ASSESSING RELIABILITY OF SPMDS FOR MONITORING PCDDS, PCDFS AND DIOXIN-LIKE PCBS VIA REPLICATE ANALYSIS

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Introduction

Traditional methods for analysis of aqueous samples in order to determine levels of organic contaminants typically involved one litre or smaller grab samples. In the case of Persistent Organic Pollutants (POPs) such as PCDDFs and PCBs, the issue was complicated by the need for quantitation at sub parts per quadrillion (ppq) levels and this sampling protocol generally proved inadequate. Moreover grab samples are discrete and fail to account for temporal fluctuations. Whilst the use of high volume sampling improves detection limits they suffer from issues of practicality and expense and the need for further sample pre-treatment to separate out particulate.
Consequently, quantification of these hydrophobic compounds in order to gauge the health of an aquatic environment often entailed analysis of sediments or biota. Whilst sediment samples provide an indication of anthropogenic pollutants in a given area they do not accurately measure the levels of dissolved organic contaminants within the water column. The reliability of biomonitoring organisms such as bivalves to assess the extent of pollution is limited by their ability to metabolise organic contaminants. The full extent of the environmental impact on an aquatic system resulting from contamination cannot be fully assessed when only a limited number of species have been investigated.
More recently alternative passive samplers have been adopted to help overcome these problems. The introduction of semipermeable membrane devices (SPMDs) enables pre-concentration of target analytes improving detection limits by 2-3 orders of magnitude and unlike biomonitors they are not subject to selective uptake as a result of metabolic pathways. Possibly the most important advantage of SPMDs is that they only sample the dissolved (most readily bioavailable) phase.[1]
The upper reaches of Sydney Harbour in particular the area around Homebush Bay was the site of extensive heavy industry including production of chlorinated hydrocarbons for several decades last century**.** This has resulted in significant contamination to this waterway leading to the cessation of commercial fishing within the harbour.[2] SPMD samplers were deployed on three separate occasions over a five year period for the determination of PCDD/Fs and dioxin-like PCBs. The first deployment in June 2006 involved five sets of spatially replicated sampling cages.[3] The deployment in May 2011 involved duplicate samples at one location inside the Bay. In August of 2011 another 6 sampling sites were selected across a much greater expanse of Sydney Harbour for the deployment of duplicate samples. Water temperature, weather conditions, water depth and complex hydrodynamics could possibly have significant impacts on the concentrations of POPs that can dissolve in water. Here we present the raw data from each of the deployments focusing only on sampling reproducibility comparing the quasi-duplicates of 2006 and duplicates in 2011. Results are reported per cage basis. Calculations of sampling rates and estimated water concentrations for the 2006 results have been reported previously. [3]

Methods and Materials

Standard SPMDs with a surface area of 460 cm2 were prepared using LDPE tubing (Brentwood Plastics, USA) containing 1 mL triolein (99%,Sigma Aldrich). For all three deployments cages were loaded with 3 SPMDs for collecting PCDD/Fs and PCBs. On each occasion field blanks were also prepared and analysed alongside samples according to standardised protocol. Following retrieval samples were treated in accordance with Huckins et al[4] prior to extraction. Samples were spiked with C13 labelled surrogates and extracted by hexane dialysis. Clean-up was effected with GPC Envirogel™ followed by Power-Prep™ (Fluid Management Systems,USA). All samples were analysed by HRGC/HRMS. The relative percent difference (%RPD) between cage pairs in tables 1and 2 is calculated as follows:

$$\%RPD = \frac{|X_1 - X_2|}{\overline{X}}$$

where X_1 and X_2 = cage 1 and 2 respectively

Results and discussion.

During the 2006 deployment the combined total of toxic PCDDF and dioxin-like PCB congeners per cage ranged from 15000 to 31000 pg. Laboratory recoveries ranged from 48% to 127% with a mean recovery of 73%. In 2011, the sampling locations spread as far as 20 km from the Homebush Bay, the sum ranged from 9700 to 54000 pg. Laboratory recoveries ranged from 26% to 103% with a mean recovery of 57%. Field blanks were prepared and analysed alongside samples with levels of PCDD/Fs and PCBs all below limit of detection. For samples with results below the LOD the mean was calculated based on LOD values.

Replicate comparison

The relative percent difference (%RPD) between cages separated from 130-410m showed considerable variation amongst sites and compounds ranging from 2% -59% (Table 1). The results from 2006 showed no one set of replicates with consistently higher or lower RPDs than other sites[3] despite the varying range of separation between replicates. Sample 3w showed the least variation and it was suggested this could reflect that the location within the Bay experienced the lowest current speed[3]. It may also reflect the depth of the bay in relation to outside. Sections of Homebush Bay are only 1-2m deep at low tide and the sample cages proximity to the sediment would impact on the way the SPMD functions. Rantalainen[5] reported impact on uptake rates when SPMDs were buried in the sediment as opposed to being suspended above the sediment. The relative percent difference (%RPD) between duplicate samples cages in 2011 (Table 2) range from 2% -23%. No one set of duplicate results yielded lower RPDs.

Table 1
Relative percent difference among spatially replicated cages for 2006.

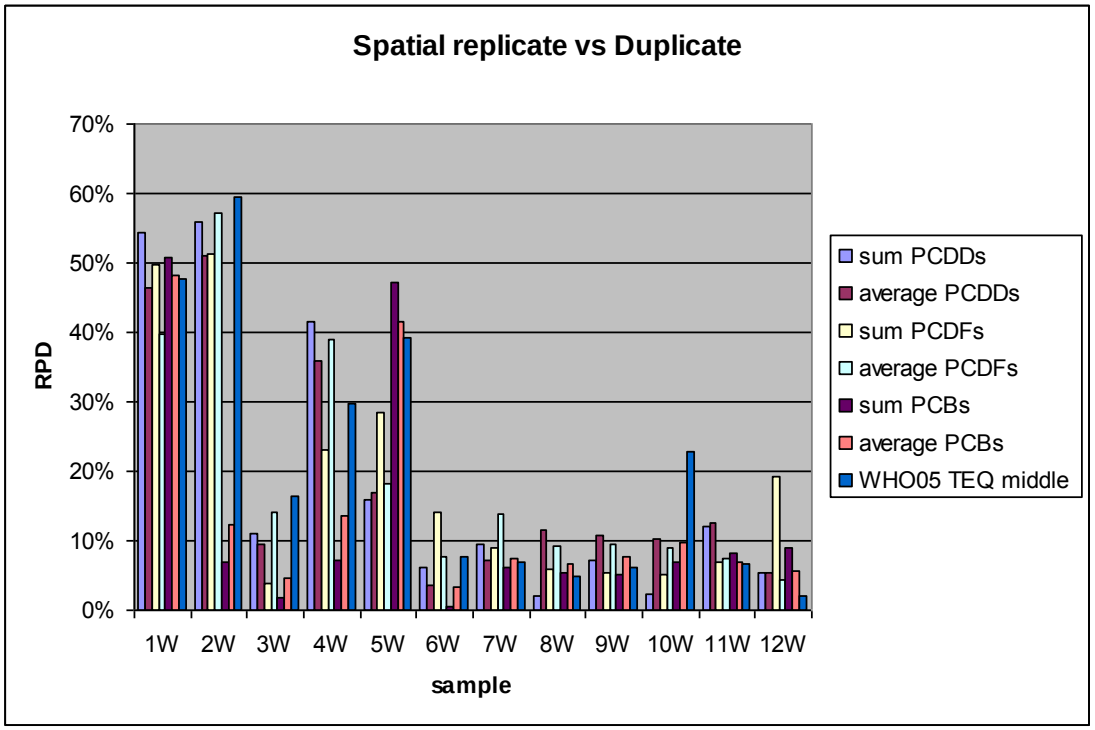
	1W	2W	3W	4W	5W
Separation between cages (m)	130	210	290	140	410
Contaminant group	%RPD	%RPD	%RPD	%RPD	%RPD
Σ PCDDs	54%	56%	11%	41%	16%
average PCDDs	46%	51%	10%	36%	17%
Σ PCDFs	50%	51%	4%	23%	28%
average PCDFs	40%	57%	14%	39%	18%
Σ PCBs	51%	7%	2%	7%	47%
average PCBs	48%	12%	5%	14%	42%
WHO_{05} TEQ	48%	59%	16%	30%	39%

Table 2
Relative percent difference for duplicate cages in 2011.

	6W	7W	8W	9W	10W	11W	12W
Contaminant group	%RPD	%RPD	%RPD	%RPD	%RPD	%RPD	%RPD
Σ PCDDs	6%	9%	2%	7%	2%	12%	5%
average PCDDs	4%	7%	12%	11%	10%	13%	5%
Σ PCDFs	14%	9%	6%	5%	5%	7%	19%
average PCDFs	8%	14%	9%	10%	9%	7%	4%
Σ PCBs	0%	6%	6%	5%	7%	8%	9%
average PCBs	3%	8%	7%	8%	10%	7%	6%
WHO_{05} TEQ	8%	7%	5%	6%	23%	7%	2%

In both 2006 and 2011 RPDs were lower for PCBs than for either PCDDs or PCDFs. PCB levels are also more consistent across the sites and are less correlated as distance increases from Homebush Bay. This most likely reflects that PCBs have entered the harbour from numerous locations along the shoreline.
Sample 12w was the furthest sample from Homebush Bay and consequently yielded the lowest levels of PCDDFs and PCBs with 40% of all results recorded as LODs.

Figure 1
Variation in RPD between the 2006 spatially replicated samples and the 2011 duplicates.



Sample 6w from inside the Bay was the highest sample and yet there was no was significant difference in RPDs between these two sets of duplicates. This reinforces the claims of superior sampling reproducibility when compared the use of living organisms[5]. Roach et al[3] were working toward establishing a sampling protocol to enable future monitoring of contaminant levels in this aquatic system. They concluded that while a single cage per sampling location would provide adequate approximation of spatial change in water concentrations, replicate analysis would yield a more statistically robust set of data. The 2011 sampling round was designed to investigate this issue. By comparing the 2006 and 2011 data we are able to attribute <10% RPD to replicate variation ie SPMD preparation, laboratory and instrumental analysis and upto 40% RPD to the spatial differences (130-410m) where factors such as different hydrodynamic conditions, depth of estuary, level of boat traffic, proximity to the shore line and risk from biofouling have the potential to effect the level of uptake by the SPMD.
This reinforces the reliability of SPMDs as a sampling technique capable of accumulating a broad range of hydrophobic contaminants in aquatic environments but highlights the need for increased number of samples to accurately survey a complex tidal environment like Sydney Harbour.

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