tissue or serum of organisms consuming contaminated micro plastics is a possibility, but no studies have been done demonstrating that this actually takes place in fish or marine invertebrates, although increased consumption of plastics has been shown to elevate PCB levels in seabirds.<sup>12</sup>

Every plastic object is produced to fill a particular perceived need and is given unique properties by the producer to fulfill its purpose. These properties are often achieved by the use of additives, which are extremely diverse and include compounds used to assist in processing the polymers involved.<sup>13</sup> Further research needs to be done to determine if plastic additives transported by plastic fragments leach into the water column or contribute to POPs levels in the sea surface microlayer or in sediments. The idea that plastics should be found in sediments runs counter to the common perception that they are positively buoyant, but only 46% of plastic resin pellets actually are (USEPA, 1992). Many objects are products such as Styrofoam, in which injected air makes the objects buoyant. As these products break down, they lose air pockets, and may eventually lose their buoyancy. Furthermore, small particles of heavier sediments such as sand, can be caught in plastic bags and other plastics and cause them to settle to the bottom.<sup>14</sup> Fouling organisms such as diatoms and bryozoans contain carbonates and silicates, which are heavier than seawater and may also contribute to the settling of pelagic plastics. Furthermore, plastics that float in the surface microlayer may be creating a sort of “floating sediment” whose characteristics warrant further study.

Micro plastics in the North Pacific have tripled during the last decade<sup>2</sup>, and near the coast of Japan, gone up by a factor of 10 every 2-3 years during the same period.<sup>3</sup> If this trend continues, the importance of understanding their effects on aquatic and marine environments will also increase. Notwithstanding the likelihood of increasing pelagic plastics, no government or industry programs for monitoring micro plastics in the environment currently exist, in sharp contrast to the widespread efforts that monitor airborne contaminants, sewage, and stormwater runoff. Without such programs, the unintended consequences to the environment of the “Plastic Age” will never be known, nor will strategies be developed to mitigate them.

## Citations

<sup>1</sup>Thompson, Richard C., et al, Lost at Sea: Where Is All the Plastic?, *Science*, Vol. 304, 2004, 843

<sup>2</sup>Moore, Charles J., et al, Density of Plastic Particles found in zooplankton trawls from Coastal Waters of California to the North Pacific Central Gyre, in *Proceedings of the Plastic Debris Rivers to Sea Conference*, 2005

<sup>3</sup>Ogi, Haruo and Fukumoto, Yuri, A Sorting Method for Small Plastic Debris Floating on the Sea Surface and Stranded on Sandy Beaches, *Bulletin of the Faculty of Fisheries, Hokkaido university* 51(2), 2000, 71-93

<sup>4</sup>Copello, Sofia, and Quintara, Favio, Marine debris ingestion by Southern Giant Petrels and its potential relationships with fisheries in the Southern Atlantic Ocean, *Marine Pollution Bulletin* 46 (2003) 1513-1515

<sup>5</sup>Mato, Y. et al, Plastic resin pellets as a transport medium for toxic chemicals in the marine environment, *Environmental Science Technology*, 35, (2001) 318-324

<sup>6</sup>Moore, Charles J. et al, A comparison of plastic and plankton in the North Pacific central gyre, *Marine Pollution Bulletin* 42-12 (2001) 1297-1300

<sup>7</sup>Mai, B et al, Distribution of Polycyclic Aromatic Hydrocarbons in the Coastal Region of Macao, China: Assessment of Input Sources and Transport Pathways Using Compositional Analysis. *Environmental Science Technology* 37, (2003) 4855-4863

<sup>8</sup>Agency for Toxic Substances and Disease Registry, (1996), <http://www.atsdr.cdc.gov/tfacts69.html>

<sup>9</sup>Gosset, Richard, CRG Project ID# 2454, August 30, (2004) 1-2

<sup>10</sup>Stein, Eric, personal communication, Principal Scientist, Southern California Coastal Water Research Project, (2005)

<sup>11</sup>Carpenter, E.J. et al, Polystyrene spherules in coastal waters, *Science* 178 (1972) 749-750

<sup>12</sup>Ryan, P.G. et al, Plastic Ingestion and PCBs in Seabirds: Is There a Relationship? *Marine Pollution Bulletin*, 19 (1988) 174-176

<sup>13</sup>Carraher, Charles E., Giant Molecules, second edition, Wiley Interscience (2003), 426

<sup>14</sup>Moore, Charles J. et al, A comparison of neustonic plastic and zooplankton at different depths near the southern California shore, *Marine Pollution Bulletin*, 49 (2004) 291-294

<sup>15</sup>Moore, C.J., G.L. Lattin, A.F. Zellers, Measuring the Effectiveness of Voluntary Plastic Industry Efforts: AMRF'S Analysis of Operation Clean Sweep, in *Proceedings of the Plastic Debris Rivers to Sea Conference*, 2005

### **Appendix (available from AMRF upon request)**

P2454 Algalita Final Report

P2454c CRG Final Report

P2538 CRG Final Report