Chlorinated, brominated, and perfluorinated compounds, polycyclic aromatic hydrocarbons and trace elements in livers of sea otters from California, Washington, and Alaska (USA), and Kamchatka (Russia)†

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Received 3rd December 2007, Accepted 26th February 2008
First published as an Advance Article on the web 12th March 2008
DOI: 10.1039/b718596k

Concentrations of organochlorine pesticides (DDTs, HCHs, and chlordanes), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs), and 20 trace elements were determined in livers of 3- to 5-year old stranded sea otters collected from the coastal waters of California, Washington, and Alaska (USA) and from Kamchatka (Russia). Concentrations of organochlorine pesticides, PCBs, and PBDEs were high in sea otters collected from the California coast. Concentrations of DDTs were 10-fold higher in California sea otters than in otters from other locations; PCB concentrations were 5-fold higher, and PBDE concentrations were 2-fold higher, in California sea otters than in otters from other locations. Concentrations of PAHs were higher in sea otters from Prince William Sound than in sea otters from other locations. Concentrations of several trace elements were elevated in sea otters collected from California and Prince William Sound. Elevated concentrations of Mn and Zn in sea otters from California and Prince William Sound were indicative of oxidative stress-related injuries in these two populations. Concentrations of all of the target compounds, including trace elements, that were analyzed in sea otters from Kamchatka were lower than those found from the US coastal locations.

Introduction

Sea otters (*Enhydra lutris*) were once distributed along the coastal regions of the North Pacific Ocean, from the Kuril Islands to Baja California.[1] However, due to commercial hunting in the 18th and 19th centuries, sea otters were extirpated from most of their historical range. Sea otters have been legally protected since 1911 under the International Fur Seal Treaty by the United States, Russia, Great Britain, and Japan.[1] Nevertheless, by the 1950s, sea otters had become extinct along the Pacific coast from Prince William Sound to Baja California, with the exception of one remnant population in the central California coast. The home range of sea otters is now divided into subregions, according to which the three subspecies, namely, the southern or California sea otter (*Enhydra lutris nereis*), the northern or Alaskan sea otter (*Enhydra lutris kenyoni*), and the Asian or Russian sea otter (*Enhydra lutris lutris*), is present. Southern sea otters are found only in California. Northern sea otters are found along the Pacific coasts of Washington, Alaska, and Canada. Asian sea otters are found in Russia and Japan. During the 1960s and 1970s, the Alaska Department of Fish and Game reintroduced sea otters into former habitats in Alaska, Canada, Washington, and Oregon, in collaboration with state and provincial wildlife management agencies. Although the reintroduction efforts have shown positive results in some areas, the rates of recovery of sea otter populations have varied from area to area.[2] The California sea otter population has increased at a rate of approximately 5% per year, compared with 17–20% per year for the northern populations.[1] Furthermore, the populations of both California and Alaskan sea otters declined again in the late 1990s.[3] Currently, the Alaskan sea otter population is listed as "threatened" under the Endangered Species Act. The decline in the populations in Alaska and California was attributed to high adult mortality rates.[4] While disease, pollution, and starvation can all influence sea otter mortality, the precise factors responsible for the recent decline in the sea otter populations are still unclear.

Sea otters are suitable indicators by which to assess the health of the coastal marine environment, because they are non-migratory, and because their diet is predominantly composed of sessile and slow-moving benthic invertebrates.[5] Thus, contaminant burdens in sea otters should reflect the animals' local habitats. Despite the reports of occurrence of contaminants in California

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† Electronic supplementary information (ESI) available: Two tables showing concentrations of contaminants in individual sea otter samples and biometric details of the sea otters analyzed are given. See DOI: 10.1039/b718596k

sea otters[6–12] prior to this study, residue concentrations of organic and inorganic contaminants in sea otters from Russia and Washington had not been measured. In this study, concentrations of organochlorine pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFCs), and 20 trace metals were measured in livers of sea otters collected from California, Washington, Alaska (Prince William Sound and Adak Island), and Kamchatka (Russia) for evaluation of geographical differences and patterns of exposures.

Materials and methods

Samples

All sea otters analyzed in this study were adult animals found stranded in coastal areas during 1995–1998. California sea otters were from Monterey Bay in central California ($n = 6$; 3M, 3F). Alaskan sea otters were collected from coastal areas of Clallam County in northern Washington ($n = 6$; 3M, 3F), Prince William Sound in southern Alaska ($n = 3$, 2M, 1F), and Adak Island in the Aleutians ($n = 2$; 2F). Russian sea otters were from the southern Kamchatka Peninsula ($n = 5$; 1M, 4F) (Fig. 1). Liver samples were collected from the carcasses at the time of necropsy, wrapped in aluminium foil, enclosed in sterile sampling bags, and stored at −20 °C until analysis.

Chemical analysis

Organochlorine pesticides, PCBs and PBDEs were analyzed following the methods described elsewhere.[8,13] Briefly, liver samples (~10 g each) were homogenized with anhydrous sodium sulfate (120 g), spiked with the internal standards PCB-30 and PCB-204 (25 ng each), and extracted with mixed solvents dichloromethane (300 mL) and hexane (100 mL) using a Soxhlet apparatus for 20 h. The solvent was concentrated (11 mL), and an aliquot (1 mL) was taken for gravimetric determination of fat content. Another aliquot (5 mL) was spiked with ^{13}C-labeled PCBs and ^{13}C-labeled PBDEs and subjected to column chromatography for removal of lipids. A third aliquot was spiked with deuterated PAHs and passed through gel permeation chromatography for the analysis of PAHs.

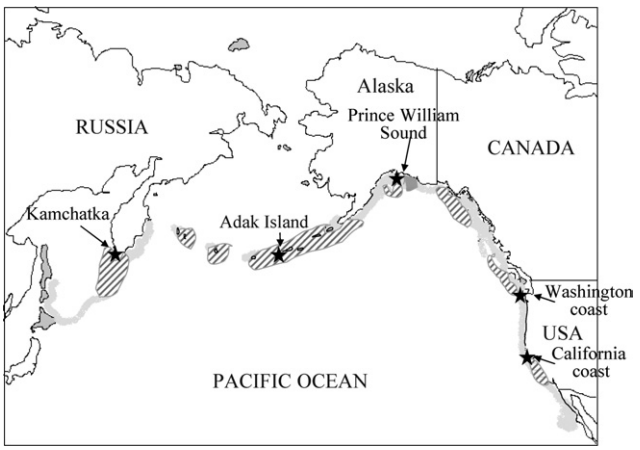

Fig. 1 Map of the Pacific Rim showing sampling locations of sea otters. Stars indicate sampling locations. Shaded, patterned areas indicate current sea otter range. Gray-shaded areas indicate historical sea otter range.

Sample extracts (2 μL each) were injected into a Hewlett-Packard 6890 gas chromatograph interfaced with a Hewlett-Packard 5973 mass spectrometer (GC-MS). Injections were made in the splitless mode, and samples were separated on a 30 m DB-5 (5% diphenyl/dimethylpolysiloxane) analytical capillary column with a 250 μm i.d. and a 0.25 μm film thickness. The MS was operated in an electron impact mode (70 eV) and selected ion monitoring mode (SIM). PBDE congeners were identified and quantified by SIM at *m*/*z* 406, 408 for triBDEs; 486, 484 for tetraBDEs; 564, 566 for pentaBDEs; and 642, 644 for hexaBDEs. Quantification was based on external calibration standard. PCB congeners were monitored at the two most intense ions of the molecular ion cluster. An equivalent mixture of Kanechlor (KC300, 400, 500, and 600), with known PCB composition, was used in the identification of PCB congeners. Quantification of PCB congeners was based on external calibration standards containing known concentrations of di- through deca-CB congeners. Concentrations of individually resolved peaks were summed to yield total PCB concentrations. Organochlorine pesticides were analyzed on an Agilent Technologies 6890 N gas chromatograph with electron capture detector. An external six-point standard calibration curve was used to quantify the sample concentrations from the peak areas for each pesticide. The term DDTs refers to the sum of *o*,*p*′-DDE, *p*,*p*′-DDE, *p*,*p*′-DDT, and *p*,*p*′-DDD. The term CHLs refers to the sum of *trans*-chlordane, *cis*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane. The term HCHs refers to the sum of α-, β-, γ-, and δ-HCH isomers. PAHs were quantified with an Agilent Technologies 6890 GC equipped with an Agilent Technologies 5973 series MS. A DB-5 fused silica capillary column coated with 5% phenyl methyl polysiloxane (30 m length × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA) was used. The PAH standards (AccuStandard, New Haven, CT, USA) consisted of 16 priority pollutant PAHs identified by the US Environmental Protection Agency (US EPA; Method 8310): naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and dibenzo[*a*,*h*]anthracene. The MS was operated under selected ion monitoring mode (SIM) for individual PAHs.

Concentrations of perfluorinated acids in liver tissue were determined by the ion pairing liquid extraction method described elsewhere.[14,15] Briefly, each liver sample (0.3 g) was homogenized in 3 mL of Milli-Q water. A 2 mL aliquot of this homogenate was spiked with 5 ng of perfluorobutanesulfonate (PFBS) and 5 ng of ^{13}C-perfluorooctanoic acid (^{13}C-PFOA) as internal standards. One millilitre of 0.5 M tetrabutylammonium hydrogen sulfate solution, 2 mL of sodium carbonate buffer (0.25 M, pH 10), and 5 mL of methyl-*tert*-butyl ether (MTBE) were added to the sample. After shaking for 30 min, the organic layer was separated by centrifugation, and the extraction was repeated with a further 5 mL of MTBE. The extracts were combined and evaporated to dryness under a gentle flow of nitrogen, before being reconstituted in 1 mL of methanol, and vortexed. The extract was filtered through a 0.2 μm nylon filter into an autosampler vial with a polypropylene cap.

Separation of perfluorinated acids was performed with an Agilent 1100 high performance liquid chromatograph (HPLC). Ten microlitres of the extracts were injected onto a 50 × 2 mm (5 μm) Keystone Betasil C_{18} column. A gradient mobile phase of methanol and 2 mM ammonium acetate was used. At a flow rate of 300 μL min^{-1}, the mobile phase gradient was ramped from 10% to 25% methanol in 7 min and then to 100% methanol at 10 min, held at 100% methanol for 2 min, and then ramped down to 10% methanol. For quantitative analysis, the HPLC was interfaced with an Applied Biosystems API 2000 tandem mass spectrometer (MS/MS). The MS/MS was operated in negative electrospray ionization mode. Analyte ions were monitored in the multiple reaction monitoring (MRM) mode. Parent and daughter ion transitions monitored for detection of PFOS, PFHS, PFBS, ^{13}C-PFOA, PFOA, and PFNA were 499 > 99, 399 > 80, 299 > 80, 370 > 170, 369 > 169, and 462 > 219, respectively. Quantitation was performed using a linear regression fit analysis weighted by $1/x$ of a single extracted calibration curve.

Trace metals were analyzed following the method described elsewhere.[16] Prior to analysis, liver samples were freeze-dried and homogenized; an aliquot (~0.1 g) of the sample was weighed in a vial lined with Teflon®. Liver samples were digested overnight in concentrated nitric acid (2 mL). Samples were then further digested in a microwave oven for 7 min at 200 W; this step was repeated three times. Concentrations of 19 trace elements (V, Cr, Mn, Co, Cu, Zn, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Tl, Pb, and Bi) were determined by an inductively coupled plasma-mass spectrometer (ICP-MS) (Hewlett Packard-4500, Avondale, PA, USA), with yttrium (Y) used as an internal standard. Concentrations of Hg were determined by a cold vapor atomic absorption spectrometer (Model HG-3000; Sanso, Tsukuba, Japan). The limit of detection for trace elements was 1 ng g^{-1}, dry wt, except for Sb and Cs (10 ng g^{-1}, dry wt) and Hg (50 ng g^{-1}, dry wt). Accuracy of the analysis was evaluated by analysis of certified reference materials: dogfish muscle (DORM2; National Research Council, Ottawa, ON, Canada) and bovine liver (SRM1577b; National Institute of Standards and Technology, Gaithersburg, MD, USA) along with the samples. Recoveries of all the elements were in the range of 89 to 104%. The results for trace elements are expressed on a dry weight basis, whereas the results for organohalogens are presented on a wet weight basis, unless specified otherwise.

Results and discussion

Organohalogens

Concentrations and profiles of organohalogen contaminants in the livers of sea otters varied by geographic location (Table 1). Sea otters from Monterey, central California, contained the highest concentrations of PCBs, DDTs, CHLs, and PBDEs, whereas sea otters from Prince William Sound, Alaska, contained the highest concentrations of PAHs (Fig. 2). Mean concentrations of organohalogens in sea otter livers from the five sampling locations were in the following order, from highest to lowest (left to right, top to bottom).

California (Monterey): DDTs > PCBs > CHLs > PBDEs > PAHs > HCHs > PFCs;

Washington (Clallam County): PCBs > DDTs > PBDEs > CHLs > HCHs = PAHs > PFCs;

Prince William Sound (Alaska): PCBs > DDTs > PAHs > CHLs > PBDEs > HCHs > PFCs;

Adak Island (Aleutian Alaska): PCBs > DDTs > PAHs > PBDEs > CHLs > HCHs > PFCs;

Kamchatka (Russia): PCBs > PAHs > DDTs > CHLs > HCHs > PFCs > PBDEs.

Geographic differences in organohalogen concentrations in sea otters suggest the importance of local sources of contamination. PCBs were the predominant contaminants in sea otter livers from all of the locations except for California (Fig. 2); DDTs were the predominant contaminants in California sea otters. Elevated concentrations of DDTs in California sea otters have

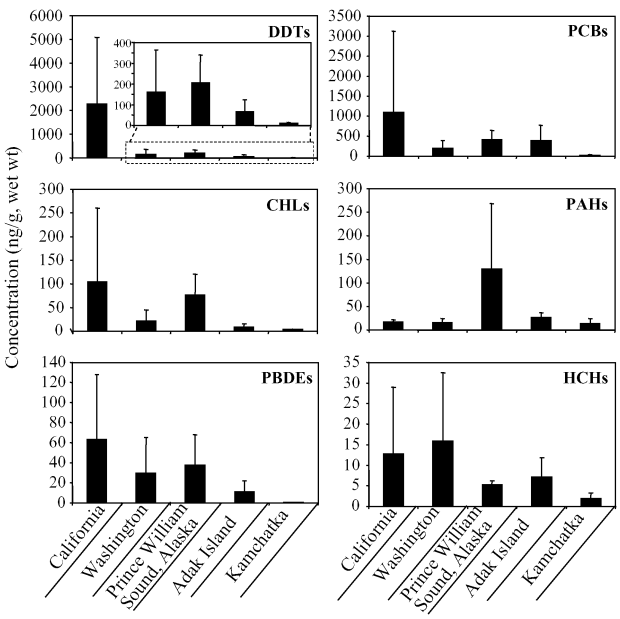

Fig. 2 Concentrations (mean ± SD) of DDTs, PCBs, CHLs, PAHs, PBDEs and HCHs in livers of sea otters from California, Washington, Alaska (Prince William Sound and Adak Island) and Kamchatka.

Table 1 Concentrations (mean ± SD) of organochlorine pesticides, PCBs, PBDEs, PAHs and PFCs (ng g^{-1}, wet wt) in livers of adult sea otters from California, Washington, Prince William Sound (PWS; Alaska), Adak Island (Alaska), and Kamchatka (Russia) collected during 1995–1998

Location	Gender	Lipid %	DDTs	HCHs	CHLs	PCBs	PBDEs	PAHs	PFCs
California ($n = 6$)	3 M, 3F	2.6 (1.6–3.8)	2300 ± 2800	13 ± 16	110 ± 160	1100 ± 2000	63 ± 65	17 ± 4.4	6.9 ± 3.8
Washington ($n = 6$)	3 M, 3F	3.3 (1.8–4.6)	160 ± 200	16 ± 17	22 ± 23	210 ± 180	30 ± 36	16 ± 8.5	8.7 ± 4.7
PWS, Alaska ($n = 3$)	2 M, 1F	3.7 (1.5–5.3)	210 ± 130	5.3 ± 1	77 ± 44	420 ± 230	38 ± 30	130 ± 140	3.6 ± 1.9
Adak Island ($n = 2$)	2F	4.0 (3.5–4.5)	65 ± 61	7.2 ± 4.6	9.2 ± 6.8	390 ± 380	11 ± 11	27 ± 11	6.5 ± 6.0
Kamchatka ($n = 5$)	1 M, 4F	3.4 (2.3–6)	11 ± 3.8	1.8 ± 1.4	4.1 ± 0.8	28 ± 9	0.5 ± 0.2	14 ± 10	1.9 ± 0.8

been attributed to past production activities along the southern California coast.[5,6,8,11,17] From 1948 to 1970, the world's largest DDT manufacturer discharged up to 20 tons of DDT wastes annually to the Los Angeles outfall on the Palos Verdes continental shelf, along southern California.[17] Marine mammals from the California coast contain some of the highest DDT concentrations ever reported.[17,18] Mean concentration of PCBs in California sea otters were 5-fold higher than the concentrations found in sea otters from the northern Washington coast. Mean concentrations of PCBs in sea otters from Prince William Sound (Alaska) and Adak Island were approximately 2-fold higher than the concentrations in sea otters from the Washington coast (Table 1; Fig. 2). Adak is a remote island, a few thousand kilometres away from mainland Alaska or Kamchatka. Adak Island was a military base from World War II until the late 1990s. Therefore, the PCB exposures of sea otters in this remote island are expected to derive from local military activities. An earlier study reported higher PCB concentrations in sea otters from Adak Island than in otters from California.[5] The mean concentration of PCBs in livers of adult sea otters from Adak Island collected during 1991–1992 was 310 ng g^{-1}, wet wt,[5] a value comparable to what was found in our study (390 ng g^{-1}, wet wt). Concentrations of PCBs and DDTs in Russian sea otters were 2 orders of magnitude lower than the concentrations found in California sea otters. Mean concentrations of total PCBs in sea otters from California, Prince William Sound, and Adak were above the toxicological threshold value of 8700 ng g^{-1}, lipid wt, reported for aquatic mammals.[19]

After PCBs and/or DDTs, PAHs showed the next highest concentrations in livers of sea otters from Prince William Sound, Adak, and Kamchatka (Table 1; Fig. 2). Concentrations of PAHs in livers of sea otters from Prince William Sound, Alaska, were significantly higher than the concentrations found in sea otters from other locations ($p < 0.05$). The high concentrations of PAHs in sea otters from Prince William Sound can be attributed to local sources. Mussels sampled in 1992 and 1993 from the beaches of Prince William Sound, that had been oiled by the massive *Exxon Valdez* oil spill of March 1989, contained total PAH concentrations ranging from 10 to 6000 ng g^{-1}, dry weight.[20] Oiled sea otters that were found dead in early April 1989 contained total PAH concentrations as great as 1780 ng g^{-1}, wet wt.[21] Although debate continues over the origin of PAHs in biota from Prince William Sound, the mean concentration of total PAHs in livers of sea otters from this location was 5- to 10-fold greater than in sea otters from other locations studied. From 1996 to 1998, wild sea otters in an area in Prince William Sound that had been oiled had significantly higher induction of cytochrome P4501A (CYP1A), a bioindicator of exposure to aromatic hydrocarbons, than did otters from an un-oiled area, indicating some level of continuing exposure in the late 1990s.[22,23] A few studies have suggested that PAHs in biota and sediments from Prince William Sound could originate from natural oil seeps, shales, and coal.[24,25] Nevertheless, the concentrations of PAHs in sea otters from Prince William Sound were greater than those reported for California sea otters, which are also exposed to natural oil seepage occurring along the California coast.[12] Our results suggest that, in addition to the natural petrogenic hydrocarbon background, sea otters from Prince William Sound are exposed to PAHs originating from oil spill-related sources. The half-lives of PAHs in marine invertebrates are on the order of a few days to few weeks,[26] and are thought to be shorter in sea otters, due to metabolism. Fish and birds contained concentrations of monohydroxylated metabolites of PAHs that were higher than the concentrations of the parent compounds.[27,28] Although un-metabolized PAHs can have toxic effects, the ability of reactive metabolites (such as hydroxides, epoxides, and dihydrodiols) of some PAHs to bind to cellular proteins and DNA can lead to mutations, developmental malformations, tumors, and cancer.[26] Although the concentrations of PAHs measured in liver tissues of sea otters suggest ongoing exposures (at least until 1996, *i.e.*, the sampling period), further studies are needed to determine hydroxylated metabolites and protein/DNA adducts in the tissues of sea otters, to assess the ecotoxicological impacts of PAHs in this species.

Concentrations of PBDEs in sea otters were, on average, 2-fold higher in urbanized areas such as central California, than in sea otters from northern Washington and Prince William Sound (Table 1). Human population densities in 2006 in Monterey County (California), Clallam County (Washington), Kenai Peninsula Borough (Prince William Sound), Adak, and Kamchatka Peninsula were 47, 14, 1, 1, and <1 per km^2, respectively. The geographical trends in PBDE concentrations in sea otters were significantly correlated with the human population densities of the study area ($p < 0.05$). Concentrations of PBDEs in Alaskan sea otter livers were two orders of magnitude greater than those reported in the livers of Alaskan polar bears,[29] suggesting that the proximity of sea otters to urban sources, and a diet dominated by benthic organisms, play important roles in determining exposure levels. Sea otters from Kamchatka contained concentrations of PBDEs two orders of magnitude lower than those in otters in California, Washington, and Alaska.

Geographical differences in the concentrations of HCHs in sea otters were minimal (Table 1; Fig. 2). This lack of variability may be due to the low bioaccumulation potential and more dispersable nature of HCHs. Similarly, concentrations of PFCs did not vary considerably among the geographical locations (Table 1). Concentrations of CHLs in sea otters from Kamchatka and Adak were 5 to 10-fold lower than those found in sea otters from the other three locations.

Isomer/congener/metabolite profiles

The composition of isomers/congeners/metabolites of organohalogens in sea otter livers varied by location. Among PCBs, hexachlorobiphenyl was the major congener in sea otter livers, accounting for 37–46% of the total PCB concentrations (Fig. 3); hexachlorobiphenyls were followed by heptachlorobiphenyls in all of the locations except for Kamchatka. Higher percentages of tri-, tetra-, and nona-chlorobiphenyls relative to total PCB concentrations were found in sea otters from Kamchatka than were found in sea otters from other locations studied, suggesting the existence of distinctive PCB sources in this location. Russian PCB formulations such as Trichlorodiphenyl and Sovol[30] are thought to be the sources of PCB exposures in Russian sea otters. Greater proportions of hexa- and hepta-chlorobiphenyls in sea otters from the United States coastal locations are similar to what was reported earlier for marine mammals from the North Pacific Ocean.[31]

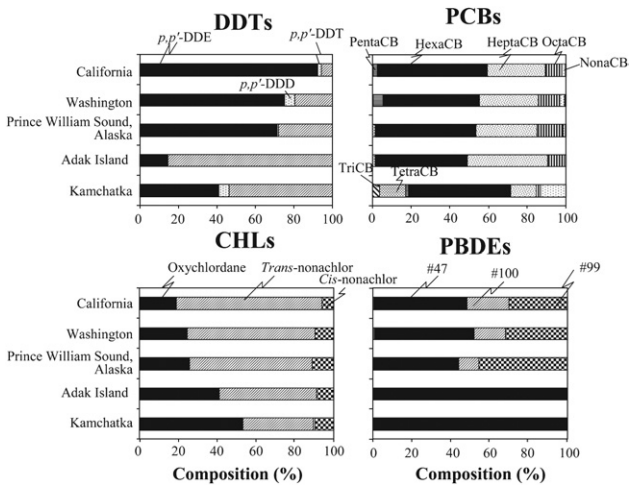

Fig. 3 Composition (%) of DDTs, PCBs, CHLs and PBDEs in the liver of sea otters from California, Washington, Alaska (Prince William Sound and Adak Island) and Kamchatka.

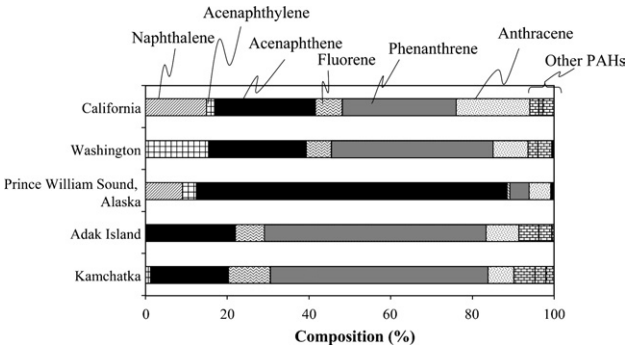

Fig. 4 Percent contributions of individual PAHs to total PAH concentrations in the livers of sea otters from California, Washington, Alaska (Prince William Sound and Adak Island) and Kamchatka.

Among DDTs, *p*,*p*′-DDE accounted for a major proportion of total DDT concentrations in all of the locations except Kamchatka and Adak Island (Fig. 3). High percentages of *p*,*p*′-DDE in sea otters from California, Washington, and Prince William Sound were suggestive of exposures to historical sources rather than current exposures. *p*,*p*′-DDE accounted for >90% of the DDT concentrations in sea otter livers from California.[5,6] *p*,*p*′-DDT accounted for a major proportion of total DDTs in livers of sea otters from Kamchatka and Adak. The latter finding suggests exposure of sea otters from Kamchatka and Adak to technical DDT preparations. As noted earlier, Adak Island was an active military base until the late 1990s, and it is probable that DDT was used on this island for the control of mosquitoes at least until 1996, when the sea otter samples were collected. Bacon *et al.*[5] reported the occurrence of greater proportions of *p*,*p*′-DDT in sea otters from Adak Island than in the sea otters from California.

Trans-nonachlor accounted for a major proportion of total CHL concentrations in our sea otters from California, Washington, and Prince William Sound (Fig. 3). This is similar to what was reported for marine mammals from the North Pacific Ocean.[6,18] *Trans*-chlordane was not found in any of the samples analyzed in the present study. Nevertheless, the proportion of oxychlordane to total CHL concentrations in sea otters from Kamchatka and Adak was higher than the proportions found in otters from the other three locations.

BDE-47 was the predominant PBDE congener in sea otters from all of the locations. Sea otters from Kamchatka and Adak contained only this congener, and at low levels (Fig. 3). Sea otters from Prince William Sound contained a high proportion of BDE-99, suggesting current exposure to PBDEs in this region of Alaska.

Among HCH isomers, β-HCH was the predominant isomer in all of the sea otters analyzed; α-HCH and γ-HCH isomers were rarely detected. These results suggest the lack of recent input of technical HCH in the coastal regions of the sea otters.

Profiles of PAHs in sea otter livers varied by location (Fig. 4). In general, di- and tri-cyclic PAHs accounted for 90–99% of the total PAH concentrations. The predominance of di- and tri-cyclic PAHs over tetra- and penta-cyclic PAHs suggests petrogenic sources of exposure. A natural oil seep has been reported to have been occurring off the coast of Santa Barbara (Coal Oil Point) for thousands of years.[32] In contrast to urban sources of PAHs, low-molecular-weight-PAHs are the primary constituents of natural petroleum seeps.[32] Similarly, sea otters from Prince William Sound contained a high proportion of acenaphthene. It is not known whether the elevated proportion of acenaphthene was due to specific sources of exposure or preferential bioaccumulation. Further studies with large number of samples are needed to examine the causes of elevated concentrations and characteristic profiles of PAHs in sea otters from Prince William Sound.

Trace elements

Concentrations of trace elements in livers of sea otters analyzed in this study are presented in Table 2. Among the 20 trace elements analyzed, In, Sb, Cs, Ba, Tl, and Bi were either rarely detected or else found at levels close to the limits of detection. Concentrations of essential elements such as Zn, Cu, and Mn varied within a 2–5 fold range among sea otters from the five sampling locations. Concentrations of these three essential elements were greater in sea otters from Prince William Sound than in the otters from other locations (Fig. 5). It has been shown earlier that diseased sea otters from the California coast contained greater concentrations of Mn and Zn than did non-diseased sea otters.[10] That finding was suggestive of induction of superoxide dismutase (SOD) enzymes, because Zn and Mn are important constituents of these enzymes. Exposure to elevated concentrations of organic pollutants, including PAHs, can induce oxidative stress, which in turn can lead to the induction of SOD. Our present finding of high concentrations of Mn and Zn in sea otters from Prince William Sound suggests that these animals have been exposed to contaminants that contribute to oxidative stress.

Liver concentrations of several toxic elements such as Hg, Cd, and Pb varied considerably among the locations. Cadmium concentrations were, in general, high in the livers of sea otters; the mean concentrations varied from 4.9 to 53 μg g^{-1} dry wt. Liver concentrations of Cd in sea otters from Alaska and Kamchatka were 3–10 fold lower than those found in sea otters

Table 2 Concentrations of trace elements (μg g^{-1}, dry wt) in livers of adult sea otters from California, Washington, Prince William Sound (PWS), Adak Island, and Kamchatka (Russia) collected during 1995–1998

Location		V	Cr	Mn	Co	Cu	Zn	Rb	Sr	Mo	Ag	Cd	Sn	Hg	Pb
California ($n = 6$)	Mean ±SD	0.36 ±0.42	4.2 ±8.4	12 ±3.5	0.10 ± 0.02	110 ±42	210 ±150	2.8 ±0.18	1.5 ±1.2	0.69 ±0.35	1.5 ±1.9	53 ±70	1.9 ±2.1	13 ±6.6	0.35 ±0.39
Washington ($n = 3$)	Mean ±SD	0.19 ±0.05	0.52 ±0.11	13 ±4.8	0.08 ±0.04	84 ±37	150 ±45	3.1 ±0.9	3.3 ±2.1	0.59 ± 0.01	0.78 ±0.34	35 ±29	0.61 ±0.11	8.6 ±8.1	0.06 ±0.02
PWS, Alaska ($n = 2$)	Mean	0.22	0.49	35	0.25	210	310	4.6	0.40	1.6	1.6	7.6	0.78	11	1.2
	Range	0.19–0.25	0.39–0.59	33–38	0.16–0.33	99–320	290–320	3.7–5.4	0.27–0.53	1.4–1.8	0.62–2.6	6.4–8.9	0.69–0.86	10–11	0.93–1.4
Adak Island ($n = 2$)	Mean	0.23	0.61	22	0.05	56	140	3.6	2.1	0.59	0.90	4.9	0.05	1.3	0.08
	Range	0.21–0.25	0.6–0.62	7.0–37	0.048–0.052	25–87	80–190	3.3–3.9	0.17–3.9	0.48–0.7	0.81–0.99	3.6–6.2	0.04–0.06	0.74–1.9	0.03–0.12
Kamchatka ($n = 5$)	Mean ±SD	0.05 ±0.04	0.49 ±0.23	8.6 ±0.85	0.05 ±0.01	47 ±13	110 ±23	3.9 ±0.63	1.1 ±0.81	0.68 ±0.14	0.84 ±0.2	15 ±12	0.14 ±0.07	1.8 ±1.8	0.23 ±0.11

Fig. 5 Concentrations (mean ± SD) of Zn, Cu, Mn, Cd, Hg and Pb in livers of sea otters from California, Washington, Alaska (Prince William Sound and Adak Island) and Kamchatka.

from California and Washington. These results suggest the existence of sources of Cd along the coasts of California and Washington. Sea otters from California accumulated some of the highest concentrations of Cd reported for any marine mammal to date;[10] this was attributed to their diet that comprises mussels and clams. In the present study, concentrations of Hg in sea otters from California, Washington, and Prince William Sound were an order of magnitude higher than in the sea otters from Adak and Kamchatka (Fig. 5). Concentrations of Pb in sea otters from Prince William Sound were an order of magnitude higher than the concentrations found in sea otters from the other four locations studied. Concentrations of Cr in California sea otters were an order of magnitude higher than the concentrations found in sea otters from the other locations.

In summary, this is a pilot study to report geographical patterns and concentrations of trace organic and inorganic contaminants in sea otter tissues. Concentrations and profiles of contaminants in sea otters varied according to the location, suggesting that sea otters are sensitive indicators of local pollution by organohalogens and toxic metals. Despite the geographical remoteness of Adak Island, concentrations of PCBs in sea otters from this location are notable. Occurrence of high concentrations of PCBs, DDTs, and Cd in California sea otters, and PAHs in sea otters from Prince William Sound suggests the need for further studies designed to assess the sources of these contaminants and the ecotoxicological implications for sea otter populations.

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