Organic contaminants of emerging concern in sediments and flatfish collected near outfalls discharging treated municipal wastewater effluent to the Southern California Bight

K.A. Maruya, D.E Vidal-Dorsch, S.M. Bay, J.W. Kwon[1], K. Xia[1] and K.L. Armbrust[1]

Abstract

To investigate the occurrence and bioaccumulation of organic contaminants of emerging concern (CECs) in the vicinity of four ocean outfalls that discharge treated wastewater effluent into the southern California Bight (U.S.A), a comprehensive suite of pharmaceutical and personal care products; current use pesticides; industrial/commercial chemicals; and legacy organic pollutants were analyzed in sediment and liver tissues of hornyhead turbot (*Pleuronichthys verticalis*), a locally abundant flatfish. Research grade GC-MS and LC-MS protocols validated using a performance based QA/QC approach were utilized. Although most CECs targeted (>75 individual analytes) were infrequently or not detected, triclosan, 4-nonylphenol (4-NP) and bis(2-ethylhexyl)phthalate were detected in all sediments analyzed at maximum concentrations of 8.6, 380 and 470 µg/kg, respectively. In liver, 4-NP and the sum of polybrominated diphenyl ether (PBDE) congeners 47 and 99 were detected in >90% of samples analyzed at maximum concentrations of 290 and 480 µg/kg, respectively. The sedative diazepam was detected in 100% of liver samples (110 µg/kg maximum concentration), but was infrequently detected in sediments. Sediment and liver concentrations ranged over several orders of magnitude across outfall locations and selected CECs (e.g. PBDEs) and legacy organochlorines were elevated relative to a reference site. Relative to sediment, accumulation in liver of PBDEs was comparable to that for legacy organochlorines (e.g. 4,4'-DDE and PCB 153), whereas triclosan and 4-NP exhibited low bioaccumulation potential. Mean tissue PBDE and diazepam concentrations were higher in livers from male vs. female *P. verticalis*, suggesting that gender differences be considered when assessing the exposure and impact of bioaccumulative CECs on sentinel fish species.

Introduction

The health of aquatic ecosystems that are subject to anthropogenic discharges, such as treated wastewater effluent and stormwater runoff, is of continuing concern. Impacts on biota (e.g., fish) in waters receiving discharge have been documented, particularly in effluent dominated streams, rivers and lakes (Desbrow *et al*. 1998, Kidd *et al*. 2007, Hinck *et al*. 2011). The primary focus of recent studies has been on responses related to modification of endocrinology, growth and/or reproductive health of fish exposed to environmental endocrine-disrupting chemicals (Scott *et al*. 2007, Bjorkblom *et al*. 2009,

[1] *Mississippi State Chemical Laboratory, Mississippi State, MS*

Evrard *et al*. 2010). Because of their potential for inducing such responses, contaminants of emerging concern (or CECs) such as pharmaceutical and personal care products (PPCPs), industrial and commercial chemicals (ICCs) and current use pesticides (CUPs) have garnered the majority of research and monitoring attention.

Little attention, however, has focused on the potential for exposure and impacts due to CECs associated with discharges into coastal and marine environments, particularly in highly urbanized regions that discharge very large volumes of wastewater and un- or minimally treated stormwater. Investigations first initiated in 2000 off the coast of southern California suggested exposure to endocrine disrupting chemicals as evidenced by the presence of biomarkers (e.g. vitellogenin) in male specimens of hornyhead turbot (*Pleuronichthys verticalis*), a marine flatfish that has been the subject of intensive monitoring in this region for decades (Bay *et al*. 2011). Although concentrations of legacy pollutants (e.g., DDTs and PCBs) were unquestionably elevated in the vicinity of these outfalls (Zeng and Tran 2002), no information was available for unregulated or infrequently monitored chemicals, and in particular, those CECs with known higher occurrence in treated wastewater effluent and receiving waters (Vanderford *et al*. 2003) and/or endocrine modulating activity (Schlenk *et al*. 2005).

In response, a multi-faceted study was designed and carried out in which over 400 samples of treated wastewater effluent, (receiving) seawater, sediment and fish tissue were collected in the vicinity of southern California (U.S.A.) coastal marine outfalls discharging treated wastewater effluent from four major publicly owned treatment works (POTWs) over a two-year period and analyzed for a comprehensive suite of CECs (Bay *et al*. 2011, Vidal-Dorsch *et al*. 2011). In addition, biomarkers of contaminant exposure and biological condition including steroid hormone and reproductive protein levels were determined in specimens of *P. verticalis* (Bay *et al*. 2011). This study aimed to address the following questions for surface sediments and flatfish tissue collected near the aforementioned POTW outfalls: What CECs are detected most frequently in sediments and flatfish tissue? What are the concentrations of the most frequently detected CECs? Do levels vary among the POTW outfalls? Are concentrations elevated at POTW outfall sites compared with a reference site? Are tissue levels gender-specific? To accomplish this, sediment grab samples and composites of *P. verticalis* liver were analyzed for a broad suite of CECs using research grade analytical protocols.

Methods

Study Area

Samples were collected in the vicinity of four major marine outfalls (LA, PV, OC and SD) and a single reference site (DP) located off the southern California coast (Figure 1). The level of wastewater treatment among the POTWs discharging at the outfall locations varies from advanced primary to full secondary (Bay *et al*. 2011, Vidal *et al*. 2011). Nominal discharge for each of these outfalls range between 200-350 mgd for a sum total approaching 1 billion gallons per day. Outfall depths range between 50 to 100 m. Details of the sites and effluent quality for each can be found elsewhere (Bay *et al*. 2011, Vidal-Dorsch *et al*. 2011).

Sample Collection, Compositing, and Preservation

Surficial sediment samples were collected at each of the five stations during the spring and summer of 2006. Once on station, a minimum of three sediment grabs were collected within 100 m of the original station coordinates to a depth of 20 cm using a Van-Veen type grab deployed from a support research vessel. The top 2 cm of sediment from each grab was removed with a pre-cleaned stainless scoop and

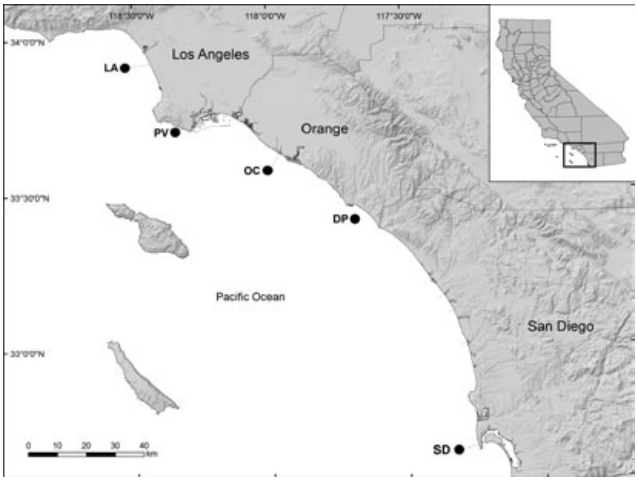

Figure 1. Study sites off the coast of southern California, USA. Four of the sites (LA, PV, OC and SD) were located adjacent to ocean outfalls discharging treated wastewater effluent. The fifth site (DP) was selected as a reference due to its non-proximity to the discharge sites.

placed into a stainless steel bowl for homogenization into a composite sample. An aliquot of the composite sample was then transferred to a 500 ml I-Chem glass jar and immediately placed in an ice-filled cooler. Between grabs, all stainless steel implements were carefully cleaned with site water, DI water and rinsed with pesticide grade methanol. Upon delivery to the laboratory, each sediment composite sample was immediately frozen at -20°C.

P. verticalis livers were excised from individual fish collected with a 7.6 meter-wide semi-balloon otter trawl and segregated by size (retaining those conforming to the 75% size rule), sex and station for a total of ten composite samples (5 female/5 male; 5 g minimum wet tissue each). A differential Global Positioning System (dGPS) was used to locate the sampling sites and to control the trawling speed at 50-60 m/minutes. Each trawl lasted 10 minutes covering distances ranging from 500 to 600 m. A methanol rinsed stainless steel scalpel was used to excise livers. Because of their relatively small mass, a minimum of 15 and 23 individual livers were composited for each female and male sample, respectively. Composite samples were stored in pre-cleaned 500 ml glass I-Chem jars and kept frozen at -20°C during shipping to Mississippi State Chemical Laboratory (MSCL) and prior to analysis.

Analytical Protocols

A total of 98 and 79 individual compounds (Table SI-1 in Supplemental Information (SI)) were analyzed in sediment and tissue samples, respectively, by the MSCL. This listing includes 48 legacy organochlorines (PCB congeners, chlordanes, DDTs), 4 butyltin compounds (sediment only); 21 CUPs (pyrethroids, triazines and urea based herbicides), 17 ICCs (PBDEs, phthalates and 4-nonylphenol); 5 PPCPs (carbamazepine, diazepam, oxybenzone, simvastatin and triclosan); and 3 hormones (estrone, 17β-estradiol and 17α-ethinyl estradiol). For hormones, only the synthetic compound 17α-ethinyl estradiol was analyzed in tissue samples.

Fifteen MSCL standard operating procedures (SOPs) were employed to process and analyze samples in this study. Legacy organochlorines, urea herbicides (including diuron), 4-nonylphenol and PBDEs were extracted from samples by accelerated (ASE) or sequential solvent extraction and analyzed by gas chromatography with electron capture or mass spectrometric detection (GC-ECD, GC-EI-MS) or by liquid chromatography-mass spectrometry (LC-MS). Organophosphate and triazine pesticides were extracted with acetonitrile, isolated by solid phase extraction (SPE) and analyzed with GC-ECD or with thermionic specific detection (TSD). Analytical protocols for the 5 PPCP analytes, including instrumental conditions, acquisition modes, and analyte specific parent and product ions, are described in detail elsewhere (Kwon *et al*. 2009). Briefly, sediment and tissue samples were solvent extracted using ASE and manual shaking, respectively. The tissue samples were further isolated using SPE (Oasis HLB). Hormones and PPCPs were analyzed using an Alliance 2695 Quattro Micro LC/MS/MS operating in the ESI – and multiple reaction monitoring EST+ modes, respectively.

Quality Assurance and Quality Control

Analytical data validation was accomplished using a performance based approach to QA/QC that included parallel analysis of procedural blanks and matrix spikes. Reporting limits (RLs) ranged from 0.1 µg/kg for PPCPs to 50 µg/kg for selected organophosphate insecticides (Table 1). Sample concentrations for diazinon (>14 µg/kg), bis(2-ethylhexyl)phthalate (BEHP; >19 µg/kg), di-n-butylphthalate (>28 µg/kg), 4-NP (>40 µg/kg) and 4,4'-DDE (>7 µg/kg) were corrected for detectable levels (in parentheses) in procedural blanks. Mean (± sd) recoveries of target analytes spiked into sediment and tissue ranged from a low of 62 ± 0.54 % for organophosphate pesticides (OPs) to a high of 99 ±4.4% for PBDEs (Table 1).

Data Analysis

Individual and total concentrations of target analytes by chemical class (e.g. PCBs, PBDEs, organochlorine pesticides) or category (e.g CUPs, PPCPs and ICCs) were expressed on a wet weight basis. Analyte-specific biota accumulation factors (BAFs) were computed as the ratio of the mean concentrations in *P. verticalis* liver and sediment, also on a wet weight basis. Univariate and statistical comparison of concentrations by site (ANOVA) and fish sex (*t*-test) were conducted using SigmaStat (Version 2.03, SPSS Inc. Chicago, IL, USA). One half of the analyte-specific reporting limit (RL) was used for non detects in computation of the mean and standard deviation.

Table 1. Reporting limits (RLs) and matrix spike percent recoveries (% REC) for selected target analytes.

Analyte Class[a]	Sediment			Tissue		
	MDL (µg)/kg)	Spike Level (µg)/kg)	% REC	MDL (µg)/kg)	Spike Level (µg)/kg)	% REC
PBDEs	1	25	85 ± 9	1	25	99 ± 4.4
PPCPs	0.1 - 0.5	10	86 ± 12	4.0 - 10	50	80 ± 6.4
CUPs	10 - 50	500 - 1000	62 ± 0.5	10 - 50	500 - 1000	67 ± 15[b]
Hormones	0.6 - 4.0	10 - 50	91 ± 8	10[c]	50[c]	100[c]
4-nonylphenol	20	80	87.5	50	2000	100[d]

[a] polybrominated diphenyl ethers (PBDEs); pharmaceutical and personal care products (PPCPs); current use pesticides (CUPs) including atrazine, chlorpyrifos, diazinon and metalochlor

[b] metalochlor was not recovered

[c] 17α-ethinylestradiol only

[d] corrected for concentration in non-fortified matrix

Results and Discussion

Frequency of Occurrence and Concentrations

The mean percent moisture for the sediment and liver samples was 36 ±5.2% (n = 5) and 72 ±3.6% (n = 10), respectively. The mean lipid content for liver samples was 5.3 ±2.7% with a higher mean for male specimens (6.6 ±2.6%) than for female specimens (4.0 ±2.1%). Of the 98 target analytes, only 6 were detected in greater than 50% of the sediment samples (Table 2). Bis(2-ethylhexyl) phthalate, 4-NP and triclosan were observed at the highest median/mean concentrations, whereas the single highest sediment concentration was observed for 4,4'-DDE. The occurrence of 4,4'-DDE and other DDT related analytes was not uniformly distributed among study sites. PBDE congeners 47 and 99, common environmental contaminants in freshwater and coastal marine ecosystems (Hale *et al*. 2001, Kimbrough *et al*. 2009, Dodder *et al*. 2011), were found in 3 of the 5 sediments at relatively low (1 - 2 µg/kg) concentrations.

In contrast to sediments, roughly 40% (33 of 79) of the target analytes for tissue were detected (Table SI-2). Those analytes detected in 100% of tissue samples represented legacy pollutants and CECs, including 4,4'-DDE, BDE and PCB congeners as well as diazepam and 4-NP (Table 2). Median concentrations for those analytes detected with 100% frequency ranged from 10 (BDE-154) to 320 µg/kg for 4,4'DDE. Comparison of the median and mean for each of these indicated that 4,4'-DDE and PCBs were not uniformly distributed among tissue samples whereas the PBDE congeners, diazepam, and to a lesser extent 4-NP, were more uniformly distributed (Table 2).

The analysis of high production volume chemicals such as phthalates and alkylphenols presents a challenge due to their ubiquity and frequent detection in procedural blanks (Vikelsøe *et al*. 2002). Thus, it was not surprising to detect BEHP, di-n-butylphthalate and 4-NP in procedural blanks. This challenge is exacerbated by the possibility of high variability in occurrence across samples. For example, our spiking of a sediment matrix with 4-NP at 80 µg/kg resulted in 88% recovery (Table 1), suggesting quantitative recovery of the analyte and a negligible background concentration even though it was detectable in procedural blanks at up to an estimated concentration of 40 µg/kg. An alternative explanation is incomplete recovery of 4-NP (e.g., ~30 - 50%) which is then artifactually enhanced by the addition of blank contamination. In contrast to the ten-fold difference observed in sediment concentrations for BEHP, and even larger ranges for other analytes, the narrow range reported for di-n-butylphthalate (min of 28, max of 44 µg/kg; Table SI-2) suggests a higher likelihood of artifactual contamination. In either case, we consider our results to be conservative (i.e., neutral or negatively biased) by correcting for detected blank concentrations.

Table 2. Concentrations of the most frequently detected target organic analytes in sediment and liver of hornyhead turbot (*Pleuronichthys verticalis*) collected near four large POTW wastewater outfalls and a reference site.

Analyte	Median (µg/kg)	Mean (µg/kg)	Standard Dev (µg/kg)	Minimum	Maximum	Occurrence %
Sediment						
bis(2-ethylhexyl)phthalate	121	171	190	4	470	100
4-nonylphenol	30	104	161	10	380	100
Triclosan	5.1	4.96	3.06	1.7	8.6	100
4,4'-DDE	4.0	182	401	1	900	60
BDE 47	2.2	1.7	1.12	0.5	2.8	60
BDE 99	1.4	1.08	0.54	0.5	1.6	60
Diazepam	0.04	0.04	0.02	0.04	0.07	20
Tissue						
4,4'-DDE	320	12200	24700	12	64700	100
BDE 47	155	156	112	11	330	100
4-nonylphenol	85	102	82.7	25	290	90
BDE 99	55	69	53	8	150	100
Diazepam	52	56	27	23	110	100
BDE 100	46	47	31.6	4	97	100
PCB 138	25	111	143	3.5	360	100
PCB 153	23	132	177	2.3	470	100
BDE 154	10	11	7.48	1	25	100

Differences among Outfall Sites

Organochlorine pesticide (OCPs) that include DDTs, and PCBs that represent discharge of historic contamination via treated wastewater effluent show a pattern characterized by higher concentrations in both sediment and fish for the two northernmost outfalls (LA and PV), with very low and/or undetectable levels at the City of San Diego plant outfall (SD) and the reference site (DP; Figure 2). In contrast, concentrations of PBDEs and 4-NP, which represent current or more recent high volume production chemicals, are relatively uniform across all outfall sites for *P. verticalis* liver, and among the three

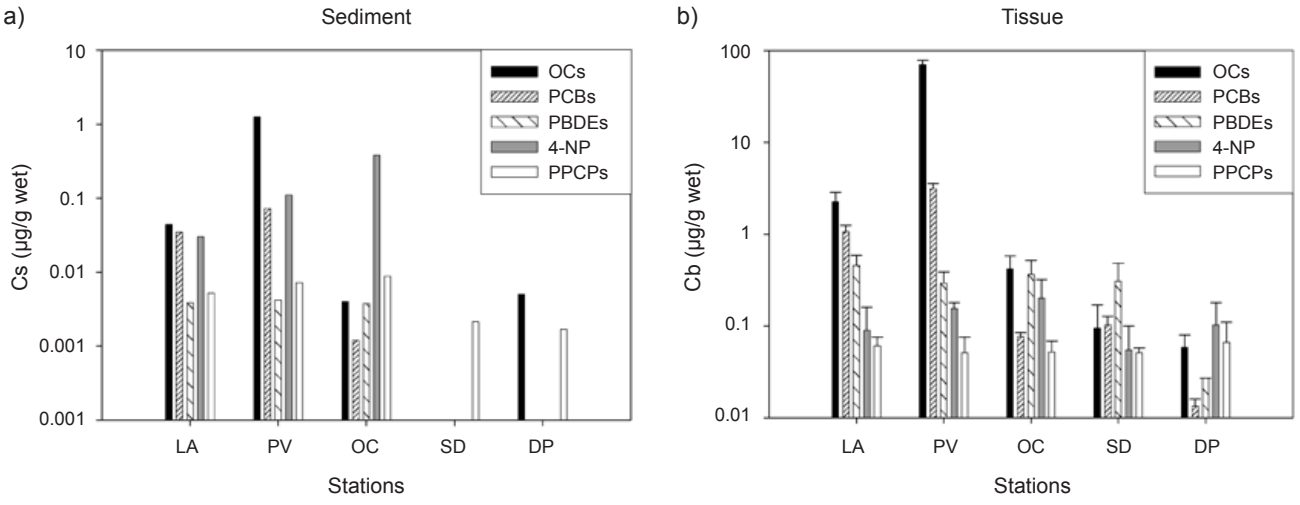

Figure 2. Summed concentrations of frequently occurring classes of organic analytes in sediment (a) and fish tissue (b) collected near four large marine POTW outfalls and a reference site (DP). OCs = organochlorine pesticides; PBDEs = polybrominated diphenyl ethers; PPCP = pharmaceutical and personal care products; 4-NP = 4-nonylphenol.

northernmost outfalls (LA, PV and OC) for sediment. PBDEs and 4-NP were not detected in sediments from SD and DP. Triclosan and diazepam were the sole PPCPs detected in sediments and tissue, respectively, with no discernable differences in concentrations between the outfall and reference sites. Sediment concentrations of triclosan (Figure 2), an antibacterial agent added to consumer products such as liquid soap, mirrored that of 4-NP, which was previously reported at mg/kg concentrations in sediments from the vicinity of the Orange County POTW outfall (OC; Schlenk *et al*. 2005).

The most striking difference in contaminant concentrations was the lower occurrence in terms of both frequency of detection and concentrations at DP (Figure 2). This is clear for sediments, and, with the possible exceptions of 4-NP and diazepam, for tissues as well. Whereas PBDE tissue concentrations were relatively uniform (10 - 100 µg/kg) at the outfall sites, levels in *P. verticalis* liver from DP were <10 µg/kg. A clear gradient was also observed for legacy pollutants (e.g., PCBs, DDTs) in both sediment and tissue with highest concentrations at the PV and LA outfall sites. The co-occurrence of CECs with legacy pollutants at some, but not all of these sites may be useful in designing subsequent field studies of contaminant responses on flatfish and other marine sentinel benthic species.

Bioaccumulation of CECs by Fish

Hornyhead turbot (*P. verticalis*) is a key monitoring species at our study sites and throughout the southern California Bight since it is widely believed to have a limited home range (Cooper 1994), and is readily captured throughout the year at these sites. Because data were based on wet weight and a small sample size, however, we present BAFs as a comparative parameter within this study, and caution the reader against comparisons to lipid and/or TOC-normalized BSAFs reported in other studies.

Liver tissue to sediment ratios, or BAFs, for BDE 47 (2,2',4,4'-tetrabromo) and 99 (2,2',4,4',5-pentabromo) were 91 and 64, respectively, which were comparable to BAFs estimated in this study for known persistent and bioaccumulative contaminants, e.g. PCBs 153 and 180 and 4,4'-DDE (Table 3). Previous studies reported that fish BSAFs for BDE 47 and 99 ranged from ~1 to 30 (Vigano *et al*. 2008, Sudaryanto *et al*. 2009), which may be expected to be lower upon normalization to tissue lipid and sediment TOC. The BAF for 4-NP was on the order of unity, suggesting it does not possess the potential for bioaccumulation, at least for a benthic-oriented fish such as *P. verticalis*. If such behavior holds true for other fish and forage species targeted by marine mammals and human consumers, 4-NP would not be expected to biomagnify to higher trophic levels. In contrast, PBDEs exhibit the persistence and bioaccumulation that warrants future research and monitoring into its occurrence, distribution and long term chronic impacts in the southern California marine environment.

Diazepam (trade name Valium), which was reported to be moderately hydrophobic (log K_{ow} ~3), particle reactive and resistant to transformation (Loeffler *et al*. 2005) presents an interesting case in that it was detected infrequently in sediments (20%)

Table 3. Bioaccumulation factors (BAFs) for organic analytes detectable in sediment and *P. verticalis* liver with a frequency of detection of 40% or greater. BAF = ratio of tissue to sediment concentration (wet weight basis).

Analyte	Tissue			Sediment			BAF
	Mean (µg/kg)	Standard Dev (µg/kg)	Occurrence %	Mean (µg/kg)	Standard Dev (µg/kg)	Occurrence %	
BDE 47	156	112	100	1.7	1.12	60	91
PCB 153	132	177	100	2.04	2.12	40	65
4,4'-DDE	12200	24700	100	189	398	80	65
BDE 99	69	53	100	1.08	0.54	60	64
PCB 180	61	81	100	1.12	0.86	40	54
PCB 118	98	155	70	2.82	3.78	40	35
2,4'-DDE	752	1561	70	38.2	79.3	40	20
4-nonylphenol	102	83	90	104	161	100	1

and at a low concentration (< 1 µg/kg). Incomplete (~50%) removal by wastewater treatment processes as reported by Carballa *et al*. (2005) supports its potential for occurrence in receiving seawater and thus exposure to *P. verticalis* at the point of discharge. Unfortunately, diazepam was not included and/or reported in a recent national pilot study on PPCP contamination in freshwater fish (Ramirez *et al*. 2009). Thus, additional research into the analytical aspects and fate of diazepam in waters receiving discharge from POTWs may be warranted.

Concentrations of PBDEs and diazepam were significantly higher in male vs. female specimens of *P. verticalis* (Figure 3). This difference for diazepam was observed for specimens collected at the reference site (DP) as well as when pooling data from the four outfall sites (*t*-test; $p = 0.0023$). For PBDEs, the difference was significant for data pooled from the 4 outfall sites (*t*-test; $p = 0.0015$). It has been shown that physiological condition and life history can profoundly influence organic contaminant body burdens in fish (Elskus *et al*. 2005), particularly when associated with fluctuations and/or large ranges in lipid content (Maruya *et al*. 2005). No association was observed between concentrations of pharmaceutical analytes (of which diazepam was not included) and lipid content for muscle and liver samples of freshwater fish in the national pilot study (Ramirez *et al*. 2009). In this study, higher mean lipid content for male *P. verticalis* could partially account for the observed difference in diazepam and PBDE concentrations. In addition, care was taken to collect and select fish that were likely to be sexually mature. Based on assessment of gonadal condition and reproductive status for the same specimens used in this study by other investigators (Bay *et al*. 2011), the vast majority of female fish were in various stages of egg production and maturation. It remains possible that females in a state of active gonad development deplete lipid from other stores (e.g., the liver), releasing associated lipophilic chemicals into the bloodstream and transporting them into other compartments (e.g. gonads). Thus, potential differences in bioaccumulation of organic contaminants within a single sentinel fish species (based on gender, sexual maturity, and/or reproductive status) should be taken into consideration when designing research and/or monitoring studies.

Literature Cited

Bay, S.M., D.E. Vidal-Dorsch, D. Schlenk, K. Kelley, M. Baker, K. Maruya and J. Gully. 2011. Sources and effects of endocrine disruptors and other contaminants of emerging concern in the Southern California Bight coastal ecosystem. Technical Report 650. Southern California Coastal Water Research. Costa Mesa, CA.

Björkblom, C., E. Högfors, L. Salste, E. Bergelin, P.-E.Olsson, I. Katsiadaki and T. Wiklund. 2009. Estrogenic and androgenic effects of municipal wastewater effluent on reproductive endpoint biomarkers in three-spined stickleback (*Gasterousteus aculeatus*). *Environmental Toxicology and Chemistry* 28:1063-1071.

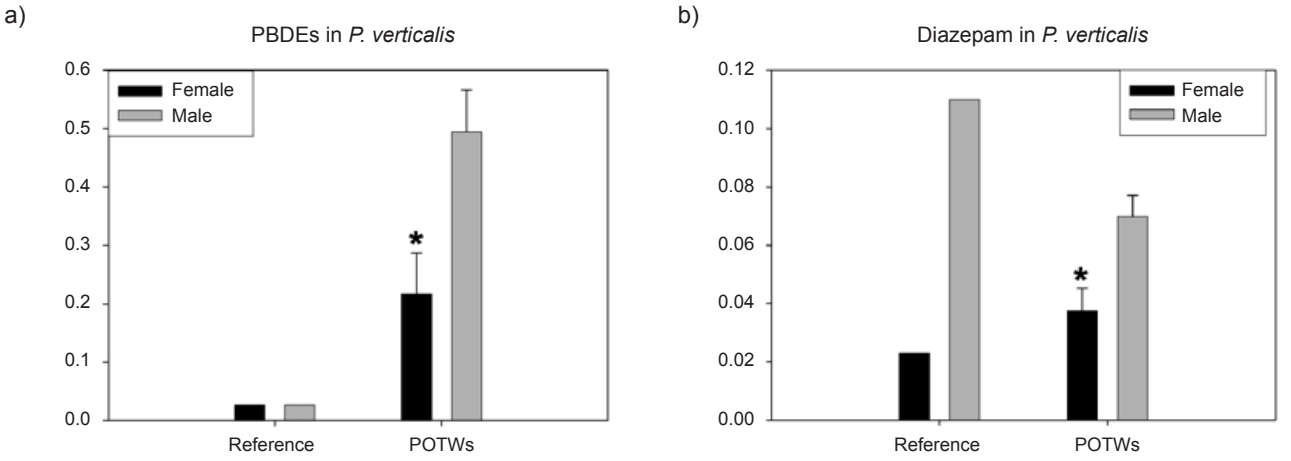

Figure 3. Concentrations (µg/gwet) of total polybrominated diphenyl ethers (a) and diazepam (b) in livers of female and male hornyhead turbot (*Pleuronichthys verticalis*) collected near four large marine POTW outfalls. * significantly different (p <0.05).

Carballa, M., F. Omil, J.M. Lema, M. Llompart, C. Garcia, I. Rodriguez, M. Gomez and T. Ternes. 2005. Behaviour of pharmaceuticals and personal care products in a sewage treatment plant of northwest Spain. *Water Science and Technology* 52:29-35.

Cooper, L. 1994. Aspect of the life history of hornyhead turbot, *Pleuronichthys verticalis*, off southern California. pp. 154-163 *in*: J.N. Cross (ed.), Southern California Coastal Water Research Project 1992-93 Annual Report. Westminster, CA.

Desbrow, C., E.J Routledge, G.C. Brighty, J.P. Sumpter and M. Waldock. 1998. Identification of estrogenic chemicals in STW effluent. 1. Chemical fractionation and *in vitro* biological screening. *Environmental Science and Technology* 32:1549-1558.

Dodder, N.G., G.G Lauenstein, J. Ramirez, K.J. Ritter, K.A. Maruya and K.C. Schiff. 2011. Distribution and sources of polybrominated diphenyl ethers in the Southern California Bight. pp. 261-270 *in*: K. Schiff and K. Miller (eds.), Southern California Coastal Water Research Project 2011 Annual Report. Costa Mesa, CA.

Elskus, A.A., T.K. Collier and E. Monosson. 2005. Interactions between lipids and persistent organic pollutants in fish. pp. 119-152 *in*: T.P. Mommsen and T.W. Moon (eds.), Biochemistry and Molecular Biology of Fishes, Volume 6, Environmental Toxicology. Elsevier Science. St. Louis, MO.

Evrard, E., A. Devaux, S. Bony, T. Burgeot, R. Riso, H. Budzinski, M. Le Du, L. Quiniou and J. Laroche. 2010. Responses of the European flounder *Platichthys flesus* to the chemical stress in estuaries: load of contaminants, gene expression, cellular impact and growth rate. *Biomarkers* 15:111-127.

Hale, R.D., M.J. La Guardia, E.P. Harvey, T. Matteson Mainor, W.M. Duff and M.O. Gaylor. 2001. Polybrominated diphenyl ether flame retardants in Virginia freshwater fishes (USA). *Environmental Science and Technology* 35:4585-4591.

Hinck, J.E., C.J. Schmitt, K.A. Chojnacki and D.E. Tillitt. 2011. Environmental contaminants in freshwater fish and their risk to piscivorous wildlife based on a national monitoring program. *Environmental Monitoring and Assessment* 152:469-494.

Kidd, K.A., P.J. Blanchfield, K.H. Mills, V.P. Palace, R.E. Evans, J.M. Lazorchak and R.W. Flick. 2007. Collapse of a fish population after exposure to a synthetic estrogen. *Proceedings of the National Academy of Sciences of the United States of America* 104:8897-8901.

Kimbrough, K.L., W.E. Johnson, G.G. Lauenstein, J.D. Christensen and D.A. Apeti. 2009. An assessment of Polybrominated Diphenyl Ethers (PBDEs) in sediments and bivalves of the U.S. coastal zone. NOAA Technical Memorandum NOS NCCOS 94. NOAA. Silver Spring, MD.

Kwon, J.W., K.L. Armbrust, D. Vidal-Dorsch, S.M. Bay and K. Xia. 2009. Determination of 17 alpha-ethynylestradiol, carbamazepine, diazepam, simvastatin, and oxybenzone in fish livers. *Journal of the Association of Official Analytical Communities International* 92:359-369.

Loeffler, D., J. Römbke, M. Meller and T.A. Ternes. 2005. Environmental fate of pharmaceuticals in water/sediment systems. *Environmental Science and Technology* 39:5209-5218.

Maruya, K.A., R.O. Manning and L. Francendese. 2005. Residues of toxaphene decrease in estuarine fish after removal of contaminated sediments. *Estuaries* 28:786-793.

Ramirez, A.J., R.A. Brain, S. Usenko, M.A. Mottaleb, J.G. O'Donnell, L.L. Stahl, J.B. Wathen, B.D. Snyder, J.L. Pitt, P. Perez-Hurtado, L.L. Dobbins, B.W. Brooks and C.K. Chambliss. 2009. The occurrence of pharmaceuticals and personal care products in fish: results of a national pilot study in the United States. *Environmental Toxicology and Chemistry* 28:2587-2597.

Schlenk, D., Y. Sapozhnikova, M.A. Irwin, L. Xie, W. Hwang, S. Reddy, B.J. Brownawell, J. Armstrong, M. Kelly, D.E. Montagne, E.P. Kolodziej, D. Sedlak and S. Snyder. 2005. *In vivo* bioassay-guided fractionation of marine sediment extracts from the Southern California Bight, USA, for estrogenic activity. *Environmental Toxicology and Chemistry* 24:2820-2826.

Scott, A.P., M. Sanders, G.D. Stentiford, R.A. Reese and I. Katsiadaki. 2007. Evidence for estrogenic endocrine disruption in an offshore flatfish, the dab (*Limanda limanda L.*). *Marine Environmental Research* 64:128-148.

Sudryanto, A., I.E. Setiawan, M. Ilya, E. Soeyanto, A.S. Riadi, T. Isobe, S. Takahashi and S. Tanabe. 2009. Levels of brominated flame retardants in sediments and their bioaccumulation potential in biota from Jakarta Bay and its surroundings, Indonesia. pp. 125-131 *in*: Y. Obayashi, T. Isobe, A. Subramanian, S. Suzuki and S. Tanabe (eds.), Interdisciplinary Studies on Environmental Chemistry — Environmental Research in Asia. Terra Scientific Publishing Company. Tokyo, Japan.

Vanderford, B.J., R.A. Pearson, D.J. Rexing and S.A. Snyder. 2003. Analysis of endocrine disruptors, pharmaceuticals, and personal care products in water using liquid chromatography/tandem mass spectrometry. *Analytical Chemistry* 75:6265-6274.

Vidal-Dorsch, D.E., S.M. Bay, K. Maruya, S.A. Snyder, R.A. Trenholm and B.J. Vanderford. Submitted. 2011. Contaminants of emerging concern in municipal wastewater effluents and marine receiving water. pp. 351-364 *in*: K. Schiff and K. Miller (eds.), Southern California Coastal Water Research Project 2011 Annual Report. Costa Mesa, CA.

Vigano, L, C. Roscioli, C. Erratico and L. Guzzella. 2008. Polybrominated Diphenyl Ethers (PBDEs) and polychlorinated biphenyls (PCBs) in 0+ juvenile cyprinids and sediments of the Po River. *Archives of Environmental Contamination and Toxicology* 55:282-294.

Vikelsøe, J., M. Thomsen and L. Carlsen. 2002. Phthalates and nonylphenols in profiles of differently dressed soils. *Science of the Total Environment* 296:105-116.

Zeng, E.Y. and K. Tran. 2002. Distribution of chlorinated hydrocarbons in overlying water, sediment, polychaete and hornyhead turbot (*Pleuronichthys verticalis*) in the coastal ocean, southern California, USA. *Environmental Toxicology and Chemistry* 21:1600-1608.

Acknowledgments

We acknowledge support from SCCWRP member agencies. We also thank the project's steering committee members for their guidance, including J. Gully of the Los Angeles County Sanitation Districts; C. Cash of the City of Los Angeles; J. Armstrong of the Orange County Sanitation Districts, and T. Stebbins of the City of San Diego; D. Schlenk of UC Riverside; and K. Kelly of CSU Long Beach.

Supplemental Information

Supplemental Information available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2011AnnualReport/ar11_SupplementalInfo_OrganicCECs.pdf