



Geography and stage of development affect persistent organic pollutants in stranded and wild-caught harbor seal pups from central California

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ARTICLE INFO

Article history:

Received 21 March 2011

Received in revised form 24 May 2011

Accepted 26 May 2011

Keywords:

PCB

DDT

PBDE

HCH

Phoca vitulina

Blubber

ABSTRACT

Persistent organic pollutants have been associated with disease susceptibility and decreased immunity in marine mammals. Concentrations of polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), polybrominated diphenyl ethers (PBDEs), chlordanes (CHLs), and hexachlorocyclohexane isomers (HCHs) were evaluated in terms of stage of development and likely exposure routes (in utero, suckling, fasting) in the blubber of 202 stranded and wild-caught, primarily young of the year ($n=177$), harbor seals (*Phoca vitulina*) in the central California coast. This is the first report of HCH concentrations in the blubber of California seals. Lipid normalized concentrations ranged from 200 to 330,000 ng/g for sum PCBs, 320–1,500,000 ng/g for sum DDTs, 23–63,000 ng/g for sum PBDEs, 29–29,000 ng/g for sum CHLs, and 2–780 ng/g for sum HCHs. The highest concentrations were observed in harbor seal pups that suckled in the wild and then lost mass during the post-weaning fast. Among the pups sampled in the wild and those released from rehabilitation, there were no differences in mass, blubber depth, or percent lipid although contaminant concentrations were significantly higher in the pups which nursed in the wild. When geographic differences were evaluated in a subset of newborn animals collected near their birth locations, the ratio of sum DDTs to sum PCBs was significantly greater in samples from an area with agricultural inputs (Monterey), than one with industrial inputs (San Francisco Bay). A principal components analysis distinguished between seals from San Francisco Bay and Monterey Bay based on specific PCB and PBDE congeners and DDT metabolites. These data illustrate the important influence of life stage, nutritional status, and location on blubber contaminant levels, and thus the need to consider these factors when interpreting single sample measurements in marine mammals.

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1. Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and polybrominated diphenyl ethers (PBDEs) are found in marine organisms throughout the world. These compounds are lipophilic and thus accumulate in the lipid rich blubber layers of marine mammals (O'Shea, 1999). Phocid seals (e.g., harbor seals, *Phoca vitulina*; gray seals, *Halichoerus grypus*) are initially exposed to contaminants transferred through the placenta and milk and then through the

prey species they ingest. The greatest exposure occurs in utero and during nursing when these seals are developing and are potentially more vulnerable to the effects of these chemicals (Debier et al., 2006). In addition, the contaminants acquired by these routes are mobilized from the blubber into the circulatory system during the post-weaning fast (Debier et al., 2003a, 2003b).

Harbor seals are born weighing 10 to 12 kg and are abruptly weaned three to five weeks later weighing 20–25 kg (Cottrell et al., 2002). In addition to the rapid mass gain and transfer of maternal antibodies, the greatest levels of contaminants are also acquired by the pups during suckling as lipid-rich seal milk is at a higher trophic level and therefore typically more contaminated than the prey species the pups will consume after weaning (Wolkers et al., 2004; Thomas et al., 2005). Pups appear to store rather than metabolize these contaminants, and at weaning, the contaminant pattern in their blubber is similar to that of the milk they ingest (Wolkers et al., 2004). Pup contaminant concentrations thus reflect maternal contaminant

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concentrations which vary as a result of exposure history and the number of pups they have nursed, with their first pup receiving the greatest contaminant concentrations (Addison and Brodie, 1977).

Little is known about the post-weaning fast in harbor seals because they do not remain ashore after weaning, but quickly disperse from their natal beaches, however the mobilization of contaminants from the blubber of gray seals and elephant seals (*Mirounga angustirostris*) during the post-weaning fast is well described (Hall et al., 2003; Debier et al., 2006). It is expected that the blubber dynamics during fasting in harbor seals are similar to gray and elephant seals, with simultaneous movement of lipids and lipophilic contaminants into the serum and concentration of contaminants in the remaining blubber.

High levels of POPs have been implicated in disease and mortality in marine mammals. PCBs were associated with mortality from infectious disease in harbor porpoises (Jepson et al., 2005) with increased concentrations associated with a greater risk of mortality (Hall et al., 2006). In California sea lions (*Zalophus californianus*), PCBs were associated with cancer deaths (Ylitalo et al., 2005a). Harbor seals that died during a phocine distemper epidemic had higher levels of PCBs and DDTs than those that survived suggesting that contaminants may have affected the ability of the seals to respond to the virus (Hall et al., 1992). In experimental studies, PCBs in contaminated fish from the Wadden and Baltic Seas were associated with reproductive failure and decreased immune system function in harbor seals (Reijnders, 1986; Ross et al., 1995; de Swart et al., 1996; Ross et al., 1996), however, the effects of environmental contaminants on marine mammal health, especially in free-ranging animals, are not well understood.

The potential role of contaminants in the births of premature harbor seal pups has long been a concern (Risebrough et al., 1980). To understand the role that contaminants might play in the health of developing seal pups in central California, differences in contaminant levels in stranded and wild-caught harbor seal pups were investigated. Our primary study objectives were to 1) consider the amount of time the pups suckled in the wild as well as the effects of growth during rehabilitation on contaminant levels; and 2) to evaluate the effect of stranding location on contaminant concentrations in newborn harbor seal pups.

2. Methods

2.1. Sample collection

Blubber was sampled from live and dead harbor seals in the same anatomical location: caudal to the left hip and lateral to the spine. For seals that were stranded dead or died during rehabilitation, the depth of the blubber layer was measured and an area of blubber (~2 cm × 2 cm) extending from the skin to the muscle layer was excised with a scalpel, wrapped in solvent-rinsed teflon sheeting (Port Plastics, San Jose, California, USA), and frozen at -80 °C until analysis. Seals that were captured in the wild, as well as rehabilitated seals that were released, were sedated with 5 mg/mL diazepam (Hospira, Inc. Lake Forest, Illinois, USA) administered intravenously at a dose of 0.25 mg/kg. The biopsy site was shaved, a 1 mL dose of local anesthesia was administered (2% lidocaine, Sparhawk Laboratories, Inc. Lenexa, Kansas, USA), and the blubber layer was visualized and its thickness measured using ultrasound (Sonovet 2000, BCF Technology, Livingston, United Kingdom). A sterile 8 mm dermal biopsy punch (Miltex, Inc. York, Pennsylvania, USA) was used to obtain the blubber sample which was wrapped in solvent-rinsed teflon and frozen at -80 °C until analysis. At the time of sampling all animals were weighed and measured (length and axillary girth).

2.2. Sample analysis

Persistent organic pollutants were extracted from blubber samples of harbor seals using a gas chromatography/mass spectrometry (GC/MS)

method (Sloan et al., 2005). Briefly, each tissue sample was mixed with drying agents (sodium sulfate and magnesium sulfate), transferred to a 33-mL accelerated solvent extraction (ASE) cell and surrogate standards (PCB 103 and 4,4'-dibromooctafluorobiphenyl) were added to the top of each sample cell. Using the ASE, the POPs and lipids were sequentially extracted at 2000 psi and 100 °C with two cell volumes using dichloromethane and the combined extract (~50 mL) collected in a 60-mL collection tube. The extract was thoroughly mixed using a Vortex mixer and a 1–2 mL aliquot of each sample extract was transferred to a GC vial for lipid quantitation by thin-layer chromatography/flame ionization detection (TLC/FID) (Ylitalo et al., 2005b). The remaining non-lipid sample extract was filtered through a column of silica gel and alumina to remove polar compounds and concentrated for further cleanup to remove interfering lipid compounds. Size exclusion chromatography with high-performance liquid chromatography (HPLC) was used to collect the fraction containing the POPs (Sloan et al., 2005). The HPLC fraction was analyzed for POPs by capillary column GC/MS. The analytes were separated on a 60-m DB-5 capillary column (0.25-mm i.d., 25- μ m film thickness) and analyzed by GC/MS (Agilent 5973 N Mass Selective Detector® Agilent Technologies) operated in the electron impact (EI) selected ion monitoring (SIM) mode (Sloan et al., 2005). The instrument was calibrated using a series of five or more multi-level calibration standard solutions containing known amounts of several different POPs from which response factors relative to PCB 103 were computed.

Each lipid sample was spotted on a Chromarod (Type SIII) and developed in a chromatography tank containing 60:10:0.02 hexane: diethyl ether:formic acid (v/v/v). Various classes of lipids (e.g., wax esters/sterol esters, triglycerides, free fatty acids, cholesterol and polar lipids) were separated based on polarity, with the nonpolar compounds (e.g., wax esters/sterol esters) eluting first, followed by the more polar lipids (e.g., phospholipids). The lipid classes were measured by flame ionization using a Mark 6 Iatroscan. Total lipid concentrations were calculated by adding the concentrations of the five lipid classes for each sample and were reported as percent lipid.

2.3. Quality assurance and quality control

The quality assurance criteria for analysis of samples for POPs by gas chromatography/mass spectrometry followed the protocol described in Sloan et al. (2006). A National Institute of Standards and Technology (NIST) blubber Standard Reference Material (SRM 1945) was analyzed with each batch of samples to confirm accuracy of POP analysis. Each sample batch consisted of 10–12 field samples. For the NIST SRM analyzed with each batch of samples, the concentrations of $\geq 70\%$ of the individual analytes were within 30% of either end of the 95% confidence interval range of the NIST certified values. Approximately 10% of the seal samples were analyzed in duplicate to measure precision of the analytical method. For duplicates, the relative percent difference was $\leq 30\%$ for $\geq 90\%$ of each of the analytes measured. A method blank was analyzed with each batch of field samples to monitor for laboratory contamination sources. Each method blank contained no more than five analytes that exceeded two times the lower limit of quantitation (LOQ). The recoveries of the surrogate standards ranged from 60 to 130%. For 0.25–0.5 g blubber samples, the LOQ for POPs ranged from approximately 1.0–6.5 ng/g, wet weight.

2.4. Data analysis

In this study, sum PCBs is the sum of congeners 17, 18, 28, 31, 33, 44, 49, 52, 66, 70, 74, 82, 87, 95, 99, 101/90, 105, 110, 118, 128, 138/163/164, 149, 151, 153/132, 156, 158, 170, 171, 177, 180, 183, 187/159/182, 191, 194, 195, 199, 205, 206, 208, and 209. Congeners are numbered according to Ballschmitter et al. (1992). Sum DDTs is the sum of *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT; sum CHLDs is the sum of oxychlordane, γ -chlordane, heptachlor,

heptachlor epoxide, nona-III-chlordane, α -chlordane, *trans*-nonachlor and *cis*-nonachlor; sum hexachlorocyclohexanes (HCHs) is the sum of α -, β -, and γ -HCH isomers; and finally, sum PBDEs is the sum of congeners 28, 47, 49, 66, 85, 99, 100, 153, 154, and 183 (numbered following the PCB numbering system). Values for individual congeners that were below the LOQ were treated as zeroes when summing.

Young of the year animals ($n=180$ excluding two fetuses) were placed into the following seven groups based on age and potential for contaminant exposure during suckling:

1. Neonate carcasses (NC) included newborn pups found dead on the beach and newborn pups that were stranded alive, but died in rehabilitation without gaining more than ten percent of their body mass at the time of admission (i.e. little or no suckling, little or no effect from a rehabilitation diet of artificial milk matrix (Zoologic, Hampshire, IL), salmon oil and frozen herring). Many of these pups were premature (i.e. stranded before viable pups were born in the wild), and this group also included 4 pups (near full term) that were found in utero after traumatic maternal death. We defined newborn as less than 5 days old based on mass, time of year, and the presence of an umbilical cord or patent umbilicus.
2. Neonate died (ND) were newborn pups that were stranded alive and gained some mass in rehabilitation, but died before release (i.e. little or no suckling, some effect from rehabilitation diet).
3. Neonate released (NR) were newborn pups that survived rehabilitation (i.e. little or no suckling, strong rehabilitation effect as pups doubled or tripled their mass).
4. Suckled died (SD) were those that were stranded in May or later, either as carcasses or died during rehabilitation (i.e. some suckling, no rehabilitation effect). They were expected to have suckled, but not necessarily weaned, in the wild as maximum pup numbers in the San Francisco Bay area occur from the third week in April to the third week in May (Allen et al., 2004). The category also included those that were stranded in May or later, gained more than 10% of their admit body mass in rehabilitation and then died (i.e. some suckling, some rehabilitation effect).
5. Weaned wild-caught (WW) were recently weaned pups that were captured and sampled in the field (i.e. full lactational input of contaminants, no rehabilitation effect).
6. Weaned died (WD) were those that weaned in the wild, then were stranded, but died before re-gaining any mass (i.e. full lactational input of contaminants, followed by post-weaning mass loss, no rehabilitation effect).
7. Weaned released (WR) were those that weaned in the wild, were stranded, and survived rehabilitation (i.e. full lactational input of contaminants, post-weaning mass loss, followed by a rehabilitation effect during mass gain).

Other age classes (fetuses, yearlings, subadults and adults) of seals were evaluated separately.

Mass, blubber depth, percent lipid and sampling date were summarized for each group. The geometric mean and 95% confidence intervals for POP concentrations were calculated for each group eliminating values below the LOQ. Mean contaminant concentrations were compared among groups using analysis of variance (ANOVA) with Tukey's Honest Significant Difference method (HSD) for multiple comparisons.

The effect of stranding location was evaluated for the neonate carcass group only ($n=50$) as the site of stranding for these newborns was likely to be close to their birth location and there was no effect from rehabilitation. This group was divided into five locations based on known harbor seal haulout locations: San Francisco Bay (SFB), North of San Francisco Bay (SFN), Tomales Bay north (TBN), South of San Francisco Bay (OCSSF), and Monterey south (MTY, Fig. 1). Geometric mean contaminants and the ratios of DDTs:PCBs and *p,p'*-DDE:*p,p'*-DDT were compared among locations using ANOVA with Tukey's HSD. A principal components analysis (PCA) was then used to compare

the individual analytes by location. To prevent biasing the results with analytes that were rarely detected, only analytes for which 48 or more samples were above the LOQ were used in the PCA analysis: a value equal to one half of the LOQ was used for two PBDE99 samples, one PBDE100 sample, and one nona-III-chlordane sample. The PCA was run on log-transformed concentrations using the R function "prcomp" which scales the variables to a unit variance.

Statistical analyses were performed using the R programming language (R Development Core Team, 2009).

3. Results

Contaminants were measured in blubber samples from 202 animals, of which 177 were young of the year, 23 were older age classes and two were fetuses. Most of the lipids detected (>98%) were triglycerides (see Supporting Information Table SI-1 for the breakdown by pup group). Heptachlor, aldrin, and endosulfan I and BDE183 were below the LOQ for all blubber samples analyzed. Hexachlorobenzene, and mirex were detected in >85% of the samples, but at low levels ranging from 2 to 958 ng/g lipid weight; dieldrin was detected in >70% of the samples at levels ranging from 2 to 89 ng/g lipid weight. PCB 153/132 was the greatest contributor to the sum PCBs (27%) followed by PCB 138 (19%), PCB 180 (10%) and PCB 187 (9% each), PCB99 (6%), PCBs 101, 170, 183, 149 (3%), and PCBs 177, 128, 199, 188 (2% each). Sum DDTs were primarily *p,p'*-DDE (97%) and *p,p'*-DDT (2%). *Trans*-nonachlor (56%) and oxychlordane (29%) were the predominant contributors to sum chlordane values. Sum PBDEs were primarily PBDE 47 (83%), PBDE 99 (8%), and PBDE 100 (6%). The majority of the HCHs detected were α (51%)

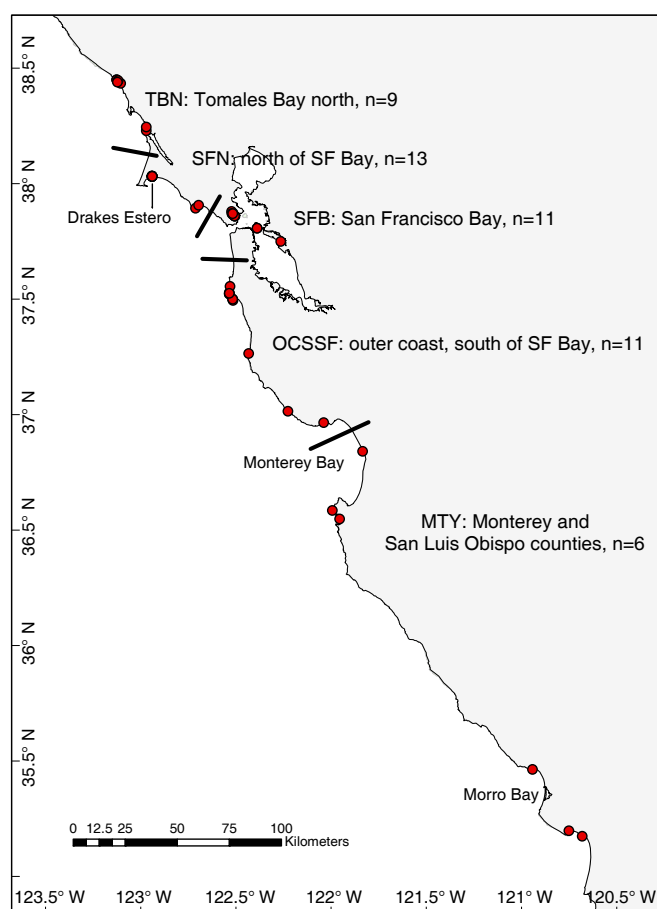


Fig. 1. Locations where harbor seal pups in the carcass group were stranded ($n=50$). Black bars delineate the five geographical strata used in the statistical analyses (MTY, OCSSF, SFB, SFN and TBN).

Table 1
Geometric mean contaminant concentrations and ranges in ng/g lipid weight for 177 harbor seal pups.

Compound	No suckling			Suckling unknown			Weaned			WR					
	NC			SD			WW			WD			WR		
	n	mean (range)	NR	n	mean (range)	NR	n	mean (range)	NR	n	mean (range)	NR	n	mean (range)	NR
HCb	37	6 (2–31)	11	16 (11–19)	45	11 (8–18)	12	7 (3–14)	33	6 (3–27)	9	5 (2–9)	11	11 (8–13)	
α-HCH	48	10 (4–26)	12	8 (2–20)	45	11 (5–21)	12	14 (6–41)	35	15 (6–35)	12	57 (16–320)	11	15 (10–24)	
β-HCH	45	10 (2–35)	12	10 (2–48)	42	11 (5–34)	9	21 (10–130)	34	14 (6–35)	11	77 (18–460)	10	16 (9–29)	
γ-HCH	13	1 (1–3)	0	<10Q	11	2 (1–2)	1	2 (2–2)	7	2 (1–3)	4	3 (2–9)	1	2 (2–2)	
α-Chlordane	22	4 (1–21)	11	8 (4–14)	36	4 (2–8)	11	7 (2–21)	20	4 (2–34)	8	5 (2–18)	9	4 (3–8)	
cis-Nonachlor	47	9 (2–69)	12	9 (3–29)	42	6 (3–22)	12	29 (7–440)	35	15 (4–120)	12	63 (8–600)	11	9 (5–16)	
γ-chlordane	2	1 (1–3)	2	2 (2–3)	0	<10Q	2	2 (2–3)	1	2 (2–3)	0	<10Q	0	<10Q	
Heptachlor epoxide	47	11 (5–52)	11	10 (4–32)	42	6 (3–19)	12	22 (8–83)	35	18 (8–40)	12	80 (5–790)	11	16 (8–46)	
Nona-III-chlordane	49	14 (5–72)	12	14 (2–74)	42	6 (3–27)	12	38 (9–240)	35	19 (7–74)	12	180 (12–2500)	11	25 (11–42)	
Oxychlorane	50	63 (18–290)	12	49 (4–220)	45	21 (6–150)	12	160 (20–810)	35	100 (32–360)	12	550 (29–5800)	11	120 (31–830)	
trans-Nonachlor	50	120 (26–780)	12	100 (20–370)	45	53 (22–250)	12	390 (61–2800)	35	200 (68–1100)	12	1400 (120–19,000)	11	220 (100–920)	
Dieldrin	40	6 (2–26)	11	10 (5–19)	44	8 (5–23)	12	16 (3–89)	34	12 (4–61)	12	16 (3–75)	11	8 (5–16)	
Mirex	37	4 (2–26)	9	5 (2–13)	16	3 (1–7)	11	13 (4–83)	30	5 (2–30)	12	57 (3–960)	11	10 (2–32)	
PCB17	19	1 (0–2)	10	1 (0–2)	29	1 (0–2)	8	1 (0–1)	27	1 (0–2)	8	1 (0–7)	11	1 (0–3)	
PCB18	14	2 (1–5)	3	2 (1–3)	20	2 (1–2)	4	4 (2–8)	8	3 (2–5)	3	3 (2–8)	5	3 (2–6)	
PCB28	44	5 (1–13)	12	5 (2–11)	43	5 (3–9)	12	10 (4–42)	35	8 (3–26)	12	18 (4–71)	11	6 (4–10)	
PCB31	35	2 (1–12)	11	4 (1–9)	41	3 (2–7)	10	5 (1–15)	35	3 (2–8)	11	5 (2–29)	11	4 (3–9)	
PCB33	7	1 (1–4)	4	2 (2–2)	4	1 (1–2)	1	2 (2–2)	2	2 (1–2)	0	<10Q	2	3 (1–6)	
PCB44	29	3 (1–12)	10	5 (3–9)	37	4 (3–6)	10	9 (3–30)	33	6 (3–18)	12	11 (2–63)	11	4 (3–7)	
PCB49	50	16 (3–95)	12	11 (4–31)	44	8 (4–37)	12	48 (7–400)	35	40 (5–230)	12	120 (12–1400)	11	21 (10–73)	
PCB52	50	46 (11–330)	12	34 (9–89)	45	23 (10–120)	12	140 (17–1800)	35	120 (14–680)	12	380 (34–4400)	11	77 (25–350)	
PCB66	39	4 (1–15)	11	6 (3–10)	38	4 (3–6)	11	11 (3–50)	33	7 (4–24)	12	19 (3–67)	11	5 (3–8)	
PCB70	37	4 (1–22)	11	7 (5–14)	44	6 (4–10)	10	10 (3–46)	34	6 (3–19)	12	13 (3–56)	11	5 (4–9)	
PCB74	50	18 (4–78)	12	15 (4–47)	44	8 (4–33)	10	48 (9–270)	35	34 (6–180)	12	160 (15–1600)	11	22 (12–55)	
PCB82	30	1 (0–2)	7	1 (1–2)	21	1 (1–2)	10	2 (0–10)	30	1 (1–4)	9	3 (0–18)	9	1 (1–2)	
PCB87	50	16 (3–65)	12	13 (5–37)	44	9 (4–35)	12	48 (9–280)	35	30 (5–130)	12	140 (14–1300)	11	20 (12–57)	
PCB95	50	17 (3–110)	12	14 (4–30)	45	13 (7–61)	12	59 (9–550)	35	43 (4–260)	12	150 (18–1600)	11	30 (14–110)	
PCB99	50	180 (31–1300)	12	120 (10–360)	45	61 (14–630)	12	590 (54–5800)	35	410 (45–2800)	12	1900 (82–25,000)	11	350 (87–2800)	
PCB101	50	150 (26–740)	12	110 (16–300)	45	59 (20–400)	12	430 (63–2700)	35	310 (34–1900)	12	1300 (98–14,000)	11	220 (74–1000)	
PCB105	50	31 (5–110)	12	23 (4–58)	45	13 (5–57)	12	82 (13–570)	35	58 (10–210)	12	260 (25–2500)	11	38 (19–85)	
PCB110	50	22 (4–89)	12	18 (6–38)	45	16 (8–48)	12	60 (12–480)	35	47 (5–170)	12	150 (18–980)	11	26 (18–43)	
PCB118	50	87 (13–390)	12	66 (12–170)	45	37 (14–180)	12	250 (43–2000)	35	160 (26–620)	12	790 (70–7100)	11	100 (46–290)	
PCB128	50	61 (7–480)	12	36 (2–89)	45	19 (4–260)	12	210 (17–2100)	35	130 (10–1000)	12	680 (34–9800)	11	120 (33–990)	
PCB138/163/164	50	560 (84–4200)	12	360 (26–970)	45	180 (33–2400)	12	1800 (150–18,000)	35	1200 (110–9130)	12	5800 (230–71,000)	11	1100 (250–9900)	
PCB149	50	85 (8–520)	12	52 (7–110)	45	39 (11–500)	12	290 (39–2700)	35	210 (14–1900)	12	840 (53–8300)	11	140 (58–1100)	
PCB151	50	25 (2–160)	12	15 (2–33)	44	11 (3–130)	12	81 (7–650)	35	61 (4–500)	12	240 (16–2000)	11	36 (15–340)	
PCB153/132	50	840 (130–6100)	12	540 (38–1400)	45	270 (46–3500)	12	2500 (203–25,000)	35	1800 (160–13,000)	12	7900 (310–90,000)	11	1600 (380–14,000)	
PCB156	50	22 (3–160)	11	17 (4–36)	39	8 (2–97)	12	61 (4–560)	35	47 (3–300)	12	190 (10–2300)	11	34 (10–250)	
PCB158	50	28 (3–220)	11	21 (6–47)	42	9 (3–120)	12	73 (4–840)	35	62 (4–540)	12	200 (10–2400)	11	41 (9–390)	
PCB170	50	85 (10–650)	12	49 (3–130)	45	25 (3–420)	12	250 (18–3200)	35	190 (11–1600)	12	790 (32–7900)	11	170 (38–1800)	

PCB171	50	18 (2-170)	11	12 (4-29)	29	8 (2-120)	11	71 (5-760)	33	51 (3-470)	12	160 (7-1600)	11	34 (8-390)
PCB177	50	51 (3-520)	11	32 (13-73)	43	16 (3-390)	12	170 (10-2700)	35	140 (4-1600)	12	520 (20-5200)	11	100 (27-1400)
PCB180	50	260 (35-1600)	12	150 (9-410)	45	76 (10-1300)	12	770 (56-8200)	35	580 (38-4700)	12	2500 (89-27,000)	11	540 (130-5200)
PCB183	50	72 (9-560)	12	40 (2-110)	45	20 (3-400)	12	220 (14-2700)	35	180 (10-1600)	12	670 (26-7500)	11	140 (31-1700)
PCB187/159/182	50	230 (25-1600)	12	120 (6-320)	45	69 (8-1300)	12	720 (52-8200)	35	540 (31-5000)	12	2300 (94-23,000)	11	470 (120-5200)
PCB191	31	6 (2-32)	7	3 (2-6)	9	4 (2-24)	9	21 (3-120)	29	12 (3-73)	9	61 (8-410)	8	8 (1-78)
PCB194	50	28 (2-170)	11	18 (8-32)	38	10 (3-140)	12	87 (6-1000)	35	60 (4-470)	12	330 (13-3800)	11	67 (15-710)
PCB195	44	9 (1-56)	10	5 (3-10)	19	5 (1-42)	9	48 (6-320)	31	25 (5-150)	10	77 (3-1100)	10	19 (3-210)
PCB199	50	40 (4-230)	12	21 (1-50)	44	12 (2-220)	12	130 (8-1500)	35	90 (5-760)	11	490 (20-5400)	11	97 (27-1100)
PCB205	17	3 (1-12)	2	3 (2-6)	3	4 (4-5)	4	20 (8-37)	20	4 (2-18)	8	25 (4-140)	3	14 (5-28)
PCB206	41	10 (1-43)	9	4 (2-8)	23	4 (2-16)	8	33 (4-370)	31	21 (5-130)	12	72 (4-1400)	10	21 (4-230)
PCB208	30	5 (1-16)	2	3 (2-3)	7	4 (2-16)	8	23 (3-140)	28	11 (3-60)	12	34 (2-510)	10	8 (2-98)
PCB209	23	4 (1-10)	1	3 (3-3)	5	3 (2-9)	8	15 (2-150)	27	6 (2-39)	9	36 (4-370)	7	8 (1-62)
o,p'-DDD	7	4 (1-19)	11	8 (4-16)	9	3 (2-6)	5	6 (1-15)	4	2 (1-6)	1	2 (2-2)	1	4 (4-4)
o,p'-DDE	17	2 (1-10)	5	3 (2-5)	1	2 (2-2)	5	4 (2-9)	5	4 (2-15)	7	9 (2-52)	0	<LOQ
o,p'-DDT	7	2 (1-3)	0	<LOQ	1	16 (16-16)	4	4 (3-8)	6	7 (2-16)	4	4 (3-7)	0	<LOQ
p,p'-DDD	50	30 (4-130)	12	44 (5-97)	45	25 (14-53)	12	100 (18-1110)	35	64 (5-530)	12	150 (14-1500)	11	23 (15-38)
p,p'-DDE	50	4700 (750-19,000)	12	3600 (579-14,000)	45	1600 (290-9500)	12	9500 (2000-44,000)	35	6210 (900-23,000)	12	56,000 (3900-15,000,000)	11	8500 (2000-26,000)
p,p'-DDT	50	84 (15-380)	12	60 (7-260)	45	32 (10-530)	12	220 (27-2700)	35	160 (32-1600)	12	770 (39-10,000)	11	150 (38-570)
PBDE28	6	3 (1-7)	0	<LOQ	2	3 (3-4)	6	12 (4-37)	15	7 (4-15)	8	28 (12-80)	1	3 (3-3)
PBDE47	50	280 (38-1600)	12	180 (23-670)	45	130 (44-810)	12	870 (170-8300)	35	650 (40-3900)	12	3500 (240-54,000)	11	540 (180-1800)
PBDE49	9	5 (2-9)	2	4 (4-4)	22	6 (4-12)	5	9 (6-18)	16	7 (4-32)	6	11 (6-17)	8	7 (4-10)
PBDE66	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	1	8 (8-8)	0	<LOQ
PBDE85	1	6 (6-6)	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ
PBDE99	48	23 (4-130)	11	16 (8-63)	44	20 (8-50)	12	86 (18-800)	32	64 (10-300)	12	260 (16-4400)	11	51 (22-390)
PBDE100	49	24 (4-104)	11	19 (10-63)	44	15 (6-110)	12	78 (20-1100)	32	59 (10-370)	12	270 (23-3500)	11	36 (19-140)
PBDE153	22	9 (2-33)	4	5 (3-9)	7	8 (4-18)	9	30 (4-230)	27	21 (6-79)	10	110 (6-1300)	9	18 (5-130)
PBDE154	4	4 (2-7)	0	<LOQ	1	4 (4-4)	5	12 (3-67)	6	5 (3-18)	7	17 (8-51)	1	5 (5-5)
PBDE183	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ	0	<LOQ
Sum.PCBs,ww	50	1100 (240-10,000)	12	820 (120-1700)	45	550 (180-7000)	12	3700 (380-45,000)	35	3300 (260-27,000)	12	7500 (1000-83,000)	11	2500 (650-25,000)
Sum.DDTs,ww	50	1800 (420-5800)	12	1600 (380-3800)	45	860 (250-4300)	12	3900 (1200-19,000)	35	3200 (520-13,000)	12	14,000 (2300-70,000)	11	3700 (1100-14,000)
Sum.PBDEs,ww	50	120 (24-830)	12	87 (14-220)	45	87 (21-640)	12	430 (110-3000)	35	370 (21-2500)	12	1000 (160-6100)	11	280 (120-1200)
Sum.CHLDs,ww	50	80 (25-330)	12	82 (22-190)	45	48 (18-220)	12	260 (47-1400)	35	170 (48-900)	12	570 (110-1800)	11	170 (80-810)
Sum.HCHs,ww	50	7 (1-23)	12	7 (3-26)	45	11 (6-28)	12	10 (4-25)	35	14 (6-33)	12	30 (10-60)	11	12 (6-23)
Sum.PCBs	50	3100 (440-21,000)	12	2000 (200-4700)	45	1100 (230-13,000)	12	9300 (860-86,000)	35	9300 (860-86,000)	12	30,000 (1300-330,000)	11	5900 (1500-48,000)
Sum.DDTs	50	4800 (810-19,000)	12	3800 (630-14,000)	45	1700 (320-10,000)	12	10,000 (2130-46,000)	35	10,000 (2100-46,000)	12	57,000 (3900-1,500,000)	11	8700 (2000-28,000)
Sum.PBDEs	50	330 (46-1900)	12	210 (23-820)	45	170 (61-960)	12	1100 (210-10,000)	35	1100 (200-10,000)	12	4200 (270-63,000)	11	660 (250-2100)
Sum.CHLDs	50	220 (57-1300)	12	200 (36-700)	45	94 (29-460)	12	670 (110-4100)	35	670 (110-4100)	12	2300 (180-29,000)	11	410 (180-1900)
Sum.HCHs	50	18 (2-63)	12	18 (5-69)	45	22 (10-53)	12	26 (6-170)	35	26 (6-170)	12	120 (17-780)	11	29 (10-51)

Pup groups are neonate carcass (NC), neonate died (ND), neonate released (NR), suckled died (SD), weaned died (WD), weaned released (WR). All values are in ng/g lipid weight unless indicated as wet weight (ww) in the compound name. PCB congeners are numbered according to Ballschmiter et al. (1992); PBDE congeners are numbered following the PCB numbering system.

and β (48%) isomers, with γ -HCH (lindane) detected in a small subset of animals (39 out of 205). Among the pups, contaminant concentrations followed the same rank order: DDTs>PCBs>PBDEs>CHLDs>HCHs except for the WW group of pups which had higher PCBs than other compounds (Table 1). The highest prevalence of γ -HCH was detected in the WD group (33%). Among the other age classes, γ -HCH was only detected in one fetus, and 2 wild-caught yearlings from SFB.

3.1. Pup morphology and blubber contaminants by group

Mass, blubber depth, percent lipid and sampling date differed by group (Table 2). Among the pups that were stranded without suckling (NC, ND, NR), mass, blubber depth, percent lipid, and sampling date increased between NC and NR (adjusted $p < 0.0005$ for all four parameters). Likewise, among the pups that weaned (WW, WD, WR), the wild-caught pups (WW) had greater mass, blubber depth, and percent lipid than the weaned pups that were stranded and died (WD). Among the pups sampled in the wild (WW) and the pups released from rehabilitation (NR and WR), there were no differences in mass, blubber depth, or percent lipid although there were differences in contaminant concentrations. The weaned pups that were stranded and died (WD) were larger and sampled later in the year than the neonate carcasses, but the blubber depth and percent lipid values were similar between the two seal groups (Table 2). Because of variability in percent lipid between groups, analyses of contaminants by group were based on lipid-normalized values.

Among the three groups that were stranded without receiving contaminants from milk, those that died soon after birth (NC) had significantly higher concentrations (except for HCHs) than those that increased their body mass in rehabilitation prior to release (NR, Table 2). This trend was significant for PCBs (adjusted $p < 0.005$), DDTs (adjusted $p < 0.005$), PBDEs (adjusted $p = 0.01$) and CHLDs (adjusted $p < 0.005$) but not for HCHs (Figs. 2–4). Pups sampled in the wild soon after weaning (WW) had greater PCBs and PBDEs than the pup groups that did not suckle although DDTs were not significantly greater than detected in the neonate carcass or neonate died groups. The weaned pups that were stranded after losing mass (WD), with blubber depth and percent lipid equivalent to the newborn carcass group, had significantly greater contaminant concentrations than all pup groups in all contaminant classes (Figs. 2–4). Some of the WD pups had values exceeding those detected in stranded adults (Table 3).

3.2. Summed contaminant compounds in the carcass group by strand location

There were no statistically significant differences in percent lipid by location (anova, $df = 4$, $p = 0.073$), although the pups from SFN had greater percent lipid than OCSF (adjusted $p = 0.05$). There were, however, differences between the wet weight and lipid weight contaminant classes by location so both wet weight and lipid weight analyses are presented in this section. Concentrations of PCBs in seals

from SFB were significantly greater than those from MTY on a wet weight basis (adjusted $p = 0.035$, Supporting Information Figure SI-1) and there was a wide range of PCB concentrations detected in seals from SFN. No differences in the lipid-normalized PCB values, as well as DDTs, CHLDs, or PBDEs (based on wet or lipid weights) were found among sampling locations. Wet weight HCHs were significantly greater in pups from north of SFB (SFN, $p = 0.009$ and TBN, $p = 0.026$); but, for lipid normalized HCHs, only TBN was greater than SFB ($p = 0.036$, Fig. 5). The ratio of DDTs to PCBs was significantly different between locations for wet weight and lipid weight concentrations ($p < 0.0005$); MTY was significantly greater and SFB significantly less than all other locations (Fig. 6). There were no differences in DDT:PCB among TBN, SFN and OCSF. There were no differences by location in the ratio of p,p' -DDE to p,p' -DDT.

3.3. Individual blubber contaminant compounds by sampling location

The first principal component explained 79% of the variability in the analytes and was negatively associated with all individual contaminants, most strongly with the PCB congeners. The second principal component explained an additional 7% of the variability in the dataset and was positively associated with most of the PCB congeners and negatively associated with the chlordanes, DDTs, PBDEs and some of the lower chlorinated PCB congeners (see Supporting Information Table SI-2). These principal components were able to distinguish the animals from SFB and MTY (Fig. 7). The variability in the SFN samples is also evident in Fig. 7 indicating that animals just to the north of San Francisco Bay are likely made up of a combination of animals from the more PCB-contaminated SFB as well as those from the more pesticide dominated areas to the north.

4. Discussion

This is the first study to compare contaminant levels among harbor seal pups based on stage of development and extent of suckling which is an important route of exposure. Blubber contaminant concentrations in harbor seal pups varied dramatically across a two to three week time scale depending on whether the animal was nursing, fasting, or fed an artificial diet during that time. This has consequences for how contaminant concentrations are compared among studies and locations as well as for evaluating the health risks to these animals from exposure to POPs.

Based on the decreased levels of contaminants in the pups released from rehabilitation (NR) compared with the neonatal carcass group, it appears that there is a dilution effect on the contaminants acquired during fetal growth for the seals fed milk matrix, salmon oil, and frozen herring in rehabilitation. Alternatively, it is possible, that the carcass group acquired greater concentrations of contaminants in utero than the other groups. Nevertheless, exposure through nursing exceeds exposure through prey consumption (Wolkers et al., 2004; Thomas et al., 2005) and pups entering rehabilitation may lower their

Table 2
Summary of the mass, blubber depth, percent lipid, and Julian day sampled for 177 harbor seal pups. Different lower case letters indicate significant differences between groups within the corresponding column.

Group	n	Mass (kg)	Blubber depth (mm)	Lipid (%)	Julian day sampled
		Mean \pm sd (range)	Mean \pm sd (range)	Mean \pm sd (range)	Mean \pm sd (range)
NC	50	7.4 \pm 2.2 ^a (4.0–13.3)*	9 \pm 4 ^a (3–23)*	39 \pm 14 ^a (18–69)	89 \pm 25 ^a (35–121)
ND	12	9.2 \pm 2.5 ^{a,b} (6.7–16.4)	12 \pm 7 ^{a,b} (4–29)	44 \pm 13 ^{a,b} (26–65)	114 \pm 30 ^b (64–166)
NR	45	18.0 \pm 2.4 ^d (12.9–25.0)	17 \pm 2 ^{c,d} (12–22)*	53 \pm 12 ^b (26–79)	176 \pm 22 ^d (122–206)
SD	12	11.2 \pm 5.8 ^{a,b} (7.9–27.0)*	13 \pm 9 ^{a,b,c} (1–30)	46 \pm 18 ^{a,b} (5–84)	144 \pm 18 ^c (125–198)
WW	35	19.2 \pm 3.8 ^d (12.8–26.8)	19 \pm 3 ^d (14–25)*	50 \pm 11 ^b (30–69)	143 \pm 13 ^c (126–171)
WD	12	13.2 \pm 4.0 ^{b,c} (8.3–18.7)	12 \pm 9 ^{a,b} (3–30)	34 \pm 23 ^a (5–74)	183 \pm 28 ^{d,e} (142–233)
WR	11	17.7 \pm 4.1 ^{c,d} (12.3–27.1)	16 \pm 4 ^{b,c,d} (11–25)	43 \pm 11 ^{a,b} (23–56)	210 \pm 26 ^e (179–256)

For mass: NC n = 38, SD n = 10; for blubber depth: NC n = 49, NR n = 44, WW n = 34.

* Indicates a decreased sample size.

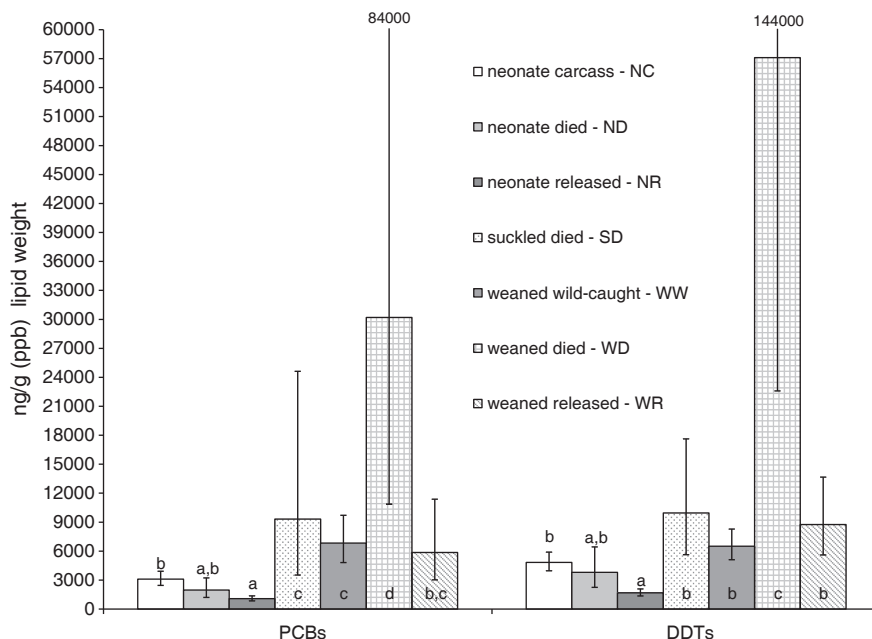


Fig. 2. Geometric mean summed PCBs and DDTs by contaminant exposure group. Error bars are 95% confidence intervals (values for upper levels are written in where they extend beyond the figure). Lower case letters in common mean no significant difference between those groups.

lifetime exposure to contaminants because they are not acquiring a substantial maternal legacy through milk. This point is illustrated by the 6- to 9-fold difference (Figs. 2–4) in blubber concentrations between the pups released from rehabilitation (NR) and the weaned wild-caught pups (WW) with equivalent mass, blubber depth and percent lipid.

Although lower concentrations of contaminants are stored in the blubber before birth than through nursing, this does not rule out the possibility of exposure effects in utero. Compared with a study in the River Tees of contaminants associated with pups aged 2 to 5 days that failed to thrive, PCB concentrations in our NC pups were lower, but

DDT concentrations were higher (Wilson, 2001). The seal from the NC group with the highest PCBs, DDTs, PBDEs and CHLDs on a lipid weight (lw) basis was a pup from San Francisco Bay with a severe congenital defect although the cause of the defect is not known (Harris et al., 2011).

Among the seal pup groups, blubber contaminant concentrations were highest in the weaned pups; and, in the weaned pups that lost mass, stranded, and died, concentrations were comparable to levels measured in the blubber of stranded adults. In addition to concentrating to high levels in the blubber, POPs are likely mobilized into the blood during this period of mass loss with the potential to exert health

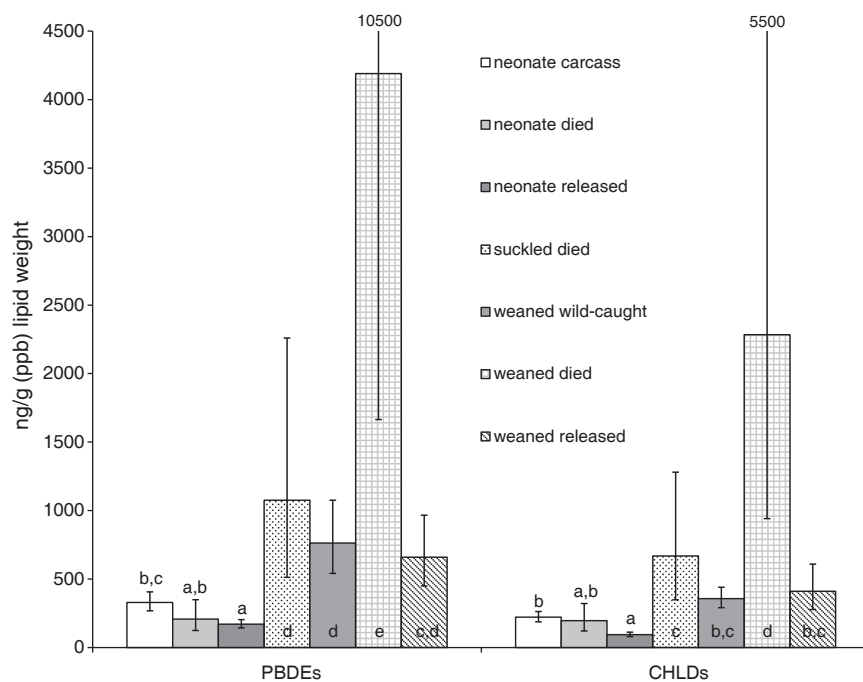


Fig. 3. Geometric mean summed PBDEs and CHLDs by contaminant exposure group. Error bars are 95% confidence intervals. Lower case letters in common mean no significant difference between those groups.

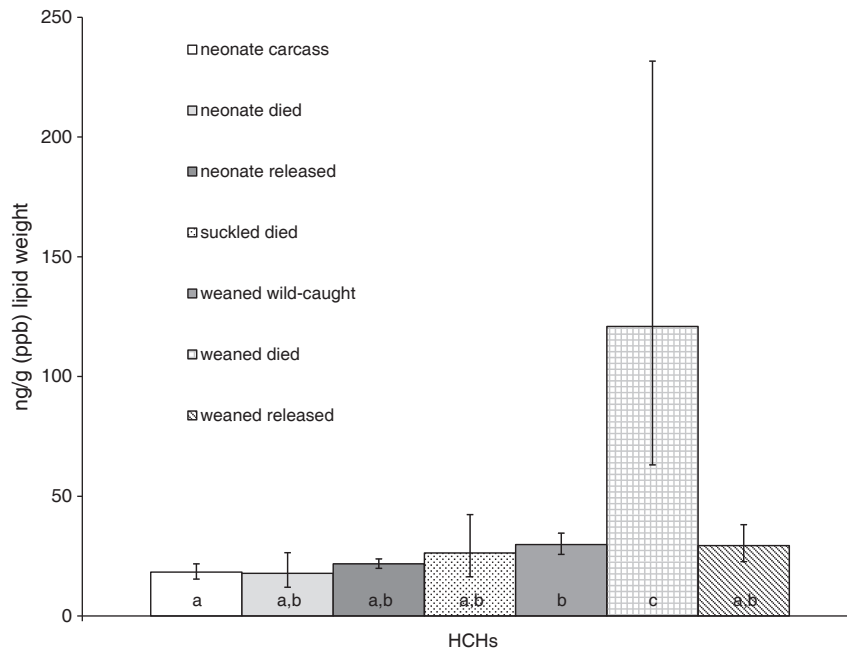


Fig. 4. Geometric mean summed HCHs by contaminant exposure group. Error bars are 95% confidence intervals (values for upper levels are written in where they extend beyond the figure). Lower case letters in common mean no significant difference between those groups.

effects on various systems just when these pups are learning to forage and fighting their first parasitic infections. In a previous study, [de Swart et al. \(1995\)](#) did not observe any changes in immune function with fasting and mobilization of contaminants into the blood of harbor seals; however, the seals in their study were older (over 3 years) and only lost 16% of their body mass. In elephant seals, [Debier et al. \(2006\)](#) found that greater concentrations of PCBs were mobilized into the serum of fasting females during late lactation. This increase in serum PCBs was more pronounced in leaner elephant seals suggesting that the retention capacity of the blubber was reduced more quickly in seals with lower lipid reserves ([Debier et al., 2006](#)). In the current study, the harbor seal pups were stranded near birth mass 3 to 8 weeks after weaning. Assuming a normal mass at weaning, these pups lost more than 50% of their body mass potentially mobilizing a large portion of the lipophilic contaminants acquired in utero and from milk into the serum where it has the potential to affect target organs.

Relatively few blubber contaminant concentrations have been reported for harbor seal pups in central California. Blubber contam-

inant concentrations were measured in eleven harbor seal pups in rehabilitation at TMMC in 1990 and 1991 similar to our ND and NR groups ([Shaw, 1998; Shaw, 2001](#)). Blubber concentrations of PCBs (1400–5300 ng/g lw) and DDE (700–13,000 ng/g lw) in this study compared with PCBs (200–13,000 ng/g lw) and DDE (520–9500 ng/g lw) reported by Shaw, suggest a possible decrease in PCBs over the years among seal pups entering rehabilitation, but little change in DDTs. [Risebrough et al. \(1980\)](#) measured blubber PCBs and DDTs from four dead pups from south San Francisco Bay and one from Double Point, Point Reyes National Seashore in 1976 which can be compared to our NC pups from SFB and SFN. PCBs (approximating Aroclor 1260) ranged from 4500 to 120,000 ng/g lw (this study 439–21,000 ng/g lw) and DDTs ranged from 7200 to 21,000 ng/g lw (this study 950–19,000 ng/g lw). Also within SFB, the PBDE concentration (sum of congeners 47, 99, 100, 153, and 154) for one full-term fetus (collected in April 1992) was 430 ng/g lw (66.9% lipid, [She et al., 2002](#)). This data point fits within our range of 49–1900 ng/g lw PBDEs. Recently PBDEs were reported in the blubber of harbor seal pups that were stranded off the coast of southern California ([Meng et al., 2009](#)).

Table 3

Mean (\pm sd) and ranges for mass (kg), blubber depth (mm), and lipid (%) and range for the summed contaminant classes in ng/g wet weight (ww) and lipid weight (lw) for age classes other than pups (nd = none detected). All samples were from stranded animals that died in rehabilitation except for the yearlings denoted with an asterisk that were captured and released in the wild.

	Fetus	Yearling	Yearling*	Subadult	Adult
n	2	3	9	2	9
Mass (kg)	1.5–3.4	26.5 \pm 3.5 (24.0–29.0)	28.9 \pm 2.7 (26.0–34.0)	35.5–39.0	64.0 \pm 18.3 (32.7–88.5)
Blubber depth	2–4	19 \pm 9 (11–29)	14 \pm 2 (10–17)	19–22	32 \pm 17 (5–60)
Lipid (%)	17–31	65 \pm 9 (58–76)	49 \pm 14 (22–71)	55–60	61 \pm 13 (39–73)
SumPCBs.ww	1200–1700	3100 (1500–6900)	3000 (610–13,000)	1900–6100	5200 (850–97,000)
SumDDTs.ww	1000–2100	4600 (1800–12,000)	4100 (2100–8400)	4400–10,000	5400 (2000–28,000)
SumPBDEs.ww	120–180	490 (240–720)	340 (93–1300)	190–620	580 (200–4300)
SumCHLDs.ww	52–120	190 (120–270)	160 (78–500)	90–280	220 (85–1900)
SumHCHs.ww	<LOQ–5.7	13 (10–19)	9 (5–12)	11–12	8 (4–19)
SumPCBs.lw	3900–9900	4800 (2000–12,000)	6300 (1500–29,000)	3200–11,000	8800 (1300–250,000)
SumDDTs.lw	5800–6800	7000 (2400–19,000)	8600 (4600–14,000)	7400–18,000	8971 (2900–73,000)
SumPBDEs.lw	580–700	750 (320–1200)	730 (310–2200)	320–1100	970 (300–11,000)
SumCHLDs.lw	300–390	290 (160–440)	340 (150–850)	150–510	370 (130–4900)
SumHCHs.lw	<LOQ–18	20 (16–31)	19 (11–51)	18–22	14 (5–45)

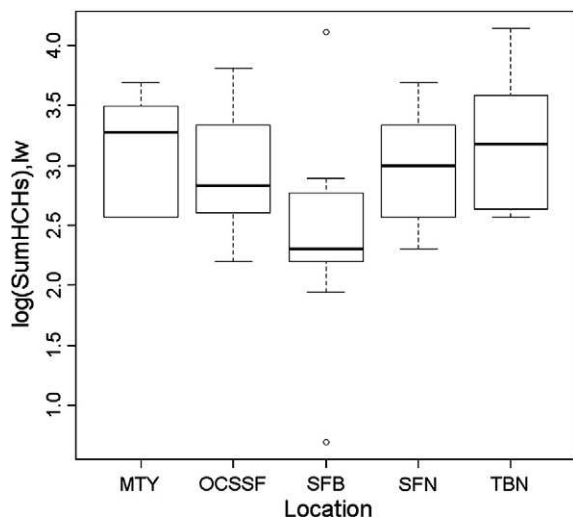


Fig. 5. Log transformed SumHCHs (ng/g lipid weight) by location. Locations are displayed from south to north. The plot shows the median value, the 25th and 75th percentiles, and maximum and minimum PCB values for each location. For SFB, the whiskers are 1.5 times the interquartile range of the data and two outliers are plotted individually.

It is not clear which of the groups the pups would be most comparable to in terms of nutritional history, but levels were similar to our most contaminated group (WD). Based on comparison with the Risebrough data from the 1970s, it appears that PCBs have declined in harbor seal pups from SFB, but DDTs are highly variable and in some cases are similar to the levels reported in seals during the peak of pesticide use.

With the exception of the wild-caught group of pups, the rank order of lipid weight contaminant classes reported in the current study is different than previously described from the livers of stranded harbor seals in California (PCBs > DDTs > CHLDS > HCHs, Kajiwara et al., 2001). In this study, DDTs were greater than PCBs as was reported in the livers of stranded sea lions and elephant seals from California (Kajiwara et al., 2001). The higher PCB concentrations in the wild-caught seal group (even greater than DDTs for the wet weight concentrations) may be a location effect, as most of the WW pups were sampled in SFB. Among the PCB congeners, the pattern was similar to that reported around the world with 153 and 138 as the biggest contributors (Debieer et al.,

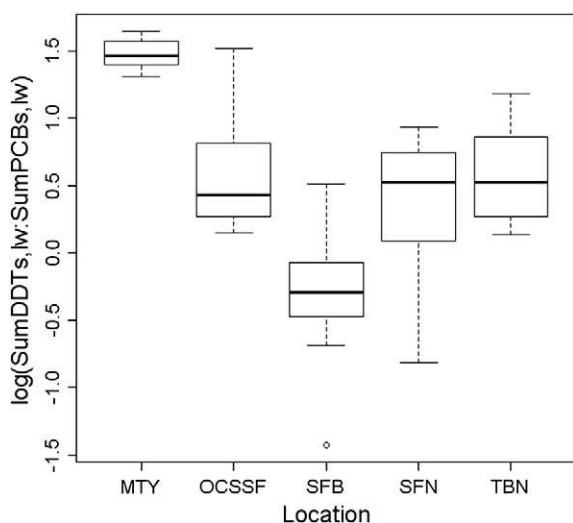


Fig. 6. SumDDTs:SumPCBs (ng/g lipid weight) by location. Locations are displayed from south to north. The plot shows the median value, the 25th and 75th percentiles, and maximum and minimum PCB values for each location. For SFB, the whiskers are 1.5 times the interquartile range of the data and one outlier is plotted individually.

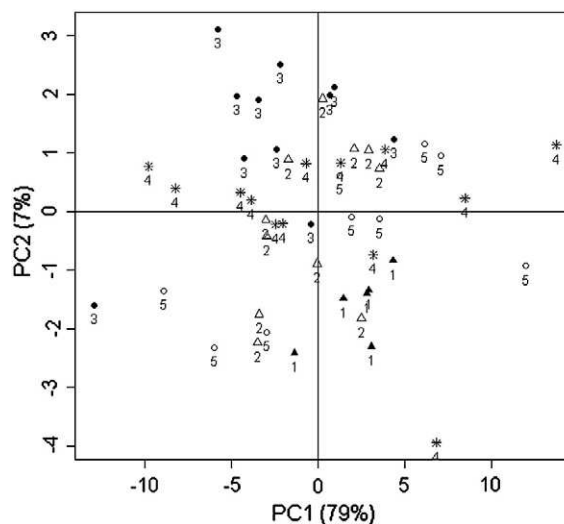


Fig. 7. The location of each sample (lipid weight) plotted by the first and second principal components (PC1 and PC2). 1 (filled triangle) = MTY, 2 (unfilled triangle) = OCSSF, 3 (filled circle) = SFB, 4 (asterisk) = SFN, 5 (unfilled circle) = TBN.

2003b). As seen in other studies, *trans*-nonachlor was the main contributor to sum CHLDS (Miranda Filho et al., 2009). We detected almost equal amounts of α - and β -HCH isomers in harbor seals in California which is an increase in the percent composition of β -HCH previously reported in harbor seal livers (Kajiwara et al., 2001). Kajiwara et al. (2001) reported a greater α -HCH in harbor seals compared with elephant seals and California sea lions, and α -HCH also is the predominant isomer in ringed seals in the Arctic (Kucklick et al., 2002; Addison et al., 2009). These species differences may reflect differences in HCH metabolism or differences in exposure level based on foraging locations. Exposure to the different isomers at different locations may also be a function of transport processes with atmospheric transport driving α -HCH levels and ocean current transport driving β -HCH levels (Li et al., 2002; Addison et al., 2009).

The current study is the first to report data on concentrations of CHLDS and HCHs in blubber of California harbor seals. In southern elephant seals (*Mirounga leonina*), HCHs (especially α -HCH) have a high transfer rate from maternal blubber to pup blubber during lactation (Miranda Filho et al., 2009). The seals that did not suckle (NC, ND, and NR) were therefore expected to have less HCH in their blubber than was measured in the recently weaned pups in the wild (WW), however no differences were observed. Overall, HCH levels were lower than the other contaminant classes. Concentrations of lindane (γ -HCH), the most potent HCH isomer, were substantially lower than levels found in UK harbor seals (Hall and Thomas, 2007), but even low doses of γ -HCH have been shown to be potent endocrine disruptors. For example, these compounds have been shown to cause chromosomal changes in human breast and prostate carcinoma cell lines such as inducing the formation of micronuclei and increasing gene expression of the BCL-2 protein (Kalantzi et al., 2004).

Differences in blubber contaminant concentrations by location among the pups that were likely stranded near where they were born (NC) presumably reflect maternal contaminant concentrations. This suggests that exposure levels among adults vary along the central California coast, with increased exposure to PCBs in SFB and increased exposure to DDTs to the south in MTY. These geographical patterns are consistent with those reported by NOAA's Mussel Watch Program which uses shellfish to monitor coastal contaminant trends. They detected medium to high levels of CHLDS, DDTs and dieldrin in mussels collected at sites in Monterey Bay; medium levels of DDTs and PCBs in SFB; and medium levels of CHLDS, DDTs, and dieldrin at sites north of Tomales Bay (Kimbrough et al., 2008). Differences in

harbor seal contaminant concentrations based on sampling locations were also reported by Ross et al. (2004) for harbor seals from the Puget Sound area. Ross et al. (2004) separated samples taken from seals in industrialized regions from those collected in more remote areas based on PCB homologue groups, with the higher chlorinated compounds more prevalent in their industrialized location. We observed some of the lower chlorinated PCBs (74 and 95) grouping with the pesticides in less industrialized locations (i.e. away from SFB), however others were part of the industrial signal (PCB 99, 101, 105).

The high variability in contaminant concentrations and contaminant profiles detected from the SFN location is informative in terms of maternal harbor seal movements and exposures. Most of the SFN pups (11 of 13) were recovered from a single beach at the mouth of Drakes Estero which is the largest nursery area for harbor seals in California with 300–500 pups born each year (Allen et al., 2004). The contaminant profiles of the pups from this location suggest that harbor seals from SFB as well as those from the less PCB-contaminated areas travel to Drakes Estero to give birth and nurse their pups emphasizing the importance of this nursery area for the harbor seal population especially for those seals inhabiting SFB that have lost much of their nursery habitat to human development (Allen, 1991). Individual variability may also reflect maternal characteristics such as birth order which we were not able to quantify in this study.

Differences in contaminant concentrations based on sampling location were not as distinct in this study as differences reported among three areas in Denmark (Storr-Hansen and Spliid, 1993). While there were differences in exposure that varied with location in our study, many harbor seals in central California likely use a combination of various locations that have different levels and proportions of POPs and may show less site fidelity than the seals sampled in Denmark. This is consistent with data from harbor seals tagged in Drakes Estero which showed three separate movement patterns: resident, breeder, and transient (Allen et al., 1987). In another study, a pregnant female that was routinely observed in Elkhorn Slough (MTY) traveled to SFB approximately 200 km away and gave birth and nursed her pup before returning to MTY (Greig, 2002).

In conclusion, contaminant concentrations in blubber of harbor seal pups from Central California vary dramatically based on age, extent of suckling and nutritional status, with the highest concentrations observed in harbor seal pups that suckled in the wild and then lost considerable mass during the post-weaning fast. This group is likely the most vulnerable to contaminant effects as these compounds also were likely circulating in high levels as the pups mobilized the fat stored in their blubber during fasting. However, contaminant effects on health and survival cannot be ruled out for any of the groups, and in the case of the neonatal carcass group, pups born in San Francisco Bay were exposed to higher concentrations in utero than pups born in other locations along the central California coast. High levels of DDTs were detected and it is unknown what effect these compounds may have on the health of developing harbor seals. Recent studies on rat models have shown synergistic effects between DDTs and biotoxins in utero (Tiedeken and Ramsdell, 2009, 2010) which has implications for marine mammals in central California that are routinely exposed to domoic acid (de la Riva et al., 2009). This study provides a comprehensive dataset of baseline contaminant concentrations stratified by important life history characteristics that can be used for future health and risk assessment work.

Role of the funding sources

Funding was provided by the Valentine Family Foundation (DG salary), The John H. Prescott Marine Mammal Rescue Assistance Grant Program (sample collection and DG salary), and The Marine Mammal Health and Stranding Response Program (sample analyses). None of the sponsors were involved in study design; collection, analysis, and

interpretation of data; writing the manuscript, or the decision to submit the paper for publication.

Acknowledgments

We thank everyone who helped with carcass retrieval, seal captures, and sampling including staff, volunteers, and interns from The Marine Mammal Center and Moss Landing Marine Labs, Point Reyes National Seashore, Fitzgerald Marine Reserve, California Academy of Science with special thanks to Tenaya Norris, Suzanne Manugian, Emily Andrews, Marjorie Boor, Sarah Allen, Sarah Codde, and Sarah Lenz. We appreciate the contaminant and data analyses provided by Bernie Anulacion, Richard Boyer, Jennie Bolton, Ron Pearce, Catherine Sloan and Karen Tilbury from NOAA Fisheries's Northwest Fisheries Science Center, and we are grateful to Catherine Sloan for improvements to the manuscript. Thanks to the Valentine Family Foundation, the John H Prescott Marine Mammal Rescue Assistance Grant Program for funding sampling, sample analyses and salary for DG. For the contaminant and lipid analyses, we are grateful to Dr. Teri Rowles of the NOAA Fisheries's Office of Protected Resources for her financial support under the Marine Mammal Health and Stranding Response Program.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2011.05.047.

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