Science of the Total Environment 407 (2009) 3721–3730

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Bioactivity of POPs and their effects in mosquitofish in Sydney Olympic Park, Australia

Christopher A. Rawson [a], Louis A. Tremblay [b], Michael St. J. Warne [c], Guang-guo Ying [c], Rai Kookana [c], Edwina Laginestra [d,1], John C. Chapman [e], Richard P. Lim [a,*]

[a] Institute of Water and Environmental Resource Management (IWERM) and Department of Environmental Sciences, University of Technology, Sydney (UTS), PO Box 123 Broadway, NSW, 2001, Australia
[b] Landcare Research, PO Box 40, Lincoln 7616, New Zealand
[c] CSIRO, Centre for Environmental Contaminants Research, PMB 2, Glen Osmond SA, 5064, Australia
[d] Sydney Olympic Park Authority, Figtree Drive, Sydney Olympic Park, NSW, 2127, Australia
[e] Department of Environment and Climate Change, NSW, 59-61 Goulburn St. Sydney South, NSW, 1232, Australia

ARTICLE INFO

Article history:
Received 16 December 2008
Received in revised form 10 February 2009
Accepted 10 February 2009
Available online 20 March 2009

Keywords:
Remediated land
Dioxin
PAH
PCB
DDT
H4IIE
EROD

ABSTRACT

The site of the 2000 Olympic Games (Sydney Olympic Park (SOP), Sydney, Australia) was contaminated by persistent organic pollutants (POPs) prior to remediation in the 1990s. This study investigates the bioactivity of POPs in the sediment and water of wetlands across SOP by *in vitro* 2,3,7,8-TCDD equivalence (TCDDeq) measurement (H4IIE cell line bioassay). Further, it examines whether disturbance of these sediments is likely to mobilise ligands for this receptor into the water column. Exposure to aryl hydrocarbon receptor (AhR) ligands was measured *in vivo* using hepatic cytochrome P4501A (CYP1A) induction (EROD) in the mosquitofish (*Gambusia holbrooki*). Aqueous TCDDeq ranged from 0.013 to 0.057 pM in SOP wetlands which was significantly ($p<0.05$) less that in urban reference sites. These concentrations were not correlated to physical or chemical characteristics of the wetlands. In the sediments, TCDDeq ranged from 0.0016 to 7.06 μg/kg and these were not significantly ($p\geq0.05$) different to that measured in urban reference sites. Simulated disturbance of small quantities of sediment in water samples significantly ($p<0.05$) increased the levels of TCDDeq measured in the water. Sediment TCDDeq was correlated to sediment ΣPAH concentration in 2006 and sediment ΣPCB, ΣDDT concentrations and fine sediment grain size in 2005. While fish at one SOP wetland had hepatic EROD activity elevated above the estimated basal level for this species, these were at the lower end of the range measured in urban impacted, non-remediated wetlands. EROD activity was positively correlated with both the sediment ΣPCB load and aqueous TCDDeq. Increased catchment size was correlated with increased EROD activity suggesting an even spread of POPs throughout the residential areas of the Sydney metropolitan area. The concentration of bioactive POPs in the wetlands of SOP is therefore low relative to urban reference sites demonstrating the ongoing success of the remediation program.

1. Introduction

Sydney Olympic Park (SOP) was highly contaminated with commercial, industrial and domestic wastes prior to its remediation in the 1990s in the lead up to the Sydney 2000 Olympic and Paralympic Games. Amongst the persistent organic pollutants (POPs) found at the site were organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs or dioxins) and polycyclic aromatic hydrocarbons (PAHs) (Laginestra et al., 2001) (Table 1). Exposure to POPs can cause major physiological damage through carcinogenic, teratogenic, and genotoxic mechanisms and has been shown to cause reproductive impairment at low concentrations (reviewed by Delzell et al., 1994a,b,c). At SOP their sources were from industrial processes including chemical manufacture (Rubenstein and Wicklund, 1991) and uncontrolled industrial and municipal dumping (Waste Services NSW, 1994). In particular, the herbicides 2,4-D and 2,4,5-T (the active ingredients of 'Agent Orange' of which 2,3,7,8-TCDD is both a by-product and contaminant (Barsotti et al., 1979)), PCBs and phenols were manufactured adjacent to the site (Rubenstein and Wicklund, 1991). As part of the remediation process, soils and sediments with a total concentration of 'scheduled compounds' (including OCPs and PCBs) greater than 2 ppm were treated by thermal desorption and base-catalysed decomposition in an on-site facility.

Four hundred tonnes of scheduled chemical waste were excavated, treated and combined with non-treated excavated material in large containment mounds. The containment mounds were clay-capped and geotextile-lined to avoid infiltration and leaching of contaminants to the groundwater (OCA, 1997; OCA and ADI, 1999). Leachate drains were installed and their contents have been reported to contain measurable levels of POPs (e.g., SKM and EVS, 2001). The remediation established terrestrial and aquatic habitats throughout SOP, which are

* Corresponding author. Tel.: +61 2 9514 4037; fax: +61 2 0514 4079.
E-mail address: Richard.Lim@uts.edu.au (R.P. Lim).
[1] Current Address: Graduate School of the Environment, Macquarie University, North Ryde, NSW, 2109, Australia.

0048-9697/$ – see front matter.
doi:10.1016/j.scitotenv.2009.02.015

Table 1
Organic compounds found in Sydney Olympic Park groundwater, surface waters and sediments samples prior to remediation and leachate from containment mounds post-remediation with Log K_{ow}.

Compound	Groundwater (μg/L)	Sediment (μg/Kg)	Surface Water (μg/L)	Leachate (μg/L)	Log K_{ow}
TPH[a]	1,025,000	30,000,000[b]	1×10^6	6,159,000	
Total PAH	182,200	430,800	43	5763	3.35[c]
Benzo(a)pyrene	4900	28,000	30	33.4	6.35
Benzene	92,000	300	160,000	77,848	2.03
Toluene	58,000	200	150	3740	2.73
Ethylbenzene	4600	26,000	4800	1920	3.15
Xylene	5357	2000	52	1301	3.12
Phenolics	82,700	19,600	50	1171	5.76
Total dioxins/furans	5.8	316,258[b]	<2	1.3×10^{-10}	
TCDDeq			0.246[b]	0.000176	
TCDD	0.0092	190[b]	0.232[b]	0.000029	6.42
Total PCB	<0.03	14000	10140[b]	<0.01	4.51[d]–7.88[e]
Total OCP	<600	1500	6800[b]	<0.02	
DDT	<40	700	446[b]	ND	6.8[f]
DDE	<40	1500	744[b]	ND	6.9[f]
DDD	<40	16000	1044[b]	ND	6.2[f]
Organophosphates	2700	180	ND	ND	<1–5.5[f,g]

Unless otherwise specified, data was sourced from the Sydney Olympic Park Ecology Databank. ND = No Data.
[a] Total Petroleum Hydrocarbons.
[b] Results from estuarine samples from Homebush Bay and Parramatta River.
[c] Value for naphthalene.
[d] Minimum reported value (PCB1) (Hansen et al., 1999).
[e] Maximum reported value (PCB209) (Hansen et al., 1999).
[f] Finizio et al., 1997.
[g] Maximum reported value for jodfenphos.

now habitat for a variety of wildlife including migratory birds and the endangered green and golden bell frog (*Litoria aurea*) (OCA, 2000). Given the current high ecological value of SOP, it is essential that the monitoring of the presence of POPs is continued.

A common method for the remediation of contaminated sediment is removal by dredging. Previous work has suggested that migration and increased bioavailability of contaminants may occur as a result of such disturbance (Rice and White, 1987; Latimer et al., 1999). In SOP, wetlands designed to intercept urban contaminated sediments (by settlement in ponded areas) may require future alterations to deal with reductions in stream/pond depth. The eastern shore of Homebush Bay, a heavily POP contaminated site (Birch et al., 2007), is currently subject to remediation by sediment dredging and treatment by directly heated thermal desorption. It is important that the potential of these processes to increase the bioavailability of sediment-bound contaminants be assessed and relayed to site managers.

Planar, aromatic hydrocarbons (including PCBs, PAHs, PCDD/Fs and some OCPs) are high affinity ligands for the endogenous aryl hydrocarbon receptor (AhR) (Denison and Heath-Pagliuso, 1998; Sierra-Santoyo et al., 2000; Oropeza-Hernandez et al., 2003). The AhR/ligand complex modulates expression of the 1A family of cytochrome P450 mRNA (CYP1AmRNA), which translates to CYP1A, a xenobiotically active enzyme present in many taxa (Hahn, 1998). While the direct toxicological implications of small increases in CYP1A concentrations are relatively minor (e.g., CYP1A metabolism of xenobiotics can lead to oxidative stress (Nebert et al., 2000; Dalton et al., 2002)), the induction of CYP1A above background levels has been used (*in vitro* and *in vivo*) as a biomarker for exposure to POPs (see Whyte et al., 2000, 2004 for reviews).

Previous studies (Ying et al., in preparation) have shown that PCBs, PAHs, DDT and dioxins are present in the sediments of SOP wetlands. The current study investigated the potential biological effects of these compounds by 1. quantifying their affinity for the AhR in aqueous and sediment fractions of the wetlands in SOP and urban-impacted reference sites; 2. assessing the potential for sediment bound POPs to be remobilized through anthropogenic disturbance (e.g., dredging); and 3. examining the exposure of mosquitofish, (*Gambusia holbrooki*, Poeciliidae) inhabiting the wetlands of SOP to POPs using EROD activity as a biomarker of exposure. It was anticipated that the results would provide important information regarding the success of the remediation program in closing pre-remediation contaminant pathways.

2. Materials and methods

2.1. Study sites

Three sets of study sites were selected for study: 1) nine SOP wetlands to cover a range of surface water catchments, contamination and remediation histories, 2) four unremediated sites from the adjacent Parramatta River with a known contamination history, and 3) eighteen urban impacted wetlands across the Sydney metropolitan area a geographically diverse range of urban impacted wetlands. These reference sites were selected to provide a baseline representing wetlands subject to urban impacts such as aerial deposition of industrial products and catchment runoff.

2.2. Water and sediment sample collection

Duplicate water samples were collected in washed and solvent (methanol and dichloromethane) rinsed amber glass bottles (1 L) with Teflon-lined lids and transported on ice to the laboratory where they were stored at 4 °C for no more than 48 h prior to extraction. Composite sediment grab samples from the top 5 cm of the sediment over an area of approximately 225 m^2, were collected using a 10 cm diameter grab sampler and sieved (2-mm mesh) on-site.

2.3. Sediment disturbance experiment

Water:sediment (30 g:1 L) suspensions were prepared for seven study sites (i.e., Boundary Creek, Eastern Water Quality Control Pond (EWQCP), Southern Water Quality Control Pond (SWQCP), Northern Water Feature, Bicentennial Park., Narrawang 22 and Macquarie University) using both field and reverse osmosis (RO) water. Suspensions were allowed to settle for 1 week then orbitally shaken for 48 h and centrifuged (1710 ×g, 20 min), after which the supernatant was collected for extraction.

2.4. Sample extraction and elution

Aqueous samples were filtered (1.2 μm, GFC) and POPs extracted onto C18 Empore disks. Disks were air dried (1 h) and stored at −20 °C for a maximum of 28 days before elution. The disks were thawed and dried on a drying plate for 1 h at 40 °C, twice eluted with 10 ml dichloromethane (DCM) and solvent exchanged under a nitrogen gas stream to 500 μL DMSO for storage at −80 °C.

Wet sediment sub-samples (500 ml) were freeze-dried for one week and POPs extracted with DCM using a Dionex ASE300 Accelerated Solvent Extractor (ASE). Five grams of each sample were weighed into each extraction cell having a filter pad at the bottom and the cell was filled up using diatomaceous earth from Dionex. The ASE used an oven temperature of 100 °C with 10 MPa (1500 psi) pressure. The heat-up time was 5 min and the static time was 5 min for 2 cycles. The extracts were concentrated in collection bottles under nitrogen gas using a Dionex SE500 Solvent Evaporator. Final extracts were redissolved in 1 ml of hexane. Some dirty extracts were further cleaned up using solid phase extraction (SPE) silica cartridges. Extracts were stored at −80 °C prior to analysis.