

## INTERNATIONAL PELLET WATCH: APPLICATION TO AUSTRALIA

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### Introduction

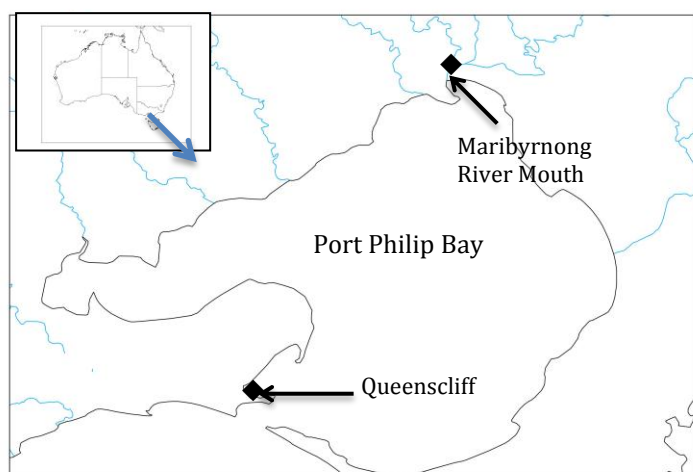
The Stockholm Convention obliges signatories to monitor persistent organic pollutants (POPs) of anthropogenic origin, although not all countries expend the time and resources to monitor these contaminants to the same extent. In this context, there is relatively little POPs monitoring in Australia relative to other jurisdictions. Grab (or spot) samples are commonly used to characterize chemical residues in surface waters. The advantage is that the matrix itself is analyzed and concentrations can be easily related to toxicity values for assessing exceedances of regulatory threshold values (TVs). One disadvantage is the cost of analysis. While the measurement of nutrients and salts in surface and groundwater is now routine and offered cheaply by many commercial laboratories in Australia, this is not so for many other contaminants of concern, such as many persistent chemicals. There are a number of modified or new approaches for sampling strategies, which would facilitate cost-effective monitoring of POPs concentrations in Australian waters, one of which is integrative sampling with passive samplers (or passive sampling).

A 'passive sampler' can be defined as a device that is able to acquire a sample from discrete location without the active media transport induced by pumping or purge techniques<sup>1</sup>. Passive sampling devices allow measurement of an average, pseudo-bioavailable concentration over a long period of time, typically in the order of days to several weeks. Most passive samplers are constructed in the laboratory and transported to the field, but in recent years the use of anthropogenic materials found in aquatic ecosystems as sampling systems ('serendipitous' passive samplers), such as beached plastic resin pellets, has been investigated, and found to be a cost-effective way to sample waters for a range of persistent organic chemicals.

Plastic resin pellets are small plastic granules used as an industrial raw material, which are transported to manufacturing sites where "user plastics" are made by re-melting and molding the pellets. Resin pellets were first observed in marine waters in the 1970s. They are unintentionally released into the environment during transport, and can be carried by surface run-off into rivers and oceans, or directly enter the ocean through accidental spills that may occur during shipping. Plastic resin pellets are now distributed widely in the oceans and found on beaches worldwide<sup>2</sup>.

International Pellet Watch was established in 2005, and uses beached plastic resin pellets as a tool to monitor POPs in coastal waters worldwide. Modelled on the long-standing International Mussel Watch program for monitoring POPs, Pellet Watch has a network of citizens and scientists that collect beached resin pellets from their local beaches and send them to the Laboratory of Organic Geochemistry (LOG) at Tokyo University of Agriculture and Technology (TUAT). Multiple 10-piece pools of pellets from each site are then extracted, and global POPs pollution mapped<sup>3</sup>. One of the advantages of Pellet Watch for participants over other programs is the low cost for sampling and shipping, particularly the ease with which samples can be collected by people with no special training, compared to the existing monitoring protocols and monitoring media (e.g., water, sediment, biological samples such as mussels). In this context, this study was initiated to assess the potential for use of beached plastic resin pellets to cost-effectively monitor POPs in Port Philip Bay in Victoria. This presentation will present data for total and congener specific concentrations of PCBs, DDT and other organochlorine chemicals in samples collected in 2010-2011, and compare Victorian data with that obtained elsewhere in Australia and Japan.

## Materials and methods



**Figure 1** Port Philip Bay, Victoria and Sampling Sites

Beached plastic resin pellets were collected from eight locations in Port Philip Bay, Victoria, in 2010 and 2011, although at the time of writing (10/05/12) samples from only two sites had been analyzed – pellets collected from a beach at the mouth of the Maribyrnong River in Melbourne, and from beaches at Queenscliff (Fig. 1). Pellets were collected according to Pellet Watch protocols, with several hundreds of resin pellets collected along the high tide line using solvent-rinsed stainless steel tweezers, and stored in aluminum foil bags. After being air-dried in the DPI Queenscliff laboratory, pellets were transported to TUAT for chemical analysis.

Pellets are classified according to their polymer types, with the two main types being polyethylene (PE) and polypropylene (PP) based pellets. After being sorted using near-infrared spectroscopy (Plascan-WTM OPT Research Inc., Tokyo, Japan) into PE, PP, and other polymers, yellowing PE pellets (yellowness of 40 or more) were selected by naked eye by comparison with reference pellets whose yellowness had been determined by a Handy Colorimeter (NR-3000, Nippon Denshoku Ind., Ltd., Japan).

Median values for contaminants were obtained by analysing at least 5 sub-sets of pellets (normally five pellets each) from each site. Each group of pellets was extracted in hexane twice, with the combined solvent concentrated by rotary evaporator, re-dissolved into ~0.5 mL of hexane and the sample applied to a fully activated silica gel column (0.47 cm i.d. x 18 cm; SilA200; Sigma). Three fractions were eluted from the column. The first fraction, containing n-alkanes and hopanes, was eluted with 5 mL hexane. The second fraction, containing PCBs and p,p'-DDE, was eluted with another 30 mL hexane. The third fraction, containing p,p'-DDT, p,p'-DDD, 4 HCH isomers ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ), and polycyclic aromatic hydrocarbons (PAHs) was eluted with 20 mL hexane/DCM (3:1, v/v). The second and third fractions were evaporated to ~0.5 mL and transferred into 1.5 mL vial for further analyses.

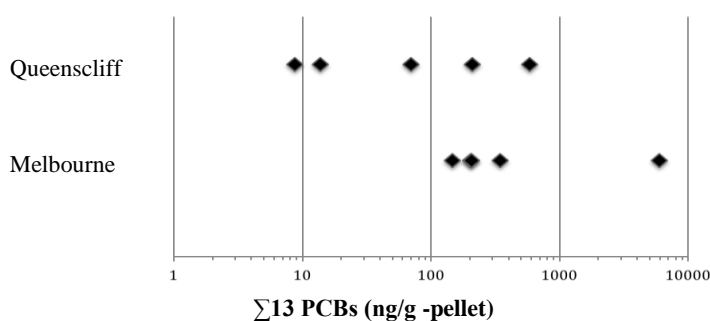
For analysis of PCBs and DDE, the solvent was evaporated to dryness under a nitrogen stream, and the residue re-dissolved in 50–3000  $\mu$ L isooctane containing 40 ppb  $^{13}\text{C}$ -CB#32,  $^{13}\text{C}$ -CB#141 and  $^{13}\text{C}$ -CB#208 as injection internal standards. Tetra- to nona-CB congeners (CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170 and 206) and DDE were analyzed on a Thermo-Fisher Polaris Q ion-trap mass spectrometer fitted with gas chromatograph (GC-MS). A J&W Scientific Durabond HP-5 MS 30-m fused silica capillary column (0.25 mm i.d., 0.25  $\mu$ m film the target compounds were 1–15%.

DDT and DDD and  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -HCH isomers were determined using a gas chromatograph-electron capture detector (GC-ECD; Hewlett Packard HP 1 electron capture detector fitted with an HP 7890 A J&W Scientific Durabond DB-5 30-m fused silica capillary column (0.25 mm i.d., 0.25  $\mu$ m film thickness)) with helium as the carrier gas at 140 kPa. The injection port was maintained at 250  $^{\circ}\text{C}$ , and the sample was injected in splitless mode, then purged 2 min after injection. The column temperature was held at 90  $^{\circ}\text{C}$  for 1 min, rose at 30  $^{\circ}\text{C}/\text{min}$  to 160  $^{\circ}\text{C}$ , at 1  $^{\circ}\text{C}/\text{min}$  to 180  $^{\circ}\text{C}$ , and at 3  $^{\circ}\text{C}/\text{min}$  to 280  $^{\circ}\text{C}$ , and was then held for 5 min. They were quantified by comparing the integrated height of the peaks of standard solutions for calibration (DDT, DDD and 4 HCH isomers; 20 ppb each).

Recovery was tested by spiking with 100  $\mu\text{L}$  of a PCB standard mixture (Kanechlor 200 + 300 + 400 + 500 (1:1:1:1) containing 0.73–36 ppb each of target CBs, 50  $\mu\text{L}$  of DDTs mixture containing DDT, DDD, DDE (20 ppb each) and 50  $\mu\text{L}$  of HCHs isomers mixture containing  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  isomers (20 ppb each) to the aliquots of the pellet extracts. The recoveries of the target compounds were more than 80%. A procedural blank was run in every set analyzed (5 pools). Analytical values less than three times of the corresponding blank are expressed as “below the limit of quantification (LOQ)”. LOQ for  $\Sigma 13$  PCBs, DDT, DDE, DDD and HCHs (sum of 4 isomers) were normally 0.3, 0.4, 0.1, 0.2, and 0.9 ng/g, respectively.

For both Victorian sites, all sub-groups of pellets were analyzed for total PCBs (total of 13 congeners), DDTs (p,p-DDT, p,p-DDD, and p,p-DDE), HCHs ( $\alpha$ HCH,  $\beta$ HCH,  $\gamma$ HCH and  $\delta$ HCH); some chlorinated pesticides were also analyzed for one site.

## Results and discussion

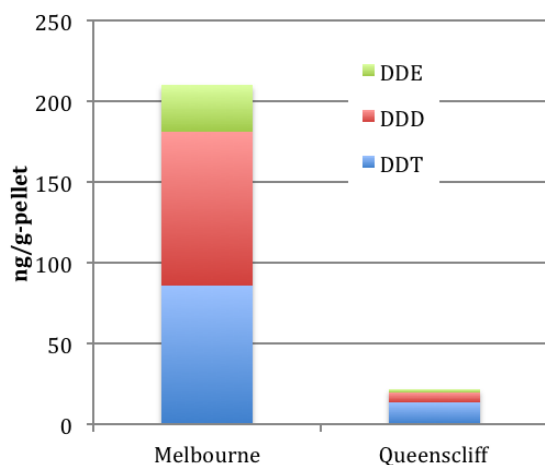


**Figure 2** Total PCB concentrations in beached plastic resin pellets from Port Philip Bay, Victoria

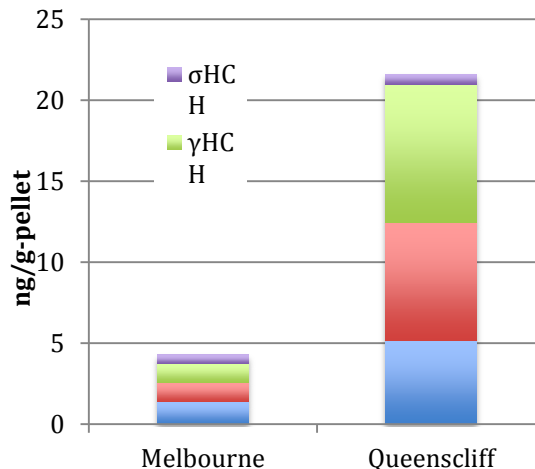
Endo et al. (2005)<sup>4</sup> suggest that analysis of 5 sub-samples of pellets is required to estimate a representative median chemical concentration for each site. Accordingly, this process was undertaken for the Queenscliff and Maribyrnong River sites. Within sample variability for total PCBs was 2 orders of magnitude at each site (Fig. 2), which is consistent with data presented by Ogata et al. (2009)<sup>5</sup>. Ogata et al. (2009)<sup>5</sup> suggest variability is a consequence of individual pellets having had different residence time in seawater, i.e. because it takes many weeks for the sorption of hydrophobic contaminants from seawater to pellets to reach equilibrium, pellets with a shorter residence time in coastal waters may have lower concentrations of contaminants than other pellets which have been in the sea for a longer time. Also, pellets pre-exposed to POPs may reach the ocean with high contaminant concentrations, and these pellets may retain their higher concentrations. PCB-138 and 153 were detected highest from both sites.

DDTs were also detected in pellets at both sites (Fig. 3), with median total DDT concentrations of 210 and 20 ng/g occurring in pellets collected from the Maribyrnong River and Queenscliff beaches, respectively. The proportion of p,p'-DDT/p,p'-DDE (DDT/DDE) has long been used as a rough indicator of the age of DDT residues in the environment, with higher ratios suggesting relatively recent DDT application. Interestingly, the DDT/DDE ratios were high, e.g. Marybrynong River 2.9, Queenscliff 5.7. However, DDT has not been registered for use in Australia for two decades, and there is no evidence of current use in Victoria, so a possible explanation for the current input of DDT is that DDT stored in sediments and/or agricultural soils may have been washed-out as run-off. There are no guidelines on 'high' and 'low' DDT/DDE ratios with respect to plastic resin pellet samples, and although DDT, DDD, and DDE are all hydrophobic (log Kow = 6.36, 5.70, and 5.50, respectively<sup>6</sup>) and so are expected to be absorbed by plastic resin pellets, further work is required to calibrate the uptake of these compounds by plastic resin pellets before observed DDT/DDE ratios can be used with any confidence to predict 'old' or 'current' use of DDT in a region.

HCHs were also detected in pellets at both sites (Fig. 4), with total HCH concentrations of 4.3 and 22 ng/g pellet at the Maribyrnong River and Queenscliff beaches, respectively.



**Figure 3** DDT concentrations in beached plastic resin pellets from Port Philip Bay, Victoria (median value)



**Figure 4** HCH concentrations in beached plastic resin pellets from Port Philip Bay, Victoria (median value)

Information on the concentration of PCBs, DDTs and HCHs in pellets can be obtained from the International Pellet Watch website Global Pollution Map<sup>3</sup>. Of particular interest to this project is the reporting of PCB, DDT and HCH concentrations in Sydney (297, 118 and 0.1 ng/g pellet, respectively) and Perth (16, 7 and 0.1 ng/g pellet, respectively), which suggests that Port Philip bay has an intermediate level of PCB contamination compared to those two cities, comparable DDT contamination but much higher HCH contamination. Moreover, median total PCBs in pellets obtained from the Maribyrnong River were as high as reported in samples collected from the west coast of the USA and some beaches in Japan<sup>5</sup>; pellets obtained from Queenscliff beaches had lower total PCB concentrations, similar to Hong Kong and South Africa<sup>5</sup>.

The aim of this project was to assess the potential for use of beached plastic resin pellets to cost-effectively monitor POPs in Port Philip Bay in Victoria. In this context, in principle, pellets may be used as a cost-effective monitoring tool, although the lack of robust uptake factors for any chemicals restricts the applicability of sampling to presence/absence investigations and qualitative comparisons.

#### Acknowledgements

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