Published in final edited form as:

Environ Sci Technol. 2008 April 1; 42(7): 2334–2341.

Atmospherically Deposited PBDEs, Pesticides, PCBs, and PAHs in Western US National Park Fish: Concentrations and Consumption Guidelines

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Abstract

Concentrations of polybrominated diphenyl ethers (PBDEs), pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons were measured in 136 fish from 14 remote lakes in 8 western US National Parks/Preserves between 2003 and 2005 and compared to human and wildlife contaminant health thresholds. A sensitive (median detection limit –18 pg/g wet weight), efficient (61% recovery at 8 ng/g), reproducible (4.1 %RSD), and accurate (7 % deviation from SRM) analytical method was developed and validated for these analyses. Concentrations of PCBs, hexachlorobenzene, hexachlorocyclohexanes, DDTs and chlordanes in western US fish were comparable to or lower than mountain fish recently collected from Europe, Canada, and Asia. Dieldrin and PBDE concentrations were higher than recent measurements in mountain fish and Pacific Ocean salmon. Concentrations of most contaminants in western US fish were 1–6 orders of magnitude below calculated recreational fishing contaminant health thresholds. However, contaminant concentrations exceeded subsistence fishing cancer screening values in 8 of 14 lakes. Average contaminant concentrations in fish exceeded wildlife contaminant health thresholds for piscivorous mammals in 5 lakes, and piscivorous birds in all 14 lakes. These results indicate that atmospherically deposited organic contaminants can accumulate in high elevation fish, reaching concentrations relevant to human and wildlife health.

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Introduction

Organic contaminant measurements in environmental compartments such as snow(1–3), water(3–5), sediment(6,7), vegetation(8,9), and fish(10–16), have demonstrated that cold, high elevation ecosystems can selectively accumulate some semi-volatile and persistent organic pollutants(4). Semi-volatile organic compounds (SOCs) volatilize at warmer temperatures, and condense or are scavenged to the earth's surface more readily at cold temperatures(17,18). Furthermore, SOCs can be magnified across elevational, temperature, and precipitation gradients(1,18) as well as up food chains. Additionally, pesticide deposition in the annual snowpack of western US high elevation ecosystems has been positively associated with proximity to past and current agricultural activity (2). Although enhanced accumulation of SOCs in high elevation fish has been observed in European mountains(10–12) and the Canadian Rockies(13), there is very limited data on the accumulation of SOCs in high elevation fish across the western US (15,19), and what, if any, risks these contaminants may pose.

Chemical fate and transport studies in ecosystems benefit from the measurement of multiple SOCs with different sources and/or physical-chemical properties which aid in understanding mechanisms of chemical emission, distribution, transport, uptake and degradation(16,20). Because fish often contain the highest concentrations of organic contaminants in aquatic ecosystems(21), and because they are relevant to human as well as wildlife health, fish are an important environmental compartment for ecosystem fate and transport studies.

To date, most multi-contaminant methods for fish have focused on similar classes of SOCs (22,23) or are used as commercial food safety screening methods with high part-per-billion (ppb) detection limits(24,25). These methods can fail to detect analytes in a large number of environmental samples(26,27). Few methods have been shown to quantify more than two classes of SOCs at concentrations below 1 ppb (1 ng/g) in fish (28). Because pesticides and other SOCs are often estimated at less than 1 ppb in fish tissues, analytical methods are needed to quantify SOCs in fish at these concentrations (10,11,29).

Our objectives were to develop and validate an analytical method to measure PBDEs, pesticides, PCBs, and PAHs in fish, including concentrations below 1 ppb, and to assess if measured SOC concentrations in fish from remote western US National Park/preserve lakes were relevant to human and wildlife health.

Experimental

Materials

Approximately 130 fish from 14 lakes in 8 U.S. National Parks/preserves (Table S1, Figure S1) were collected as described previously(30) or by gillnet and setline (Denali National Park). Field blanks were obtained by exposing foil, bags, and scalpels to air and water in the same manner and time as sample collection. The samples were stored in a –25 °C freezer until analysis. National Institute of standards and Technology (NIST) fish standard reference material (SRM) #1946 (Lake Superior Lake Trout -1997) was purchased from the National Institutes of Standards and Technology (NIST, Gaithersburg, MD) for method validation.

Chemical standards and reagents were purchased, prepared, and stored as described previously(3).

Sample Preparation and Analysis

Sample preparation details can be found in the supporting information. Whole fish homogenates were analyzed to better assess piscivorous wildlife contaminant exposure. Whole fish and method blanks (150 g baked sodium sulfate) were homogenized with liquid nitrogen in a food processor. Following the addition of 32 isotopically labeled recovery surrogates, samples (~20 g ww, 1.8 g SRM) were extracted using pressurized liquid extraction. Interferants were removed from extracts using silica adsorption chromatography and gel permeation chromatography. Final extracts were reduced under nitrogen and spiked with 4 isotopically labeled internal standards prior to analysis by gas chromatographic isotope dilution mass spectrometry (GC/ID-MS).

Purified extracts were analyzed by GC/ID-MS as described previously(3,31). The SOC_s measured, their characteristic ions, SIM windows, as well as the GC column and oven temperature program were previously described for the electron impact ionization MS (EI-MS) analysis(3) and in Table S2 for the electron capture negative ionization-MS (ECNI-MS) analysis. Quality assurance and control procedures were followed, including frequent analysis of calibration checks (25% of analyses), blanks (10%), duplicate injections (10%) and SRM analysis (10%), and are described elsewhere(3). All reported sample concentrations had their method blanks subtracted and were corrected by their surrogates' sample specific recoveries.

Method Validation

Estimated method detection limits (EDLs) were calculated in triplicate for three representative fish samples, lake (*Salvelinus namaycush*), brook (*Salvelinus fontinalis*), and rainbow trout (*Oncorhynchus mykiss*), collected from remote lakes in Denali, Sequoia, and Rocky Mountain National Parks respectively (Table S1). The procedure described in US EPA Method 8280A was used to calculate EDLs from each analyte's signal to noise ratios in selected ion chromatograms of each fish extract and standards(32). This estimation method was conducted for these three fish samples, (spanning species, age, and location) to assess the consistency of the EDL determination method.

An additional lake trout collected from Wonder Lake in Denali National Park was selected for method recovery experiments due to its moderately high lipid content (10%), relatively low concentrations of the target analytes, and sufficient sample mass to permit multiple analyses. Background SOC concentrations in this fish homogenate were measured in triplicate prior to triplicate fortification with target analytes (~8 ng/g ww). The three fortified aliquots were processed according to the analytical method except that recovery surrogates were not added to the sample prior to extraction to adjust for method recovery, but were added to the extract just prior to analysis in order to calculate analyte loss over the entire analytical method. Analyte specific method recoveries were calculated from method blank and background subtracted concentrations in the final extracts of these fortified aliquots.

Method precision and accuracy was assessed using five aliquots of ~1.8g of NIST SRM 1946, analyzed over a 5 month period. Less mass of the SRM was analyzed than in the US National Park fish due to higher target analyte concentrations in the SRM. The average analyte concentrations measured in NIST SRM 1946 aliquots using this method were compared to certified values for 31 comparable analytes.

Contaminant Health Thresholds

Contaminant specific health thresholds were calculated for recreational and subsistence fishing consumption patterns using US Environmental Protection Agency (EPA) risk assessment documents(33). The contaminant specific health thresholds discussed here were calculated fish contaminant concentrations that would likely lead to contaminant consumption exceeding US EPA Integrated Risk Information System (IRIS) reference doses or acceptable cancer risk levels for individual contaminants only, assuming typical recreation or subsistence fish consumption patterns(34). Additionally, lake-specific advisory fish consumption limits were calculated for recreational and subsistence fishing consumption using US EPA guidance on additive cancer risks(34). US EPA default recreational (17.5 g of fish per day) and subsistence fishing consumption rates (142 g of fish per day), adult body mass (70 kg individuals), and acceptable risk levels (lifetime excess cancer risk of 1:100,000) were used to calculate the contaminant health thresholds and likely lake specific advisory fish consumption limits(33). Contaminant health thresholds for recreational fishing were adjusted to account for differences between the measured whole fish SOC concentrations and likely exposure in trimmed and cooked fish fillets by increasing the contaminant threshold by 32%, equivalent to an average 32% reduction in organochlorine exposure estimated to be achieved due to trimming and cooking(33). Subsistence fishing health thresholds were not adjusted for reductions from whole fish SOC concentrations since subsistence consumption patterns are reported to be highly variable and often include the whole fish (soups, stews, etc.)(33, 35).

Wildlife contaminant health thresholds were derived from wildlife fish contaminant consumption criteria in the literature(36) for non-lethal reproductive and developmental wildlife health endpoints identified by the US EPA(37). For use in this work, the criteria was derived for piscivorous wildlife known to occur in the majority of National Parks and where non-lethal endpoints were used as indicators of a negative effect.

Results and Discussion

Chromotography and Blanks

This analytical method resulted in fish extract chromatograms with baseline separation of a large majority of the target analytes (Figure S2). In the few cases where complete baseline separation wasn't achieved, mass-spectral separation was achieved. Most analytes were not detected in method or field blanks, or measured concentrations were typically estimated below the quantitation limit (lowest point on the calibration curve). However, phenanthrene, PBDE 47, and PBDE 99 were measured in most method blanks with average mass corresponding to fish concentrations of 300, 15, and 25 pg/g, respectively. When analytes were quantified in method blanks, concentrations were less than 5% of sample

concentrations for all method recovery and SRM experiments, and averaged less than 5% of measured analyte values in western US National Park fish.

Method Validation

Estimated method detection limits (EDLs) for the 91 SOC ranged from 0.2 to 900 pg/g ww, with a median of 18 pg/g ww (Table S3). The EDLs were fairly consistent across the three different fish species, with an average 11% RSD (n=3). With the exception of nine PBDEs and endrin, all analyte EDLs were 100 pg/g ww or less. Analyte recovery over the entire method ranged from 31.4 to 98.3%, with an average recovery of 61.4% at environmentally relevant concentrations of ~8 ng/g ww. Analyte recoveries were reproducible, with an average standard deviation of 4.1% (n=3). Individual target analyte recoveries and their surrogate's recovery in the sample set differed by less than 12%, on average, suggesting recovery surrogates were generally representative of target analytes.

Concentrations for 19 of 31 comparable analytes with certified concentrations in NIST SRM 1946 were measured to within the NIST confidence intervals (Table S3). The concentrations of all 31 certified analytes averaged within 7%, and ranged less than 30% from NIST certified values (Table S3). Additionally, 8 SOC were measured which were not previously reported and/or certified in SRM 1946 (b-HCH, heptachlor, endrin, dacthal, endosulfan I, endosulfan sulfate, PBDE 155, PBDE 183). The polarity range of compounds measured in the SRM demonstrates the utility of this analytical method for measuring a broad range of SOC, at low concentrations in fish tissues.

SOCs in Western U.S. National Park Fish

The 10 most concentrated SOC measured in >75% of fish from western US National Parks were p,p'-DDE, dieldrin, PBDE 47, 99, PCB 153, 138, dacthal, trans-nonachlor, HCB, and endosulfan sulfate, respectively. Dieldrin, p,p'-DDE, dacthal and endosulfan sulfate concentrations were highest in Sequoia, Rocky Mountain and Glacier National Park fish (Figure 1 C and D). PBDE concentrations in fish across western US National Parks varied less than most other SOC, both within and between lakes. PBDE concentrations were highest in Mt. Rainier National Park fish, and lowest in the Alaskan National Park fish. The fish concentrations of 5 major PCB congeners were comparable between the Alaskan and Pacific Coast National Park fish (Sequoia, Olympic, Mt. Rainier National Parks), and lower in fish from the Rocky Mountains (Glacier and Rocky Mountain National Parks) (Figure 2A). In general, current use pesticide concentrations were highest in fish from Sequoia National Park, followed by Rocky Mountain and Glacier National Parks (Figure 1A and B), and lower in Pacific Northwestern (Olympic, Mt. Rainier National Parks) and Alaskan National Park fish (Denali and Noatak National Park/Preserve).

For most compounds, the variation in the fish SOC concentrations within lakes was almost as large as the variation in concentrations between lakes. Concentrations for only 28 of the most frequently detected SOC are presented here. Concentrations of PAHs and other SOC measured are not shown here because they were detected in less than 50% of samples, likely due to low ambient concentrations and rapid transformation and/or elimination from fish(38).

Comparisons to SOC_s in other Mountain Fish

When compared to salmonid fishes collected from similar high elevation lakes throughout Europe(10), PBDE concentrations measured in western US National Park fish were, on average, 3 times higher in concentration after adjusting for typical differences between muscle and whole tissue concentrations(33) (Table 1). Concentrations for most historic use SOC_s (HCB, DDTs, and HCHs) were 2–9 times lower in western US fish than European mountain fish(11). Because the European mountain fish and western US National Park fish studied here included similar fish species collected from cold, oligotrophic lakes, all within 3 years time, it is unlikely that the observed differences in the SOC concentrations are due to fish accumulation differences or potentially changing SOC emissions. Even a rapid PBDE doubling time of 6 years could not account for the 3 times higher PBDE concentrations in western US National Park fish. This may suggest that fish from western US National Parks are exposed to higher PBDE concentrations than similar European mountain fish, which is consistent with PBDE concentrations measured in other North American and European environmental compartments(39), and more recent European fish samples(16).

When compared to fish collected from a transect of mountain lakes in Canada(13), HCHs and chlordanes were, on average, 4–5 times higher in concentration in the Canadian mountain fish (Table1). The Σ DDTs and HCB concentrations in Canadian fish were comparable to western US National Park fish, while dieldrin was 3 times higher in concentration in western US National Park fish. Because the fish and lakes sampled in Canada and the western US were of similar species and productivity, and since dieldrin and chlordanes are similarly persistent and bioaccumulative, it is unlikely that differences in fish dieldrin and chlordanes concentrations are due to fish accumulation differences. This suggests that fish in western US Parks may be exposed to higher concentrations of dieldrin and/or lower concentrations of chlordanes and HCHs than similar fish from the southern Canadian Rocky Mountains. Elsewhere, fish collected from high elevation lakes in the Asian Tibetan Plateau (14) had comparable concentrations of DDTs, and 4–9 times higher concentrations of HCB and HCHs than these western US fish (Table 1).

Although dacthal and endosulfan sulfate residues were among the most concentrated and frequently detected SOC_s, it is not known if the current use pesticide concentrations measured in western U.S. high elevation fish are comparable or higher than fishes of other regions of the world due to their limited reports in the literature. Together, these comparisons suggest that fish in western US National Park lakes may be exposed to comparable or lower concentrations of most historic use pesticides than similar fish around the world, but higher concentrations of PBDEs and dieldrin.

Comparisons to SOC_s in Pacific Salmon

The average concentrations of DDTs, dieldrin, and PBDEs were 2–5 times higher in these western US National Park fish than ocean caught Pacific salmon (*Oncorhynchus* spp), while HCB, HCH and chlordanes concentrations were 3–19 times lower (Table 1) (40,41). Differences in the year of fish collection and analytical methodology likely do not account for these concentration differences because most samples were collected within a 2.5 year period and the analytical methods are similar, including the use of isotope dilution mass

spectrometry (33,41). Because the accumulation of these organohalogenes in fish is similarly affected by differences in fish lipid and age, it is not likely that lipid and age differences would explain both higher and lower SOC concentrations in the salmon. Differences in food webs, as well as ambient environmental concentrations, are likely responsible for the different SOC concentrations observed. This suggests that DDTs, dieldrin, and PBDEs are accumulated to higher concentrations in fish from high elevation aquatic ecosystems of western US National Park lakes than salmon from the Northeast Pacific Ocean.

Human Fish Consumption Criteria

Dieldrin and/or p,p'-DDE concentrations in just over half (77 of 136) of the individual fish (in 11 of 14 lakes) exceeded calculated subsistence fishing human contaminant health thresholds. Lake average dieldrin and/or p,p'-DDE concentrations in fish exceeded the contaminant health thresholds for subsistence fishing for 8 of 14 lakes. These lakes are located in Sequoia, Rocky Mountain, Denali, and Glacier National Parks, as well as Noatak National Preserve (Figure 1 C,D). The concentrations of 11 other SOC (with IRIS toxicity data) ranged 1 to 6 orders of magnitude below contaminant health thresholds for subsistence fishing (Figure 1). Additive lifetime cancer risks from each lake's average fish SOC concentrations exceeded the acceptable risk level at the subsistence fishing consumption level in all but three lakes (Table S4) largely due to cancer risk contributions from dieldrin concentrations. Additive cancer risk of subsistence fishing consumption was calculated by multiplying the fish SOC concentrations by the assumed consumption rates and each SOC's cancer slope factor, dividing it by assumed body mass (70kg), and summing these 'risks' for all SOC. Additive cancer risk exceeded acceptable thresholds when a lake's average fish SOC concentrations increased the lifetime risk of cancer by more than 1:100,000 (0.001%).

Lake average SOC concentrations in western US National Park fish were below recreational fishing contaminant health thresholds for all 13 SOC with IRIS toxicity data (Figure S3). However, average dieldrin concentrations in fish from 4 of the 14 lakes (Rocky Mountain, Glacier, and Sequoia National Parks) were within a factor of 1.5 of the contaminant health thresholds, and the concentrations of dieldrin in 13 individual fish (Rocky Mountain, Glacier, and Sequoia National Parks) exceeded the lifetime cancer contaminant health threshold for recreational fishing (Figure S3D). No other fish SOC concentrations measured in western US National Parks exceeded recreational fishing contaminant health thresholds and average concentrations in fish ranged 1 to 7 orders of magnitude below these health thresholds (Figure S3). Additive lifetime cancer risks from average fish SOC concentrations did not exceed the acceptable risk threshold for recreational fishing at any of the 14 western US National Park/preserve lakes (Table S4).

Calculated contaminant health thresholds for subsistence fishing were about one order of magnitude lower than recreational fishing due to higher estimated consumption rates and whole fish versus muscle consumption scenarios(33,35). It should be noted that the likelihood of the above risks being realized at these sites is limited by the remote locations, which limits the number of people exposed and their duration of exposure. Also, the confidence in the cancer slope factor for dieldrin has been classified as "low"(34), and there

is some debate about the accuracy in the use of upper-bound cancer slope factors and additive cancer risks employed in the US EPA risk assessment methods(42). Together, this suggests that the human health risks from fish-SOC ingestion could be lower than those calculated here(42). Although this risk estimation methodology does not fully include potential SOC interactions beyond cancer risk additivity, it remains the sole health based consumption advice that uniformly treats lifetime health risk due to fish contaminant consumption for such a broad range of chemicals. The contaminant health thresholds were risk estimations and did not characterize nutritional or health benefits associated with salmonid consumption, such as cardiac health risk reduction from increased omega-3 fatty acid consumption or potential dietary reduction in unhealthy fats due to food substitutions. These benefits from salmonid consumption may help some fish consumers more than a reduction in contaminant exposure.

Wildlife Fish Consumption Criteria

Lake average chlordane and Σ DDT concentrations in fish exceeded wildlife contaminant health thresholds for the Belted Kingfisher (*Ceryle alcyon*) in all 14 lakes studied (Figure 2B and C). However, chlordane and Σ DDT fish concentrations were below the health thresholds for mammals in the Pacific Northwest and Alaskan parks. Contaminant health thresholds for kingfishers and River Otters (*Lutra canadensis*) eating fish contaminated with dieldrin were exceeded at Sequoia, and Rocky Mountain National Parks but concentrations were sufficiently low at the other parks to be protective of wildlife health (Figure 2D). The contaminant health thresholds for the American Mink (*Mustela vison*) were exceeded only in Sequoia and Glacier National Parks and only due to Σ DDT concentrations in fish.

Comparing concentrations of historic use pesticides in fish to wildlife screening values suggests that some SOC concentrations could negatively impact piscivorous wildlife. However, it has been cautioned that the wildlife consequences of eating contaminated fish may vary with the health, sex, and reproductive status of the animal(36) as well as the amount of time the animals forage from the lake. The wildlife contaminant health thresholds(36) were developed using reproductive and developmental endpoints established by the US EPA(37); therefore, observation of changes in population numbers and health would likely be delayed. The nutrition derived from fish consumption is necessary for the survival of largely piscivorous wildlife and a balance exists between nutrition and the detrimental effects of SOC. Nonetheless, concentrations measured here suggest the potential for negative impact on wildlife due to fish SOC concentrations.

Using this multi-contaminant method and US EPA risk methodology, atmospherically deposited SOC in fish from western US National Parks were measured at concentrations relevant to human and wildlife health. The analytical method was validated to be sensitive, accurate, and reproducible and the concentrations of historic use pesticides were comparable to or lower than those measured in similar fish from Europe, Canada, and Asia. However, PBDE and dieldrin concentrations were uniformly higher in high elevation fish collected from western US National Parks/preserves than similar high elevation fish from elsewhere in the world and Pacific Ocean salmon.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Dr. Dave Stone for his assistance in interpreting US EPA contaminant consumption criteria. This work is part of the Western Airborne Contaminants Assessment Project, a collaborative venture between the National Park Service, the Environmental Protection Agency, the U.S. Geological Survey, Oregon State University, University of Washington, and the U.S.D.A. Forest Service. It was funded primarily through cooperative and interagency agreements with the National Park Service, and also included in-kind contributions from all of the project partners. Further information about WACAP can be found on the WACAP web site at: http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.cfm. This document has been subjected to appropriate institutional peer review and/or administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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FIGURE 1.

Concentrations of select current (A,B) and historic use SOC (C,D) in individual fish (symbols) and lake average fish (bars) from western US National Parks compared to estimated non-cancer (A,B) and cancer (C,D) contaminant health thresholds for subsistence fishing (lines). * - nd >50% of lake fish. SEKI – Sequoia, ROMO – Rocky Mountain, MORA - Mt. Rainier, OLYM – Olympic, GLAC – Glacier, DENA - Denali, GAAR – Gates of the Arctic National Parks, and NOAT – Noatak National Preserve

FIGURE 2.

Lipid normalized concentrations of PCBs (A), chlordanes (B), DDTs (C), and dieldrin (D) in individual whole fish (symbols), and lake average fish (bars) from Western US National Park lakes, compared to wildlife contaminant health thresholds (labeled lines). Gray bars are *Salvelinus* spp. brook trout (solid) and lake trout (hatched); white bars are *Oncorhynchus* spp. rainbow trout (solid) and cutthroat trout (hatched); the black bar is burbot and whitefish.

Table 1
Comparison of Recent Contaminant Concentrations in Fish muscle from Remote Areas (ng/g ww)

Location	Σ PBDE	dieldrin	HCB	Σ DDT	Σ HCH	Σ chlordane	Σ PCB	n	year	ref.
	average range	average range	average range	average range	average range	average range	average range			
Western US Parks ^{a,b}	1.1 0.18–5.7	0.68 0.01–9.5	0.26 0.01–1.3	4.3 0.16–34	0.063 0.001–0.52	0.058 0.005–3.5	1.1 0.10–4.6	136	2003–2005	this study
Tibetan Plateau	n/a	n/a	1.0 0.31–3.2	6.3 0.78–23	0.91 0.13–2.6	n/a	n/a	20	2005	c
European Mountains	0.38 0.07–1.1	n/a	0.42 0.14–1.0	19 0.25–65	0.54 0.10–1.6	n/a	6.3 0.68–17	163	2000–2001	d,e
Canadian Mountains	n/a	0.23 nd–1.0	0.35 0.014–1.9	5.6 0.17–52	0.25 0.023–1.2	0.23 0.03–1.0	7.7 0.5–59	91	1997,2001,03	f
Pacific Salmon	~0.2 ~0.04 ~ 5	~0.3 ~0.1 ~ 1	~0.8 ~0.3 ~ 3	~2 ~0.8 ~ 10	~0.7 ~0.4 ~ 11	~1 ~0.4 ~ 2.75	~2.5 ~1.1 ~ 10	47	2002	g,h

^a muscle tissue concentrations estimated using 68% whole fish concentrations (32% reduction);

^b Σ PCB= PCB#74,101,118, 138, 153, 183, 187;

^c (14);

^d (11);

^e (10);

^f (13);

^g (40);

^h (41);

n/a – not available