# Journal of Environmental Monitoring

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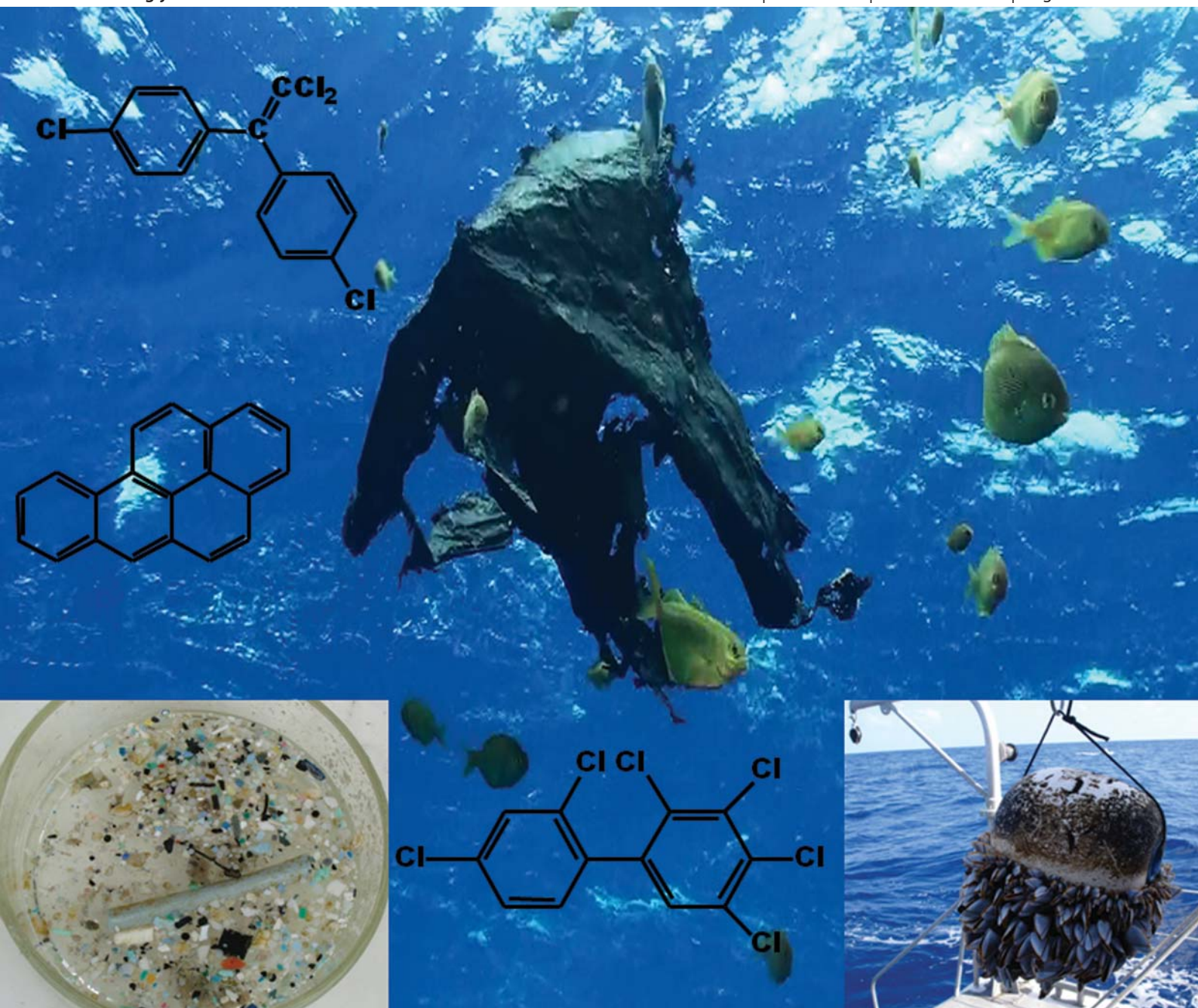
## RSC Publishing

**PAPER**
Rios *et al.*
Quantitation of persistent organic pollutants adsorbed on plastic debris from the
Northern Pacific Gyre's "eastern garbage patch"

# Quantitation of persistent organic pollutants adsorbed on plastic debris from the Northern Pacific Gyre's "eastern garbage patch"

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Floating marine plastic debris was found to function as solid-phase extraction media, adsorbing and concentrating pollutants out of the water column. Plastic debris was collected in the North Pacific Gyre, extracted, and analyzed for 36 individual PCB congeners, 17 organochlorine pesticides, and 16 EPA priority PAHs. Over 50% contained PCBs, 40% contained pesticides, and nearly 80% contained PAHs. The PAHs included 2, 3 and 4 ring congeners. The PCBs were primarily CB-11, 28, 44, 52, 66, and 101. The pesticides detected were primarily $p,p$-DDTs and its metabolite, $o,p$-DDD, as well BHC (a,b,g and d). The concentrations of pollutants found ranged from a few ppb to thousands of ppb. The types of PCBs and PAHs found were similar to those found in marine sediments. However, these plastic particles were mostly polyethylene which is resistant to degradation and although functioning similarly to sediments in accumulating pollutants, these had remained on or near the ocean surface. Particles collected included intact plastic items as well as many pieces less than 5 mm in size.

## Introduction

Plastic debris is one of the most persistent contaminants in the oceans and on beaches worldwide,[1–3] and continues to go into the oceans and persists for a very long time. The plastic particles low in density relative to seawater float, drift with wind and water currents, and as such are transported over large distances. In the process the particles are exposed to vast quantities of seawater which by dilution have very low concentrations of pollutants. However, the partitioning quotient between plastic and seawater favors the accumulation of pollutants onto the plastic particles[4] and plastic pellets.[5] The increasing rate of plastic consumption in worldwide has led the plastic production increase from 1950 with

1.5 million tons to 245 million tons in 2008. In 1988, 30 million tons of plastic were produced in the United States.[6–8]

Plastics are synthetic polymers that are typically made from non-renewable resources including crude oil, coal, and natural gas. In addition, these polymers contain other chemicals including phthalates, flame retardants, and bisphenol-A. Marine plastic debris is a new environmental problem arising from the extremely widespread usage and massive quantities of inexpensive and disposable plastic items. These highly utilitarian items have the serious side effect of serving as particles on which pollutants accumulate. In addition, floating synthetic plastic polymers such as polyethylene are slow to degrade in the marine environment.

Just as chlorofluorocarbons were once considered benign materials and only subsequently were found to be destructive of the stratospheric ozone layer, the discovery of massive amounts of plastic debris in the Northern Pacific Gyre (NPG) was believe to only cause physical blockage on ingestion, we now find quantitative evidence that the plastic particles accumulate toxic materials and have the potential for chemical damage to marine organisms.

The North Pacific Gyre is a great high pressure system in the central Pacific Ocean. For more than fifty years plastics have

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### Environmental impact

This research paper describes the analysis of persistent organic pollutants adsorbed on floating plastic debris, and demonstrates that the plastic debris functions as solid phase extraction media in a way similar to the adsorption of pollutants on particles in sediments. While these floating particles accumulate pollutants, they do not sink and instead remain on or near the surface where they are accessible to marine life and may be ingested. While it is not possible to know the time span of the accumulation process, it is clear that over 50% of the samples contained measurable amounts of PCBs, and over 75% contained PAHs. The levels of each varied from a few ppb to thousands of ppb, indicating that the levels of these pollutants are much higher in the plastic debris than expected concentrations in the water. That is, these plastic particles accumulate and concentrate pollutants out of the water column and, unlike sediments, these particles remain accessible for ingestion providing another path for entry into the marine food chain constituting an ecotoxicological concern.

found their way into this area and into a special zone called the "eastern garbage patch".[9] Plastic debris in the ocean has been found to have direct effects on seabirds, mammals, turtles and benthic organisms by ingestion, entanglement, and the accumulation of higher density plastic debris on the seafloor where it can inhibit gas exchange between the overlying waters and the pore waters of the sediments, and disrupt or smother inhabitants of the benthos.[10] These negative physical effects from plastic debris add to the effects of chemical pollution by persistent organic pollutants (POPs) and possibly for heavy metals.[11–13] Of particular concern is the accumulation on plastics of polychlorinated biphenyls, PCBs, chlorinated pesticides, and polycyclic aromatic hydrocarbons, PAHs, which are known carcinogens, and are considered endocrine disrupting chemicals, EDCs. These EDCs have the capacity to bind to estrogen and androgen receptors.[14,15]

Persistent organic pollutants include a range of very stable compounds that are typically lipid soluble and have very low water solubility. A report including plastic found on beaches indicated the accumulation of POPs[4] and the current paper finds quantitative evidence from samples gathered in the open ocean. POPs originate from a wide range of both diffuse and point sources including agriculture, combustion, industrial manufacturing, waste incineration and even reemission from surface water, and contaminated sediments and soils.[16–18]

PCBs are considered representatives of industrial POPs and were banned in 1975 in the United States. These compounds have low degradability, high toxicity, are mutagenic and have a high tendency to bioaccumulate.[19]

Polycyclic aromatic hydrocarbons (PAHs) are mixtures from a set of over 100 different PAHs compounds. They can be formed during incomplete combustion of simpler organic compounds and are even found in charcoal broiled foods. PAHs are not synthesized for large scale commercial purposes, but are isolated, concentrated and purified from coal tar products or arise from pyrolysis of organic material. Some PAHs are used as research chemicals and may be found in small amounts in drugs, dyes, pharmaceuticals, pesticides, photography chemicals, lubricating materials, and plastics. Soot, which also contains PAHs, is used in elastomeric plastics to achieve required properties, such as flexibility, damping, and solubility in the polymer matrix.[20,21] Only three PAHs are produced on a commercial basis: acenaphthene, acenaphthylene, and anthracene. There is no report of the amount of production of the first two. However, data for the production of anthracene can be found in the publication "Toxicological Profile for PAHs 1995" produced by the Agency for Toxic Substances and Disease Registry (ATSDR).[22] A set of 16 PAHs ranging from 2 to 6 rings, have been identified as priority pollutants by the US Environmental Protection Agency based on their toxicity and prevalence in the atmosphere[23,24]

Despite the fact that the pesticide DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) was banned in 1972 by the United States and subsequently banned in most countries, evidence of DDT and its metabolites DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2- bis(p-chlorophenyl)ethane) are still found in sediments and seawater. In addition, they are still used in some countries mainly for malaria vector abatement. Depending on the temperature, the half-life of DDT is from 2 to 15 years and for DDE and DDD, 3 to 10 years, respectively.[25]
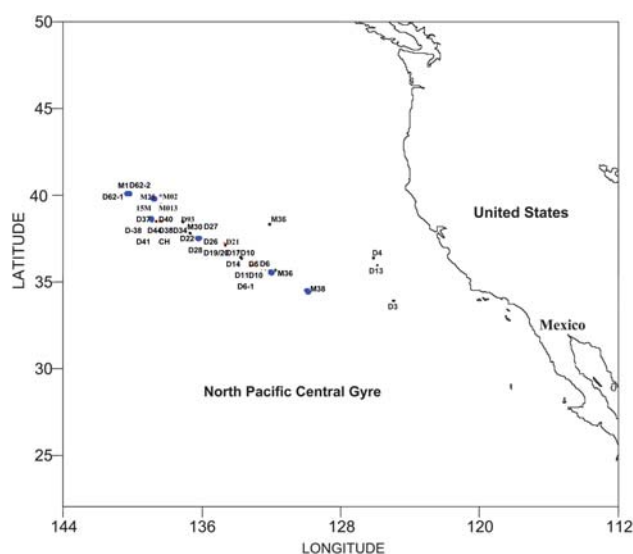


**Fig. 1** Sampling area with sample locations annotated.

*n*-Alkanes are also found associated with marine plastic debris. These originate from both biogenic and anthropogenic sources. Anthropogenic sources include fuel evaporation as well as combustion.[26]

The research reported here sought to establish the identity of adsorbed pollutants on plastic debris, and to measure quantitatively the net accumulation of these pollutants by plastic debris collected from the marine environment. The obvious question is what happens with these persistent organic pollutants if they become part of the marine food web? There is concern regarding the bioavailability of these pollutants not only for their toxicity but also for the potential harm as endocrine disrupters.

## Experimental

### Study area and sample collection

The plastic debris samples were collected in July 2005 from an area of the North Pacific Central Gyre called the "eastern garbage patch." The sampling area is located between Latitude 33° 54.486′–40° 05.399′ N and Longitude 124° 56.351′–140° 18.941′ W (Fig. 1). The North Pacific Central Gyre is part of a huge high-pressure system of the North Pacific Ocean with clockwise ocean currents. Our study area is located between San Francisco and Hawaii. A global positioning system (GPS) was employed to identify the precise location of each of the marine plastic debris samples collected. The sampling was carried out onboard the Oceanographic Research Vessel Alguita. The number of samples collected was 29 macro (greater than 5 mm) debris plastic samples, and 8 micro (less than 5 mm) debris plastic samples. These samples were collected using a hand net and a manta trawl respectively. The manta was towed horizontally at the ocean surface outside the port wake of the vessel at an average speed of 3 m s$^{-1}$ for periods between one and two hours on average. The manta had a rectangular opening of 0.9 × 0.15 m$^2$, and was 3.5 m long. At the end, there was a collecting bag of 30 × 10 cm$^2$ with a 333 micrometer mesh net. An AGO flowmeter measured the volume of water sampled. The samples were frozen at −20 °C until analysis in the lab.

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**Table 1** Individual analytes measured on plastic debris

| PCBs[a] | PAHs | Organochlorine pesticides | Aliphatic hydrocarbons |
|---|---|---|---|
| 1 | Acenaphthene | 2,4′-DDD | n-Dodecane |
| 5 | Acenaphthylene | 2,4′-DDE | n-Tetradecane |
| 8 | Anthracene | 2,4′-DDT | n-Hexadecane |
| 11 | Benzo(a)anthracene | Aldrin | n-Octadecane |
| 18 | Benzo(a)pyrene | α-BHC | n-Eicosane |
| 28 | Benzo(b+k) fluoranthene | β-BHC | n-Docosane |
| 29 | Benzo(ghi)perylene | δ-BHC | n-Tetracosane |
| 44 | Benzo(k)fluoranthene | γ-BHC | n-Hexacosane |
| 47 | Chrysene | 4,4′-DDD | n-Octacosane |
| 50 | Dibenz(a,h)anthracene | 4,4′-DDE | n-Triacontane |
| 52 | Fluoranthene | 4,4′-DDT | n-Dotriacontane |
| 66 | Fluorene | Dieldrin | n-Tetratriacontane |
| 77 | Indeno(1,2,3,c,d)pyrene | Endosulfan I | n-Hexatriacontane |
| 87 | Naphthalene | Endosulfan II | |
| 101 | Phenanthrene | Endosulfan sulfate | |
| 104 | Pyrene | Endrin | |
| 105 | | Endrin aldehido | |
| 118 | | Heptachlor | |
| 121 | | Heptachlor epoxide-isomer B | |
| 126 | | Methoxychlor | |
| 128 | | | |
| 136 | | | |
| 138 | | | |
| 153 | | | |
| 154 | | | |
| 170 | | | |
| 180 | | | |
| 185 | | | |
| 187 | | | |
| 188 | | | |
| 194 | | | |
| 195 | | | |
| 200 | | | |
| 206 | | | |
| 208 | | | |

[a] IUPAC numbers of congeners.

## Reagents and standards

All solvents used for sample processing and analysis were purchased from J. T. Baker, as pesticide HPLC chromatographic grade liquids. Silica and alumina chromatography materials were purchased from EM Science. PCBs, PAHs, DDTs, as well as individual pesticide, organochlorine, and aliphatic hydrocarbon standards were obtained from Accustandard, Inc. We also obtained surrogate internal standards used for PAHs: the deuterated standards (1,4-dichlorobenzene-d4, naphthalene-d8, phenanthrene-d10, acenaphthene-d10, perylene-d12, chrysene-d12), and a mixture of tetrachloro-m-xylene (TCMX) and PCB-209 for PCBs and organochlorine pesticides. The recovery standard was DBOFB (4,4-dibromooctafluorobiphenyl) for PCBs and pesticides, and was p-terphenyl-d14 for PAHs. These were purchased from Accustandard, Inc. For aliphatic hydrocarbons, the deuterated standard, n-dodecane-d26, was obtained from Sigma Aldrich.

## Sample analysis

The micro plastic debris was removed from seawater using a stereoscope and separated from organisms in the sample using forceps. The fragments and micro plastic were dried under a hood overnight before extraction. The larger macro plastic debris particles were cut into pieces 5 to 8 mm in size before extraction. All glassware was cleaned and baked in an annealing oven prior to use. This removed organic materials from the glass to a level below the detection limit. The samples were soxhlet extracted for 24 h with one cycle per 10 min using 150 mL of dichloromethane. The procedure used takes 1 g of the debris sample in a glass extraction thimble and adds a mixture of recovery standards. The extract was concentrated using a water bath at 50 °C. Hexane was used as exchange solvent and concentrated to a final volume of 1 mL under a gentle flow of nitrogen gas. This extract was subsequently passed through an 11 mm diameter × 300 mm long glass column packed with silica and alumina. The analytes were eluted using first 15 mL hexane (fraction 1) and then 40 mL of a hexane : dichloromethane mix (70 : 30 v/v) (fraction 2). The extract was carefully concentrated using first a water bath, and later a rotary evaporator at 35 °C until a volume of 4 mL was obtained. The final step was to reduce the volume to 1 mL under a gentle nitrogen gas flow for subsequent analysis by gas chromatography/mass spectrometry (GC/MS). The plastic samples were analyzed for PCBs, PAHs, organochlorine pesticides, compounds from fraction 2, and aliphatic hydrocarbons, from fraction 1 (Table 1).

A Shimadzu model 8300 Fourier Transform Infrared Spectrometer (FT-IR) with a diffuse reflectance accessory was used to provide evidence for the identification of the polymer material that was analyzed. Silicon carbide (SiC) was used as roughing material for the analysis of plastic samples by diffuse reflectance FT-IR. To differentiate between thermoplastic and thermoset plastics, a hot iron was used and pressed against the sample after the extraction analysis. Virgin thermoplastic pellets were used as standards to compare with the plastic debris samples.

## Instrumental analysis

The PCBs, PAHs and pesticide fractions were quantified using a gas chromatography-mass spectrometer system. The JEOL GC/Mate II™ is a double-focusing, reverse geometry mass spectrometer. The gas chromatograph was an Agilent 6890 equipped with a BPX-5 capillary column: 0.25 mm i.d., 0.5 μm film thickness, and 30 m long. The mass spectrometer was operated under selected ion monitoring mode (SIM) using three confirming ions for each analyte. The instrument was operated with a resolving power of 1000 with 10% valley, in electron ionization mode at 70 eV and 450 V setting for the photomultiplier detector. The GC interface and ion-chamber temperatures were 310 and 280 °C, respectively. The GC was operated in splitless mode with a solvent delay of 1.5 min. The injector temperature was 270 °C and transfer line was 310 °C. The column temperature was programmed from 70 °C (1 min) to 300 °C (25 min), at a rate of 5 °C min⁻¹. The carrier gas was helium (ultra high purity) and a carrier-gas purifier was also used. The carrier gas was set for constant flow mode with a flow rate of 1.2 mL min⁻¹.

## Quality assurance

A surrogate standard solution was added before extraction. The PAHs studies were done using spikes of deuterated PAHs

**Fig. 2** Some types of plastic debris collected from North Pacific Central Gyre (2005).

(1, 4-dichlorobenzene-$d$4, naphthalene-$d$8, phenanthrene-$d$10, acenaphthene-$d$10, perylene-$d$12, chrysene-$d$12). A mixture of tetrachloro-$m$-xylene (TCMX) and PCB-209 were used to spike the samples for PCBs and organochlorine pesticide samples. Recovery standards were added before instrumental analysis. The recovery standard DBOFB (4,4-dibromoocta-fluorobiphenyl) was used for PCBs and pesticides, while p-ter-phenyl-$d$14 was used for PAHs. Procedural blanks were analyzed with each batch of samples (6 samples per batch) and were taken through all phases of the analytical procedure. For every eight samples one duplicate sample was analyzed, using strict quality control measures. The samples analyzed were found to fall in the range from 70 to 98% recovery. The limit of detection (LOD) of the organic compounds was calculated according to the methods proposed by Vial and Jardy.[27] The LOD values ranged from 0.02 to 0.15 ng g$^{-1}$ for PCBs, 0.05 to 0.8 ng g$^{-1}$ for PAHs, 0.03 to 2.03 ng g$^{-1}$ for pesticides and 0.02 to 6.18 µg g$^{-1}$ for aliphatic hydrocarbons.

The quantitation was based on the integrated peak area for the appropriate $m/z$ value at the expected retention time with positive identification confirmed by the ion representing the base peak and the presence of two confirming ions for each. Any retention time shift in the chromatogram was corrected using the data for the internal standard. Positive confirmation of the analyte was based on the above criteria and retention time within 0.2 minutes of expected value.

## Results

### FT-IR analysis

Thirty-seven plastic debris samples were analyzed using GC/MS, and FT-IR spectroscopy. Fig. 2 presents photographs of selected examples of the plastic debris samples to show some of the different sizes, shapes, and colors. The sizes of plastic debris varied from whole plastic items to fragments, and pieces less than 5 mm in size. A representative spectrum obtained from the
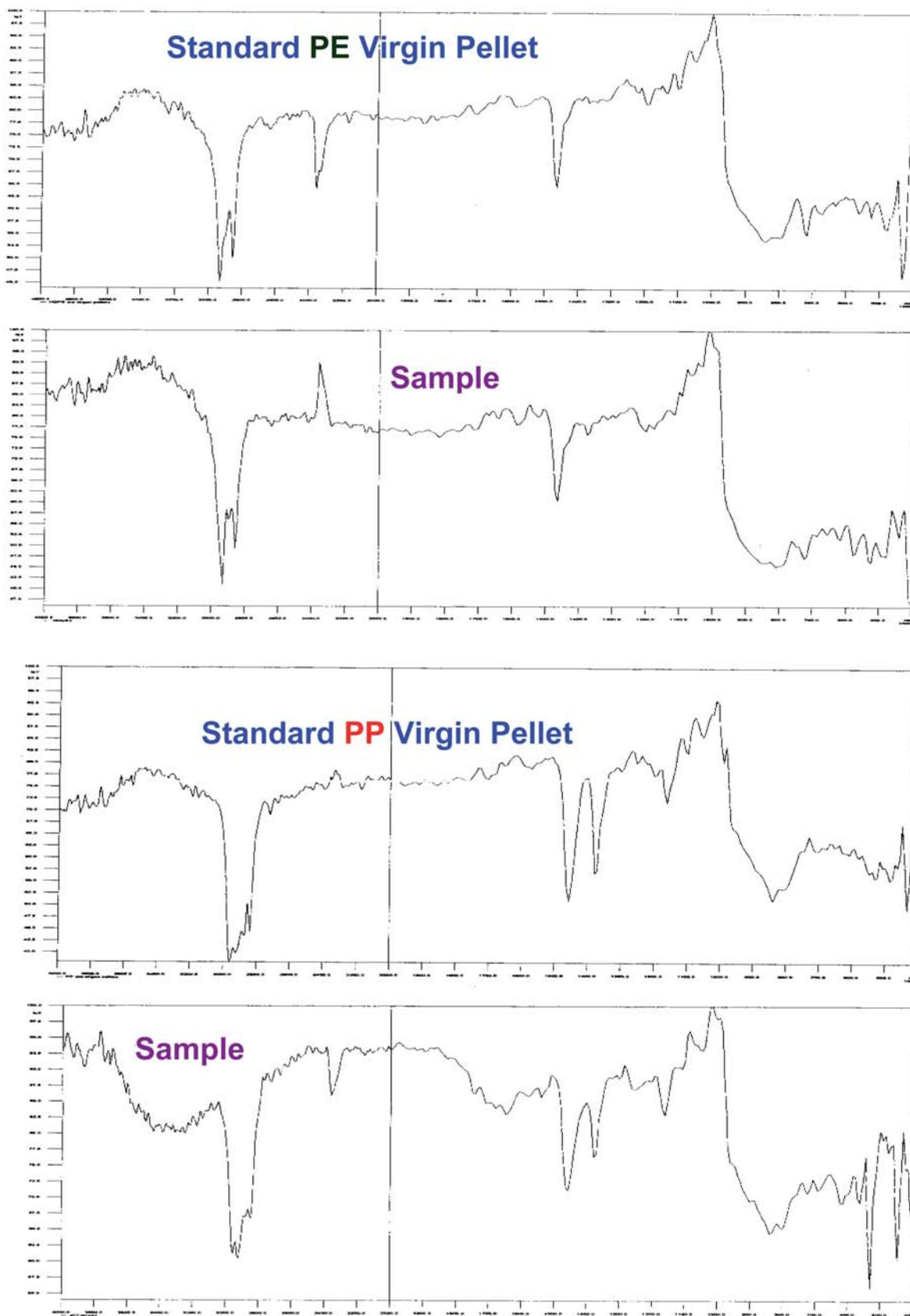
**Fig. 3** Identification of the type of plastic by comparison with standard polyethylene and polypropylene samples.

**Table 2** Identification, description, and sum of PCBs, PAHs, pesticides and aliphatic hydrocarbons on samples from North Pacific Gyre—2005[a]

| Sample ID | Plastic description | Plastic type | ΣPCBs/ng g$^{-1}$ | ΣPAHs/ng g$^{-1}$ | ΣPest/ng g$^{-1}$ | ΣAH/μg g$^{-1}$ |
|---|---|---|---|---|---|---|
| D3 | Whole-Buoy | PE | nd | 39 | nd | 6 |
| *M38 | Micro-plastic | PP | 26 | 18 | nd | 16 |
| M-36 | Micro-plastic | PE | 41 | 177 | nd | 9 |
| *M-36 | Micro-plastic | PE | nd | 399 | nd | 21 |
| D5 | Whole-Cap | PE | 3 | 132 | nd | 85 |
| D6 (Al foil) | Fragments | PE | 20 | 229 | 16 | 12 |
| D6(1 of 2) | Rope-line | PE | 114 | 14459 | 454 | 60 |
| D10 | Whole-Buoy | PE/PP | nd | 255 | nd | nd |
| *D10 | Whole-bottle | PE | nd | 219 | nd | 3609 |
| D11 | Whole-Buoy | PE | 45 | 451 | nd | 78 |
| D13 | Fragments | PP | nd | 15 | 1 | 1 |
| D14 | Rope-line | PE | nd | nd | nd | nd |
| D17 | Rope-line | PE | nd | 202 | 29 | nd |
| D4 | Whole-Cap | PP | nd | nd | nd | nd |
| D19/20 | Fragments | PE/PP | 63 | 304 | nd | 263 |
| D21 | Fragments | PE | 1193 | 45 | nd | 2 |
| D22 | Micro-plastic | PP | nd | nd | nd | 3 |
| D26 | Fragments | PE | nd | nd | nd | 78 |
| D27 | Rope-line | PP | nd | 18 | nd | 138 |
| D28 | Fragments | PE | 2856 | 451 | 8 | 967 |
| *M30 | Micro-plastic | PE/PP | 1540 | 1728 | nd | 14 |
| D93 | Whole-Cap | PE | nd | 101 | nd | nd |
| *D34 | Whole-Cap | PP | 5 | 10 | nd | 313 |
| D37 | Fragments | PE | nd | 54 | nd | 9 |
| D38 | Rope-line | PE | 8 | 513 | 214 | 121 |
| D-38 | Rope-line | PE | 8 | 76 | nd | 111 |
| D40 | Fragments | PE | nd | nd | nd | 6292 |
| D41 | Whole-Buoy | PE | nd | 128 | nd | nd |
| D44 | Fragments | PE | 33 | 100 | 354 | 60 |
| CH | Fragments | PE | nd | nd | 12 | 5 |
| M013 | Micro-plastic | PP | 16 | nd | 3 | 14 |
| 15M | Fragments | PP | nd | 68 | 3 | 106 |
| *M-025 | Micro-plastic | PE | 21 | 105 | nd | 107 |
| M25 | Micro-plastic | PE | nd | nd | 108 | nd |
| D62-1 | Fragments | PE | 6 | 26 | 1 | 14 |
| D-62-2 | Fragments | PE | 11 | nd | 175 | 15 |
| M-1 | Micro-plastic | PE | 2058 | 100 | 11 | 89 |

[a] nd = not detected at detection limit. Limit of detection for PCBs 0.02–0.15 ng g$^{-1}$, PAHs 0.05 to 0.8 ng g$^{-1}$, pesticides 0.03 to 2.03 ng g$^{-1}$, and AH 0.02 to 6.18 μg g$^{-1}$.

FT-IR analysis is shown in Fig. 3. The results of the analysis by FT-IR showed that the synthetic polymer polyethylene (PE) was present in 70% of the total samples (27 samples). Polypropylene (PP) was found as the polymer in 8 samples, and 2 samples were a mix of PE and PP (Table 2).
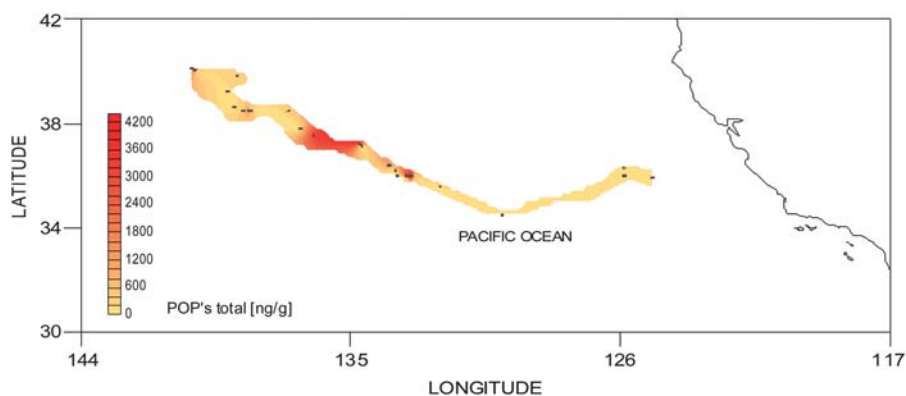
### Concentrations of PCBs

The total concentration of PCBs detected in plastic debris samples are summarized in Table 2. Approximately 51% of total samples were found to contain individual PCB *congeners* in the range of 1 to 2566 ng g$^{-1}$. Just four samples, D21, D28, *M30, M-1, showed a concentration above of 1000 ng g$^{-1}$, with a mean of 1912 ng g$^{-1}$. The rest of the samples had a mean of 28 ng g$^{-1}$. The major individual PCBs found were CB-11, 28, 44, 52, 66, and 101. PCB-11 was found in the highest amount of all the PCB congeners measured in the debris samples. The sum of all PCB congeners observed in each sample ranged from 3 to 2856 ng g$^{-1}$, where the highest total concentrations were found in locations D28 and M1. Fig. 4 presents a concentration map of the total concentration of the POPs.

### Concentrations of PAHs

The total PAHs detected on plastic debris in North Pacific Central Gyre is summarized in Table 2. Approximately 77% of the samples showed concentrations of these individual analytes in the range of 1 to 4395 ng g$^{-1}$. Samples D6(1/2) and *M30 had the highest concentrations of the sum of PAHs at 14 459 ng g$^{-1}$ and 1728 ng g$^{-1}$, respectively. Ten samples showed concentrations lower than 100 ng g$^{-1}$, with a mean of 37 ng g$^{-1}$. Sixteen samples showed concentrations above 100 ng g$^{-1}$, but lower than 1000 ng g$^{-1}$, with a mean of 242 ng g$^{-1}$. The major individual polycyclic aromatic hydrocarbons found were: naphthalene, phenanthrene, fluoranthene, and pyrene.

### Concentrations of organochlorine pesticides

Sum of pesticides found in the plastic debris samples are shown in Table 2. DDT and its metabolites, as well as BHC (α, β, δ and γ), aldrin, and methoxychlor were detected above the detection limit. The range of concentration of individual pesticides found in 15 of 37 total samples (40% of the total samples) was 1 to 176 ng g$^{-1}$. Nine samples had a sum of pesticide levels lower than

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*J. Environ. Monit.*, 2010, **12**, 2226–2236 | 2231

**Fig. 4** Total concentration map of POPs (ΣPCBs + ΣPAHs + ΣPest) and the total found on plastic debris found in the North Pacific Gyre.

100 ng g$^{-1}$ with a mean of 9 ng g$^{-1}$. In the rest of the samples, five samples had a mean of 261 ng g$^{-1}$ as the sum of total pesticides, with a mean of 45 ng g$^{-1}$. The sum of DDTs, is the sum of $o,p'$-DDD, $p,p'$-DDD, $o,p'$-DDE, $p,p'$-DDE, $o,p'$-DDT, and $p,p'$-DDT. This sum ranged from 0.1 to 336 ng g$^{-1}$. The $p,p'$-DDE and $o,p'$-DDE were most often found in samples with a range of 0.1 to 126 ng g$^{-1}$. A map of the sum of pesticide, PCBs, and PAHs concentrations is shown in Fig. 4.

#### Concentrations of aliphatic hydrocarbons

The analysis of aliphatic hydrocarbons showed a range of concentrations from 1 to 6227 µg g$^{-1}$. The total concentrations of these compounds are summarized in Table 2. The chain lengths of the most abundant alkanes were found to be between C12 and C24 for the plastic debris found at different sites in the NPG.

## Discussion

Plastic debris has been found capable of concentrating persistent organic pollutants from marine areas contaminated by these compounds.[4] The main types of synthetic polymers found in the NPG-2005 expedition were polyethylene (PE) and polypropylenes (PP), which are the most commonly used thermoplastic resins with a density less than that of seawater. There are many forms and sizes of plastic items that enter the ocean. PP and PE are polyolefins which are used mostly in packaging, and possess a special combination of properties including chemical resistance to degradation, flexibility, lightness, strength, moisture and air resistance, and ease of processing into final products. These are simple and inexpensive consumer plastics which contribute to their being found on the ocean in high concentrations. These plastics are also used in the fishing industry for nets, ropes, lines, and buoys. Both polymers are slightly buoyant, with the specific gravity of PE ranging from 0.92 to 0.97, and PP having a value of 0.91 g mL$^{-1}$. The specific gravity of seawater is approximately 1.025g mL$^{-1}$. Notably, there is a wide range of types of plastic used in plastic products, and not all float. Thompson *et al.*[28] identified microscopic plastic found in marine sediments. The environmental consequences of this contamination are not yet fully known, but it is clear that it is likely to pose a danger to marine wildlife. Most of the intact plastic objects found on our expedition were buoys or large fragments of ropes and tiny lines used by fishermen. The rest of the plastic samples were small fragments from the breakdown of diverse containers and other objects from unknown sources. The variation in sizes, shapes and colors in smaller sizes is a concern since these tiny fragments can be mistaken for food by marine organisms and seabirds. Certainly, the micro-plastic debris cannot be collected and removed from the ocean; and, it would be necessary to control plastics at the source. A method of mitigating the problem is needed.

Floating plastic debris is dispersed over the ocean and it travels long distances from its original source. The North Pacific Gyre (NPG) has received special attention because of its ability to aggregate everything that floats and persists in seawater. Fig. 5 shows the most concentrated plastic debris area. As a result of the dominant clockwise currents, the center of the NPG contains the highest concentration of plastic debris relative to the edges. Modeling studies showed that plastic debris can be retained in the NPG for more than 12 years.[29]

The air–water interface has a very important role in the transfer of contaminants from the air to the ocean. These pollutants include petroleum hydrocarbons, pesticides, chlorinated compounds, and plastic particles. The categories of persistent organic pollutants include some carcinogens and mutagens. Typically, they are lipophilic and have low chemical and biological degradation rates.[17] When POPs are in surface water, they tend to be adsorbed onto particulate materials and plastic debris is no exception.[4] Among these POPs, PCBs are the most persistent compounds. PCBs were banned in 1976 in the US, in 1970 in Canada, and in 1972 in Japan; however, these mixtures can be used in completely closed systems. The most common PCBs congeners found in our samples were classified by the USEPA as priority pollutants in the environment because they are found in high concentrations in sediments. It was observed that the dominant PCBs found in the plastic debris were the lesser chlorinated congeners (below CB-101). This suggests that these compounds came from remote areas because they are volatile and can easily travel long distances *via* the atmosphere.[17] Primbs *et al.*[30] reported that PCBs were found in air samples, and they attributed these to volatized stored surface deposits of PCBs from soil and vegetation. PCBs with low chlorinated congeners are also described as endocrine disruptors. It is well known that marine sediments are the last reservoir for
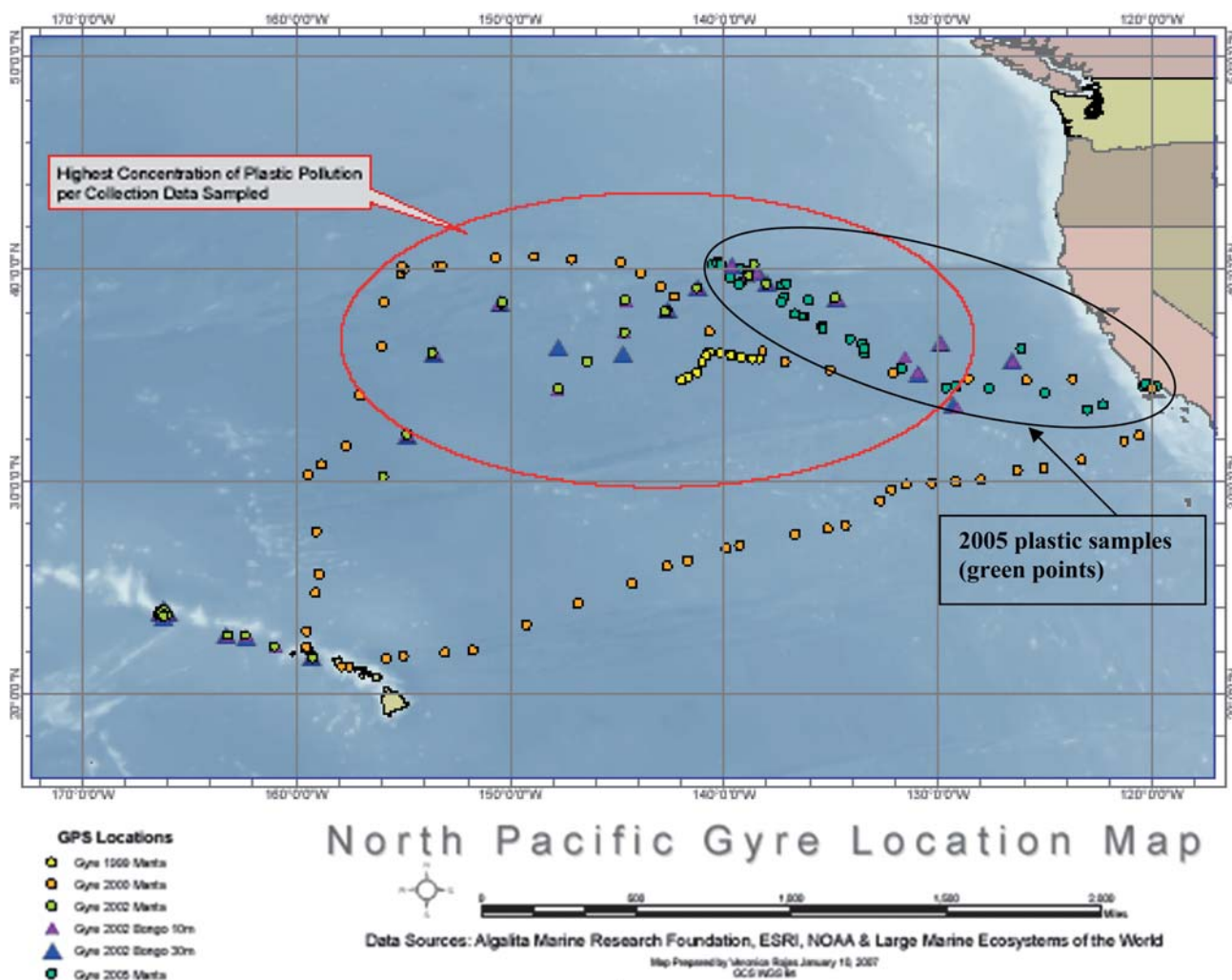
**Fig. 5** Map of plastic debris sampling sites in North Pacific Central Gyre (reproduced with the permission of the Algalita Marine Research Foundation, AMRF).

anthropogenic organic compounds because of their hydrophobic nature. The POPs in the water column tend to be adsorbed on particulate matter and finally sink becoming part of marine sediments.[31] However, in our study, plastic debris floating in oceanic surface water can persist for long periods of time and adsorb these hydrophobic compounds and behave like floating versions of the particles in sediments. PCBs and PAHs have been detected in air masses from Asia and North American regions. Particulate-phase PAHs were found emitted from Asia and transported by the atmosphere to North America.[30] The increase in atmospheric PCBs from North America may be associated with wildfires.[30] If one compares the concentrations of POPs adsorbed on plastic debris with contaminated sediments found in very contaminated areas (such as in Korea[32] where the sum of PCBs ($\Sigma$PCBs) range from 2.85–26.5 ng g$^{-1}$ which was interpreted to come from shipyard and industrial complexes), then it is clear that plastic debris is another repository of PCBs in addition to sediments. Samples of sediments taken in Alaska[33] had a range for the $\Sigma$PCBs of 0.2 to 30 ng g$^{-1}$ where the source was atmospheric. Strikingly, the values for subsurface seawater in China[34] ranged from 91.1 to1355.3 ng L$^{-1}$, with a mean of

313.6 ng L$^{-1}$, where the pollutants appeared to originate primarily from the dumping of toxic materials from industries that discharge wastewater into seawater, including factories such as fabric, paper, electronics, plastics, *etc*. Along the coast of California, USA,[31] in tidal salt marshes the range was found to be 80 to 9940 ng g$^{-1}$ of sediment where the source is also likely to be due to industrial activities.

The implication of our study is that plastic debris behaves very much like sediments, but these are floating solid phase accumulators of pollutants. In addition, these floating particles are located near the sea surface where they can accumulate PAHs and other airborne pollutants that settle into the ocean and/or are washed out of the air in rain. The amounts of pollutants on the floating plastic are also of concern since the particles are in reach of marine life forms that ingest and thereby take in these pollutant-laden particles. This situation puts at risk the health of all marine species and consequently the humans who consume seafood. The ecotoxicological potential of these pollutants on plastic debris which can be transferred to fish, and the potential effects on humans, especially infants, is beginning to receive significant attention in the literature.[10,35]

PAHs are the most commonly detected contaminants on plastic debris. They differ from other POPs in that many are not man-made for large scale industrial or agricultural use. These PAHs compounds are produced by incomplete combustion of organic materials including fossil fuels[36–38] and forests. However, PAHs present in the marine environment have to be largely attributed to anthropogenic sources. The composition of the PAHs found in the plastic debris was characterized by the predominance of two, three, and four rings, with the predominant congeners having three-rings. Naphthalene and phenanthrene were detected in more than 80% of the samples, but not acenaphthene, anthracene, or fluorene which were detected in less than 25% of the samples. The PAHs found are those that are lower in molecular weight, and have higher volatility. They are associated with gas-phase PAHs. The composition of the PAHs can be used as chemical fingerprints to identify possible sources. Fluoranthene is known to be a product of combustion of organic matter in fossil fuels. Phenanthrene comes from petroleum combustion and has a diagenetic origin. The ratios of phenanthrene : anthracene and fluoranthene : pyrene have been used to differentiate PAHs by origin.[36,39] The average range of the ratio of fluoranthene : pyrene found in the plastic debris samples was 1.4. When this ratio is greater than one, the PAHs come from pyrogenic sources. In contrast, for crude oil and refined petroleum products the ratios are less than 1.0. The observed ratio of fluoranthene/pyrene suggests anthropogenic emission of products of combustion particles, atmospheric aerosols, and sediments contaminated by pyrolitic sources that are transported to the marine environment by the atmosphere. Our data suggest that the fluoranthene : pyrene ratio indicates combustion sources rather than fossil fuel sources. Along these lines, PAHs from petrogenic origin, formed by slow maturation of organic matter have a ratio of phenanthrene : anthracene higher than 10 : 1. Our samples had a phenanthrene : anthracene ratio below 10, which supports the suggestion that combustion originated pyrogenic PAHs are more prevalent than petroleum related PAHs in the adsorbed pollutants on the plastic debris.

It is a fact that the atmosphere is a major pathway for the transport and deposition of PAHs. The half-life of PAHs in the gas phase has been estimated to be on the order of hours, whereas PAHs adsorbed on tiny particulate-phase submicron aerosols may have half-lives on the order of a week. The principal mechanism of removal of particulate-phase materials from the atmosphere is precipitation.[30] PAHs in sediments in Korea far from one edge of the NPG provide a measure of the amounts found near land. Where the sum of PAHs, $\Sigma$PAHs, in those sediment samples ranged from 10 to 1870 ng g$^{-1}$ with a mean of 309 ng g$^{-1}$. In addition, the most commonly found individual PAHs compounds were of 3 and 4 rings.[32] In California, along the coast in tidal marshes, the $\Sigma$PAHs ranged from 80 to 9940 ng g$^{-1}$ of sediment, with possible petrogenic sources.[31]

Organochlorine pesticides are also persistent organic pollutants. DDD was the most abundant metabolite of DDT found in our samples. Samples D62-2 and D6 had the highest concentrations of *p,p*-DDE, *p,p*-DDT, and BHC. It is known that DDT in the environment can be transformed by anaerobic and aerobic paths into DDD and DDE, the most stable of the metabolites. These are redistributed through the environment *via* atmospheric transport, by ocean currents, and animal migration. However,

DDD has two possible sources; one from DDT transformation, and the other from direct application. DDD has insecticidal properties and was used directly for agricultural purposes.[31,40] In our results, DDE apparently came from aerobic degradation of DDT and DDD could be from either direct input or anaerobic reductive dechlorination. An environmental-fate model has been used to calculate concentrations of DDT and its metabolites in the environment.[41] They found that DDE is more abundant in atmospheric and soil samples than DDD, but DDD was present at higher concentrations than DDE in water. When the ratio of DDT/(DDE + DDD) is less than one, this indicates aged DDT and when this ratio is greater than one, this indicates a fresh input of DDT. In our studies the DDT/(DDE + DDD) ratio was 0.5 to 1. This ratio suggests that DDE and DDD found in the plastic debris came from DDT transformation.[42]

The material benzene hexachloride (BHC) was also found in the marine plastic debris. DDT usage officially has ceased in many countries. Another organochlorine pesticide, BHC, is included in the 12 substances on the list of POPs.[43] However, on plastic debris the residues of BHC were found to be in lower concentrations than DDTs. The β-BHC isomer, the most persistent, was present in greater concentrations than α-, δ-, and γ-BHC isomers in our plastic debris samples. The comparison with other results from places close to the sampling area showed that the source of this pesticide likely was agricultural applications. In Korea,[32] concentrations of 0.5 to 8.3 ng g$^{-1}$ of DDTs and BHCs in sediments were reported; in Alaska[33] the sum of DDTs and BHCs was 0.5 to 0.8 ng g$^{-1}$ in sediments. In China[34] the $\Sigma$DDTs in seawater ranged from 27 to 956 ng g$^{-1}$, concentrations in tidal salt marshes along the coast of California were from 2 to 68 ng g$^{-1}$.[31]

Aliphatic hydrocarbons, C12 to C24 were the most abundant of the alkanes found on plastic debris samples. It has been suggested that alkanes with molecular composition lower than C22 can be attributed to emissions of unburned diesel fuel in gas phase samples.[26,44] However, one cannot discount the possibility that some of these alkanes could have come from the plastic samples themselves that were synthesized from petroleum derivatives.

## Conclusion

This study has provided data on the concentrations of selected persistent organic pollutants found on plastic debris from the North Pacific Gyre. High concentrations of PCBs, PAHs and organochlorine pesticides were found on some samples. The PCBs and PAHs found on the plastic debris are also the ones most commonly found in marine bottom sediments. Our study provides evidence showing that marine plastic debris behaves like sediments. These new "inverse sediments" were found floating on the surface and some contained high levels of persistent organic pollutants. Since these solid phase plastic materials float, they are easily mistaken for food by marine creatures. These results demonstrate there exists a clear risk for all marine species and consequently for humans as these polluted particles are ingested and transport hazardous materials into creatures in the food web. The current evidence demonstrates that marine plastic debris adsorbs pollutants, persists, and is abundant in the North Pacific Gyre. By extension, we recognize this to be a general

phenomenon. Some 40% of the world's oceans are considered subtropical gyres and each gyre tends to accumulate plastic debris,[10] making this a global problem. This is the first study to show that floating plastic debris from the NPG is an important pollutant extraction agent. The plastic serves to adsorb and accumulate persistent pollutants from the seawater. In this way, the floating plastic debris acts as like the solid particles that sink into marine sediments with the exception that these particles float and stay within reach of many marine creatures.

## Acknowledgements

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