CONTRASTING PATTERNS OF SPATIAL AUTOCORRELATION OF PCDD/FS, DIOXIN-LIKE PCBS AND PBDES IN SEDIMENTS IN SYDNEY HARBOUR, AUSTRALIA.

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Abstract
Sediments were collected from 25 sites, from five zones and across a 30 km transect of the Sydney Harbour / Parramatta River estuary. We analysed the concentrations of 34 PBDEs, 7 PCDDs, 10 PCDFs and 12 dioxin-like PCBs using HRGC/HRMS. For congeners above the LOD we used generalized additive modelling (GAM) to model their TOC normalized concentrations with respect to position in the estuary to examine how patterns of the spatial distribution and autocorrelation (Moran's I) varied among these contaminant groups. ∑PBDE, ∑PCDDs, ∑PCDFs, and PCBs concentrations spanned 1, 2, 1 and less than 1 orders of magnitude respectively, across the five sampling areas. The GAMs showed strongly contrasting spatial autocorrelation and distributions in the TOC normalised sediment concentrations both among and within PCDDs, PCDFs, dioxin-like PCBs and PBDEs. PCDD concentrations were associated with proximity to a source in Homebush Bay, whereas patterns of furan congeners were indicative either Homebush Bay sources or other sources. Dioxin-like PCBs concentrations were most highly variable indicative of more small scale sources. PBDEs also showed congener dependent spatial patterns but the main sources appeared to occur in the upper Parramatta River.

Introduction
The Sydney Harbour / Parramatta River estuary has experienced significant environmental pollution. Studies on contaminant levels in biota have found PCDDs, PCDFs, dioxin-like PCBs and PBDEs to accumulate in invertebrates, fish and birds[1,2]. Dioxin levels in fish have caused the closure of commercial fishing and restrictions to fishing and consumption of fish by recreational fishers[3,4] and increases in human blood serum levels[5]. PCDDs, PCDFs, dioxin-like PCBs and PBDEs are bioaccumulated largely via trophic uptake but species have varying behaviours such as movement and variation in diet which makes patterns of contamination in biota difficult to interpret by themselves. Environmental data (e.g. sediments and water column) provide a point of reference against which to interpret levels in biota and provide a means to identify contaminant source, behaviour and predict exposure risk. There is currently limited environmental data to adequately explain the levels of PCDDs, PCDFs, dioxin-like PCBs and PBDEs observed in biota throughout the Sydney Harbour / Parramatta River estuary.

This study investigated the spatial patterns of contamination of PCDDs, PCDFs, dioxin-like PCBs and PBDEs along a 30 km transect of Sydney Harbour / Parramatta River estuary. We measured the concentrations of these compounds and modelled their concentrations with respect to position in the estuary to examine how patterns of contamination varied among contaminants.

Materials and Methods
Sample sites were ascribed haphazardly within one of five zones in Parramatta River / Sydney Harbour system. Each zone was in the same water body and representative of areas with similar levels of urban/industrial development. This resulted in sites being located within zones but also positioned along a transect which spanned approximately 30 kms of the Parramatta River / Sydney Harbour estuary (Figure 1). At each site approximately 200-250 ml of sample from the top 3 cm of the sediment profile was taken using a stainless steel van Veen grab. This was done by compositing 50 ml of sediment from 4-5 grabs taken at random within an area of approximately 50 m^2. The samples were homogenised and then split for analysis of the organic compounds (e.g. PCDD/PCDFs, dl-PCBs and PBDEs), grain size and total organic carbon. Total organic carbon was analysed using an infrared combustion procedure following the removal of inorganic carbonates using acid-catalysed digestion (10% HCl, 1% $FeCl_2$ at 70 °C)[6]. The proportion of mud (=silt+clay <63 mm), sand (>63 mm, <2mm) and gravel (>2 mm) was determined by wet sieving.

Sample preparation and analysis
We analysed sediments for 34 PBDEs, 7 PCDDs, 10 PCDFs and 12 dioxin-like PCBs (Table 1) using HRGC/HRMS and isotope dilution methods. The sample preparation and analytical methodology for the

determination of PCDD/Fs, dioxin-like PCBs and PBDEs in sediment have previously been described in detail[7,8]. Briefly, approximately 20g of sediment was accurately weighed and a known amount of the respective PCDD/PCDF, dioxin-like PCB and PBDEs isotopically labelled $^{13}C_{12}$ surrogate spiking solution. Accelerated solvent extraction (ASE) was performed on samples using an ASE 100 (Dionex, Utah, USA) with toluene as the extracting solvent and a temperature and pressure of 150 °C and 1,500 psi, respectively. Clean up was effected by partitioning with sulphuric acid then distilled water with further purification performed using column chromatography on acid and base modified silica gels, basic alumina and carbon dispersed on celite for PCDD/Fs and PCBs and acid and base modified silica gels plus basic alumina for PBDEs. The analytes were quantified using HRGC/HRMS where analytes were separated using a HP 6890 gas chromatograph. The PCDD/Fs and non-ortho PCBs were separated on a ZB-5 (DB-5 equivalent) column (60m x 0.25mm I.D. x 0.25um film) followed by DB-Dioxin column (60m x 0.25mm I.D. x 0.15um film) to confirm specific congeners. Mono-ortho PCBs were separated on a DB-Dioxin column (60m x 0.25mm I.D. x 0.25um film) and PBDEs were separated on a DB-5 column (10m x 0.1mm I.D. x 0.1um film). Prior to injection on the GC internal standards were added to each extract, and an aliquot of the extract injected into the GC. Following separation by the GC the analytes were detected by a high-resolution (>10,000) mass spectrometery (HRGC/HRMS). All results were corrected for labelled surrogates and are reported on a dry weight basis. The detection limits and quantification levels in this method were usually dependent on the level of interferences rather than instrumental limitations. The laboratory is accredited to ISO 17025:2005 for these analytes and participates in international interlaboratory studies to benchmark its performance.

Data Analysis

Generalized additive modelling (GAM) was used to relate TOC normalized concentrations of PCDD/Fs, dioxin-like PCBs and PBDEs congeners to position along the Parramatta River / Sydney Harbour transect. Position was measured as linear distance (km) from first sampling site. GAMs are a flexible modelling approach, permitting both linear and complex additive response shapes, as well as a combination of the two within the same model and hence can fit complex spatial patterns to data[9]. It uses a link function to establish a relationship between the mean of the response variable and a "smoothed" function of the explanatory variables. Data were log (concentration+1) transformed and the model used a Gaussian error structure with an identity link function. Akaike's Information Criterion (AIC) was used as selection criterion to determine the model complexity (i.e. the penalty order/degree of smoothing). Moran's I[10] was used as a measure of global spatial autocorrelation and provided a measure of how well the adjacent observations of each congener were correlated. Values range from −1 (indicating perfect dispersion) to +1 (perfect correlation): where a zero values indicate a random spatial pattern. Only sediment values with a TOC greater than 1% were included in this analysis. Those sediments are generally indicative of sediments which are more dynamic than depositional and generally had more congeners with concentrations <LOD which made them inappropriate for modelling purposes. Where concentrations were <LOD maximum likelihood distribution regression of the left censored data was used to estimate the concentration. Congeners with more than 40% of observation < LOD were excluded from these analyses the estimation procedure was considered unreliable.

Results and Discussion

Of the 34 PBDEs, 7 PCDDs, 10 PCDFs and 12 dioxin-like PCBs which were analysed in the samples, 21 PBDEs were detected above the LOD in one or more samples and all PCDDs, PCDFs and dioxin-like PCBs were detected in one or more samples. The mean recovery rate across all congeners for PCDD/Fs, dioxin-like PCBs and PBDEs was 79%, 78% and 60% respectively. Across all sites ∑PBDE concentrations ranged from 460 - 87000 pg g-1 d.w., ∑PCDDs ranged from 480 - 258000 pg g-1 d.w., ∑PCDFs ranged from 8-4600 pg g-1 d.w., and ∑PCBs ranged from 300 - 15317 pg g-1 d.w.. Across the five sampling areas mean concentrations of ∑PBDE, ∑PCDDs, ∑PCDFs, and PCBs spanned 1, 2, 1 and less than 1 orders of magnitude respectively (Table 1) and concentrations decreased with distance down the Parramatta River. A decrease in concentration was observed for most congeners of PBDEs, PCDDs, PCDFs and dioxin-like PCBs, however, the rates of change among individual sites differed among congeners and contaminant types and was further elucidated using spatial modelling.

For all PCDD congeners generalized additive modelling (GAM) estimated that between 93.7 and 98.7 % of the variance among sites was explained by position on the transect along the Parramatta River/Sydney Harbour (Figure 1). The model plots indicate that their concentrations were strongly correlated with a sites proximity to Homebush Bay (Figure 2). Spatial autocorrelation (Moran's I) was significant ($p<0.00001$) for all congeners with values ranging between 0.43 and 0.54. GAMs of the PCDF congeners found between 77.6 and 98.9% of the variation among sites was explained by position along the estuary. The model plots

showed variation in PCDF concentration profiles along the transect with congeners such as TCDF and 1,2,3,7,8-PeCDF showing a multiple concentration peaks whereas 1,2,3,4,7,8-HxCDF and 1,2,3,4,7,8,9-HpCDF showing a single spatial peak associated with Homebush Bay (Figure 2). Spatial autocorrelation (Moran's I) was significant ($p<0.002 - 0.00001$) for all congeners the values ranged widely (0.22-0.54) with lower values found for congeners with multiple peaks were evident in the model plots indicating that these congeners have lower spatial autocorrelation among sites. GAMs of the PBDEs congeners found between 72.2 and 97.6% of the variation among sites could be explained by position along the estuary. The model plots of the PBDE congeners typically showed a simpler profile with higher concentrations in sediments from sites the upper Parramatta River / Sydney Harbour transect compared with those sites downstream. Interestingly the congeners with greater bromination, particularly BDE 209 and BDE 206, showed contamination over a wider spatial scale than the less brominated congeners (i.e. BDE153 to BDE17). Spatial autocorrelation (Moran's I) ranged from 0.09-0.56 ($p<0.002$ - 0.00001) with values typically lower for the less brominated congeners. GAM of the dioxin-like PCBs congeners found 46.76 and 78.9% of the variation among sites was explained by position along the estuary. The model plots (Figure 2) showed the greatest variation in PCB profiles with congeners ranging from single peaks associated with proximity to Homebush Bay (PCB 77), multiple peaks down along the Parramatta River / Sydney Harbour estuary (PCB 169) and marked decreases then increases in concentration (PCB 114). Spatial autocorrelation (Moran's I) ranged from (0.06-0.31; ns–$p<0.0007$) indicating that the dioxin-like PCBs typically display lower spatial autocorrelation than the other contaminant types.

These analyses showed contrasting spatial autocorrelation and distributions in the TOC normalised sediment concentrations both among and within PCDDs, PCDFs, dioxin-like PCBs and PBDEs. All PCDD congeners generally displayed a high spatial autocorrelation and had higher concentrations with proximity to Homebush Bay: the major source of PCDDs in Sydney Harbour[4]. Homebush Bay is also a source of PCDFs and PCBs[4]; however, these two contaminant groups displayed greater variation among congeners in concentration and spatial autocorrelation. The concentration of TCDF plateaued around 15 kms downstream then concentrations declined markedly along the estuary which suggests a mid river source adding to the sediment levels, whereas 1,2,3,4,7,8-HxCDF did not plateau indicating Homebush Bay is the major source (Figure 2). This indicates that for some furan congeners there are probably additional sources of contamination. The GAMs of the dioxin-like PCBs concentrations found that the position along the estuary generally explained the lowest % variation of all the contaminants. It is likely that this pattern reflects the wide use of PCBs (e.g. dielectric fluids, lubricants, sealants, flame retardants) which has led to multiple sources of PCBs in urban/industrial environments elsewhere[11] and has probably resulted in patchily distributed inputs from a range of sources in the Sydney catchment. More generally the presence of other sources of PCDFs and PCBs has implications for environmental managers as these contaminants contribute to the total TEQ. In Sydney Harbour commercial fishing has been banned and recreational catches limited because of dioxin levels in fish[4]. The contribution to the total TEQ from PCDFs and PCBs increases from 10% near Homebush Bay to 20% downstream (unpublished data). As Homebush Bay is cleaned up[4] the contribution to the TEQ from other sources may become even more important and therefore the identification and clean up of these sources may have the potential to further reduce the need to limit recreational catches. The source of PBDEs in Parramatta River / Sydney Harbour estuary is unlikely to be the related to the source of PCDDs, PCDFs and PCBs and this was reflected by the GAMs. BDE 209 was the dominant PBDE congener in the sediments making up 90% or more of the total PBDE load. BDE 209 had high concentrations along a longer proportion of the transect indicating multiple sources in the Parramatta River indicating that contamination continued further upstream but also occurred widely in this section of the Parramatta River/Sydney Harbour system. BDE 206, and to a lesser extent BDE 207 and BDE 208, displayed a similar spatial pattern which probably reflects their presence in commercial deca-PBDE mixtures along with BDE 209[12]. The less brominated congeners such as BDE 153, 49 and 17 which are either derived from octa-PBDE or penta-PBDE commercial mixtures or via microbial[12] or photolytic[13] debromination showed an initial steep decrease in concentration which plateaued at about 10 km along the transect and continued throughout the system. The modelling inferred sources occurred further upstream than was sampled.

Conclusions

PCDDs, PCDFs, dioxin-like PCBs and PBDEs displayed varying patterns of TOC normalised concentrations in sediments along the Parramatta River/Sydney Harbour system. PCDD concentrations were strongly associated with a known major source, Homebush Bay, whereas patterns of furan congeners were indicative either Homebush Bay sources or Homebush Bay and downstream sources. Dioxin-like PCBs concentrations were most highly variable indicative of more small scale sources. PBDEs also showed congener dependent spatial patterns but the main sources appeared to occur in the upper Parramatta River.

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Table 1 List of analytes. Underlined congeners are those which were not detected at concentrations above the LOD in any sample.
PCDD Congeners: TCDD, PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, HpCDD, OCDD
PCDF Congeners: TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF, OCDF
PCBs - Non-Ortho: PCB77, PCB81, PCB126, PCB169. Mono-Ortho: PCB 105, PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167, PCB 189
PBDEs: BDE17, BDE28+33, BDE30, BDE47, BDE49, BDE66, BDE71, BDE77, BDE85, BDE99, BDE100, BDE119, BDE126, BDE138+166, BDE139, BDE140, BDE153, BDE154, BDE156+169, BDE171, BDE180, BDE183, BDE184, BDE191, BDE196, BDE197, BDE201, BDE203, BDE204, BDE205, BDE206, BDE207, BDE208, BDE209

Table 2 Mean (± standard deviation) concentrations (pg g^{-1} dry weight) of ∑PBDEs, ∑PCDD, ∑PCDFs and ∑PCBs in sediments from areas 1-5 in Sydney Harbour.

	Area 1	Area 2	Area 3	Area 4	Area 5	Range
∑PCDDs	12834 ±11183	47260 ± 25348	91683 ±33082	192112 ± 39996	168829 ± 36381	481 - 258228
∑PCDFs	79 ± 83	681 ± 362	1221 ± 441	3135 ± 750	3010 ± 1000	7.9 - 4608
∑PCBs	3499 ± 2967	5634 ± 3089	8401 ± 3705	10659 ± 1369	12506 ± 2357	300 - 15317
∑PBDE	3508 ± 2828	18746 ± 9559	37254 ±16597	40578 ± 26176	45524 ± 5137	459 - 87191

Figure 1 Map of Sydney Harbour showing the sampling areas and individual sampling sites.

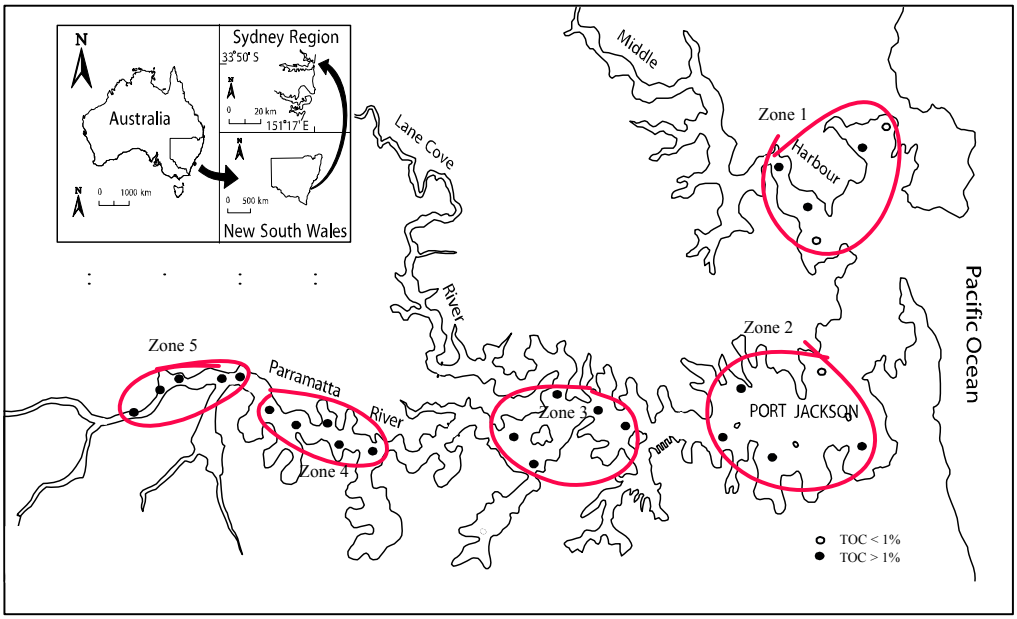

Figure 2. Plots of generalized additive model (GAM) predictions of TOC normalized sediment concentrations of selected PCDD/Fs, dioxin-like PCBs and PBDEs.