Chemical Burdens in Fish from Yosemite National Park

Compared to Human and Wildlife Health Consumption Thresholds

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Introduction

The importance of monitoring contaminants in fish has been discussed previously in Flanagan *et al*. (2014). In brief, semi-volatile organic compounds (SOCs) including pesticides, industrial by-products such as polychlorinated biphenyls (PCBs), and combustion by-products like polycyclic aromatic hydrocarbons (PAHs) may negatively impact human and wildlife health. SOCs are known to persist in the environment, bioaccumulate in food chains, and cause reproductive abnormalities, cancer, or chronic disease (Ackerman *et al.* 2008, Schwindt *et al.* 2009). Some pesticides (DDTs, chlordanes, and endosulfans) and PCBs are endocrine disruptors causing impairment to the reproductive system and other bodily functions (Schwindt *et al.* 2009).

SOCs are deposited to terrestrial ecosystems from the atmosphere in cold, high elevation and high-latitude sites. SOCs in fish were measured at national parks in the western U.S. and Alaska during WACAP. These results were compared with human and wildlife thresholds and some SOCs exceeded these limits in some fish (Ackerman *et al.* 2008, Landers *et al.* 2008, Landers *et al.* 2010, Schwindt *et al.* 2009). This report summarizes the contaminant concentrations in fish from Yosemite National Park (YOSE) collected from Vernon Lake in the Tuolumne River Watershed in 2012. The concentrations are also compared to fish from Mildred Lake collected in 2009 and other lakes within California's National Parks (NPs) including Summit Lake in Lassen Volcanic NP (LAVO) collected in 2009, Emerald Lake and Pear Lake in Sequoia and Kings Canyon NP (SEKI) collected in 2003-2007 during the Western Airborne Contaminants Assessment Project (WACAP) and also Bench Lake and Kern Point in SEKI collected in 2009. Finally, the contaminant concentrations at all these parks are compared to human and wildlife thresholds.

Study Design

The purpose of this study was to analyze the concentration of airborne contaminants from 19 fish (*Oncorhynchus mykiss spp.* (Rainbow Trout)) in YOSE from Vernon Lake (Table 1). The research stems from WACAP findings and was conducted to gain an understanding of fish contaminant burdens at Vernon Lake. Parks included in the current study and WACAP are shown in Figure 1.

Water bodies within selected parks were remote, high elevation, and removed from anthropogenic influence (e.g., roads, latrines, developed areas) to isolate the contribution of contaminant loading by atmospheric deposition. Rainbow Trout were selected because they were available within Vernon Lake.

Measurement of SOCs in Fish

The 19 fish (Table 1) were analyzed for the contaminants listed in Table 2. Whole fish homogenate was prepared, extracted, and analyzed following the method described in Ackerman *et al*. 2008 for a wide-range of pesticides, PAHs, and PCBs. Pesticides included both current-use pesticides (CUPs) and historic-use pesticides (HUPs, legacy contaminants now banned in North America). These SOCs are listed in Table 2 and are the same SOCs measured in fish collected for the WACAP study, excluding polybrominated diphenyl ethers (PBDEs) (Landers *et al*. 2008; Landers *et al*. 2010). Only fish with pesticide concentrations above the estimated detection limits (consistent with Ackerman *et al.* 2008) are shown in the figures.

Results

SOC Concentrations in Fish by Lake

Figure 2 shows the fish SOC concentrations by park. The pesticides that were measured in >75% of the fish samples at Vernon Lake included p,p'-dichlorodiphenylethene (p,p'-DDE), hexachlorobenzene (HCB), *oxy*-chlordane, *trans*-chlordane *trans*-nonachlor,

dacthal, and endosulfan 1 (Figure 1). The highest pesticide concentration (in ng/g lipid) measured was p,p'-DDE at 1310 ng/g lipid.

Comparison to WACAP Fish SOC Concentrations

Figure 3A-M show the fish pesticide concentrations in ng/g lipid measured Vernon Lake (Bench Lake and Kern Point Lake in SEKI), along with the fish pesticide concentrations measured at Summit Lake in LAVO (Flanagan Pritz *et al*. 2014), and Mildred Lake in YOSE, Pear Lake and Emerald Lake in SEKI from WACAP (Ackerman *et al*. 2008, Landers et al 2008), and also Bench Lake and Kern Point Lake in SEKI (Flanagan Pritz *et al*. 2014; Figure 1). Figure 4A-L shows the fish pesticide concentrations for these same lakes in ng/g wet weight (ww). In general, the pesticide profiles are the same for each site for both ng/g lipid and ng/g ww. To compare SOC concentrations in fish from the current study to WACAP, concentrations in ng/g lipid were used. Normalizing concentrations by lipid content of individual fish helps to account for differences in size and species between all of the fish. One fish from Vernon Lake, VERN-RN-26-4-8/4, was excluded from the statistical analysis and Figures because of low extraction efficiency of spiked isotopically-labeled compounds resulting in an inaccurate amplification of contaminant concentrations.

Concentrations (ng/g lipid) for the individual pesticides, endosulfan sulfate, total endosulfans (termed "endosulfans" - sum of endosulfan I, II and sulfate), individual and total chlordanes (termed "chlordanes" - sum of *oxy*-, *cis*,-, *trans*-chlordane, *cis*-, *trans*-nonachlor),dieldrin, pp-DDE, individual and total PCBs (termed PCBs – sum of PCB 101, 118, 138, 153, 183, and 187) were statistical different at Vernon Lake compared to Mildred Lake (p-value < 0.05) with higher concentrations measured at Mildred Lake. Mildred Lake had stastically similar concentrations of *oxy*-chlordane, endosulfan sulfate, total endosulfans as Pear and Emerald Lake at SEKI. Hexachlorocyclohexanes (HCHs) were not detected in fish from Vernon Lake, Bench Lake (SEKI), or Kern Point Lake (SEKI) but both were

detected in fish from Pear Lake and Emerald Lake while only a-HCH was only measured at Summit Lake in LAVO and Mildred Lake in YOSE.

Comparison of Fish SOC Concentrations to Human Health Thresholds

Similar to Ackerman *et al*. 2008, contaminant health thresholds for humans were adopted from the U.S. Environmental Protection Agency (EPA) to evaluate non-cancer and cancer contaminant health thresholds for recreational or subsistence fish consumption. These data are shown in Figure 4 and Tables 3 (subsistence fish consumption only). No fish SOC concentration in Vernon Lake exceeded the threshold for recreational fish consumption. The subsistence fish consumption threshold for dieldrin and pp-DDE were exceeded by 3 fish out of 19 and 7 out of 19 fish, respectively. One individual fish, Vernon-RN-12-1-8/4, had the highest concentration (1310 ng/g lipid) of pp-DDE than in any other fish collected from the 6 other lakes.

Comparison of Fish SOC Concentrations to Wildlife Health Thresholds

Similar to Ackerman *et al*. 2008, contaminant health thresholds for piscivorous wildlife (kingfisher, mink, and river otter) were derived from EPA nonlethal reproductive and developmental wildlife health end points as indicators of a negative effect. The data for chlordanes, dieldrin, and p,p'-DDE are shown in Figure 5 and Table 4. No individual fish from Vernon Lake, or the other six lakes, exceeded the chlordanes or dieldrin wildlife thresholds (Figure 5). However, one individual fish from Vernon Lake (Vernon-RN-17-5-8/4) exceeded the p,p'-DDE threshold for kingfisher. This is a lower frequency of exceedences than Pear Lake (2 out of 10), Emerald Lake (3 out of 10), and Mildred Lake in YOSE (4 out of 10). The fish from Vernon Lake had the highest lipid content (2.35g of extractable lipid) out of 19 fish collected from this lake with the average g lipid was 1.34 (±0.73 SD) g lipid. This fish likely had more capacity to store p,p'-DDE in greater quantities than the other fish

because of its higher lipid content. Established wildlife contaminant health thresholds for the remaining historic-use pesticides and for the current-use pesticides have not been developed.

Figure 1. Fish from national parks analyzed for SOC concentrations by the Simonich Lab: WACAP and additional CA parks. WACAP fish samples were collected in 2003–2006. Fish samples analyzed in the current study were collected in 2009 and 2012.

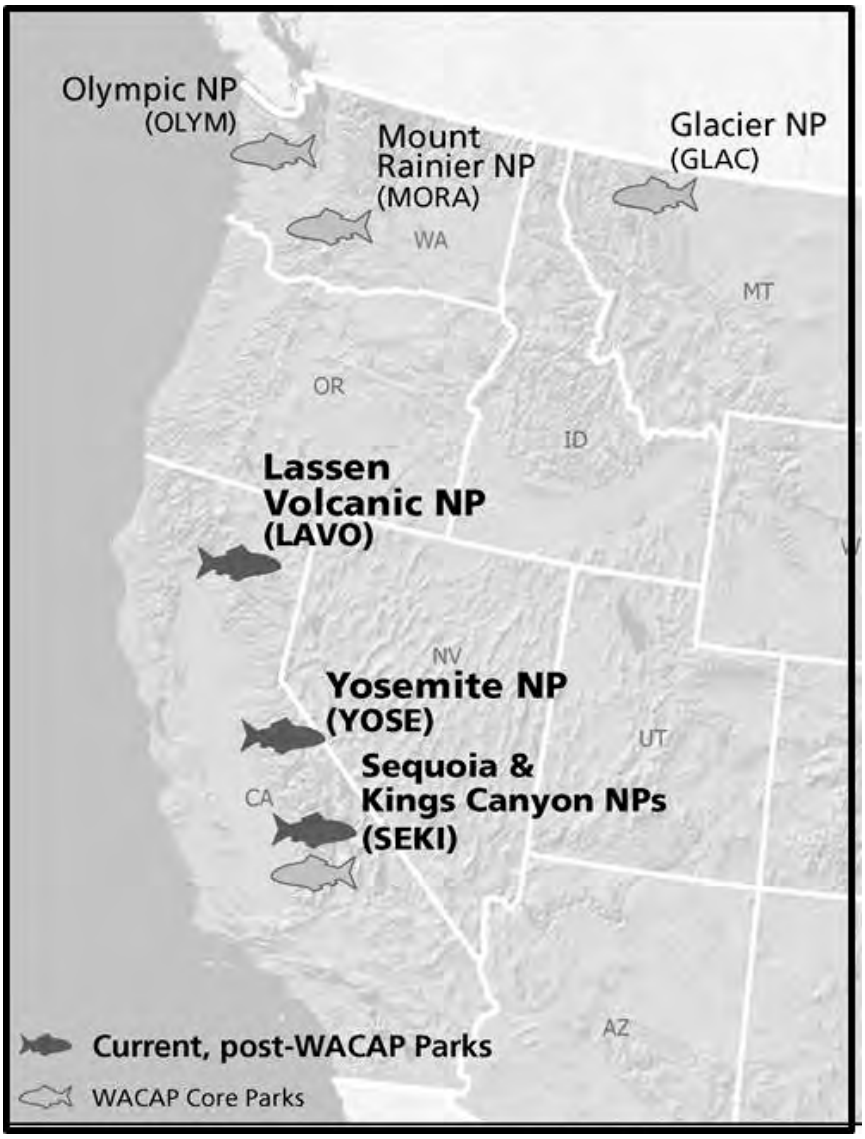


Table 1. Fish collected at Vernon Lake in YOSE in 2012. TBL: Total body length. SFL: Snout to fork length.

Sample Name	Species	TBL (mm)	SFL (mm)
VERN-RN-2-2-8/3	Rainbow Trout	170	158
VERN-RN-4-4-8/2	Rainbow Trout	172	159
VERN-RN-5-4-8/3	Rainbow Trout	148	135
VERN-RN-7-4-8/3	Rainbow Trout	150	144
VERN-RN-8-1-8/4	Rainbow Trout	276	259
VERN-RN-9-1-8/4	Rainbow Trout	245	232
VERN-RN-10-1-8/4	Rainbow Trout	322	300
VERN-RN-11-1-8/4	Rainbow Trout	375	362
VERN-RN-12-1-8/4	Rainbow Trout	352	336
VERN-RN-13-5-8/4	Rainbow Trout	150	139
VERN-RN-14-5-8/4	Rainbow Trout	167	160
VERN-RN-15-5-8/4	Rainbow Trout	210	198
VERN-RN-17-5-8/4	Rainbow Trout	311	297
VERN-RN-18-5-8/4	Rainbow Trout	435	414
VERN-RN-19-5-8/4	Rainbow Trout	343	336
VERN-RN-21-2-8/4	Rainbow Trout	270	245
VERN-RN-22-2-8/4	Rainbow Trout	370	350
VERN-RN-23-4-8/4	Rainbow Trout	224	216
VERN-RN-26-4-8/4	Rainbow Trout	381	365

Table 2. SOCs measured in fish by GC/MS using two modes of ionization.

Electron Impact Ionization	**Negative Chemical Ionization**
Pesticides and degradation products: o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, Methoxychlor, Acetochlor PAHs[1]: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene Surrogates: d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, Internal Standards: d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	Pesticides and degradation products: Hexachlorocyclohexanes (HCH) (α, β, γ, δ) Chlordanes[2] (cis, trans, oxy), Nonachlor (cis, trans), Heptachlor, Heptachlor Epoxide, Endosulfans[3] (I, II, and sulfate), Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene (HCB), Dacthal, Chlorpyrifos, Chlorpyrifos oxon, Trifluralin, Metribuzin, Triallate, Mirex PCBs[4]: PCB 74, PCB 101, PCB 118, PCB 138, PCB 153, PCB 183, and PCB 187 Surrogates: $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl), d_{10} – Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II Internal Standards: d_{14}-Trifluralin

[1] ΣPAHs= Chrysene+ Triphenylene+ Fluorene+ Phenanthrene+ Anthracene+ Fluoranthene+ Pyrene+ Retene+ Benz[a]anthracene+ Benzo[b]fluoranthene+ Benzo[k]fluoranthene+ Benzo[e]pyrene+ Benzo[a]pyrene+ Indeno[1,2,3-cd]pyrene+ Dibenz[a,h]anthracene+ Benzo[ghi]perylene

[2] Σchlordanes= *oxy*-chlordane+ *trans*-chlordane+ *cis*-chlordane+ *cis*-nonachlor+ *trans*-nonachlor

[3] Σendosulfans= endosulfan I+ endosulfan II+ endosulfan sulfate

[4] ΣPCBs= PCBs 101+ 118+ 138+ 153+ 183+ 187

Figure 2. Mean SOC concentrations in fish (ng/g lipid) for Vern Lake. Bars represent standard error. VERN-RN-26-4-8/4 was not included because of low extraction efficiency during sample preparation resulting in exaggerated contaminant concentrations.

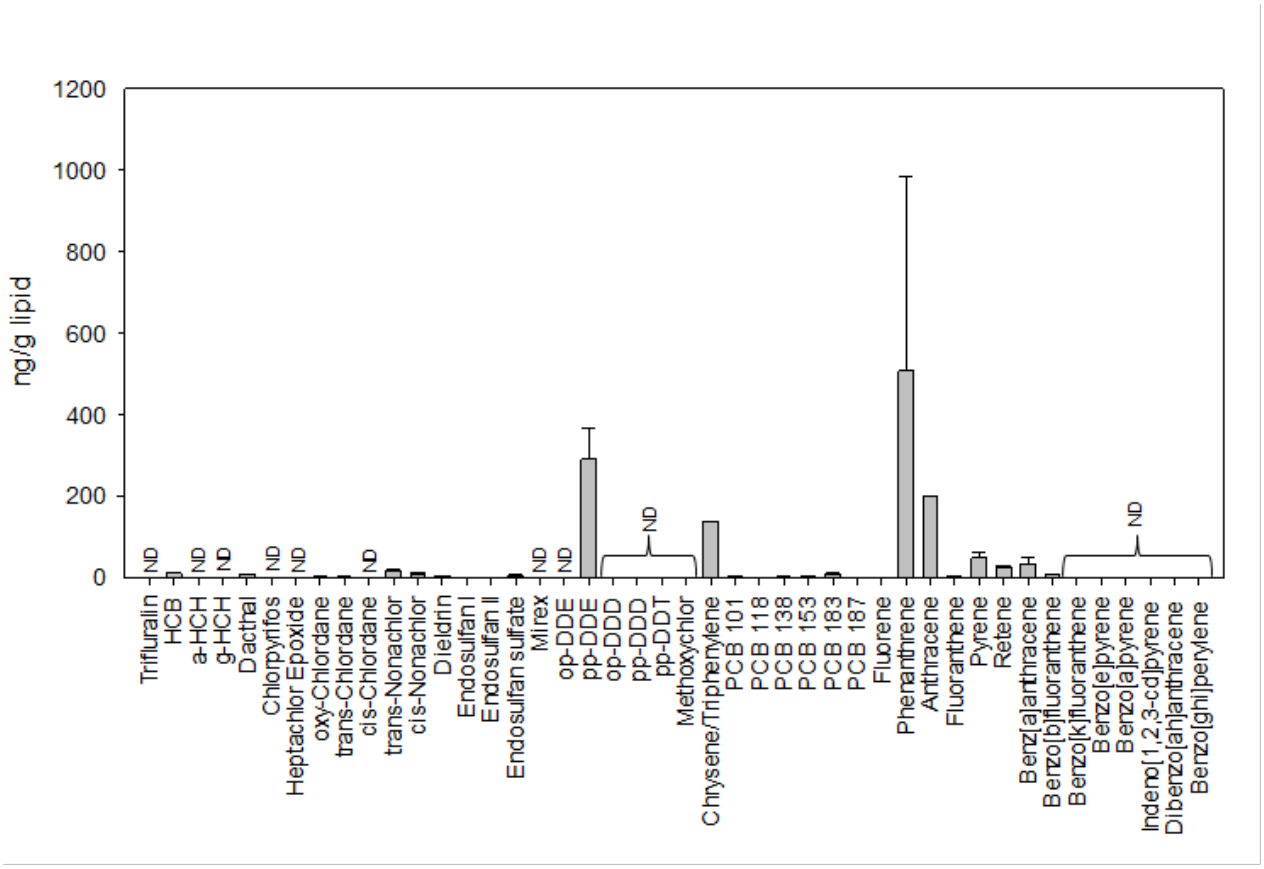
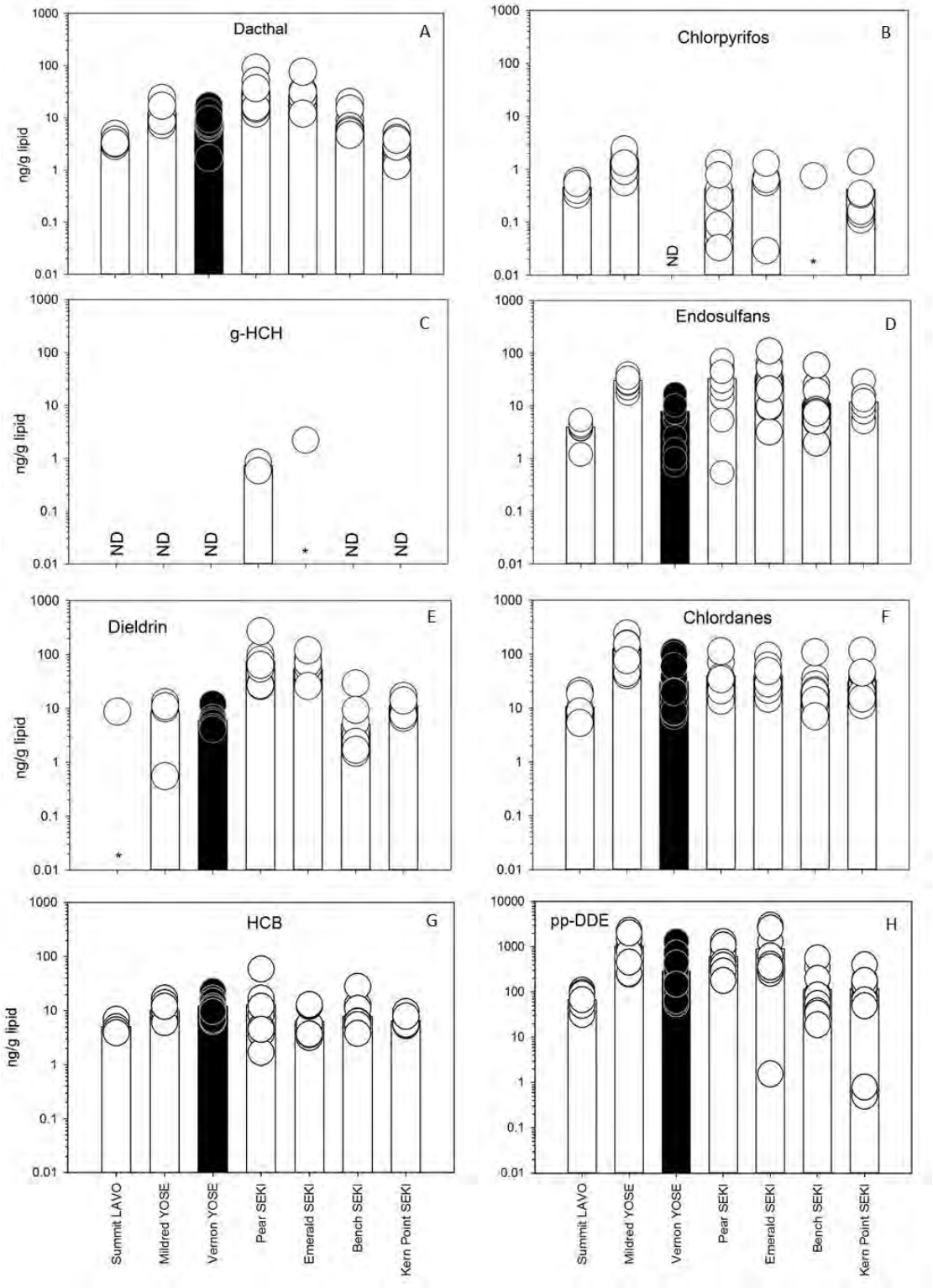


Figure 3 (A-M). Concentrations of the top 13 SOCs of concern in fish (ng/g lipid) at Summit Lake (LAVO), Mildred Lake (YOSE), Vernon Lake (YOSE) Pear Lake (SEKI), Emerald Lake (SEKI), Bench Lake (SEKI), and Kern Point Lake (SEKI). Top of bar indicates the mean concentration and the circles indicate concentrations of individual fish. Black bars depict data from current study; white bars depict previously published data from WACAP (Landers et al. 2010; Ackerman et al. 2008). ND, no detect; *, ND > 50% of lake fish.



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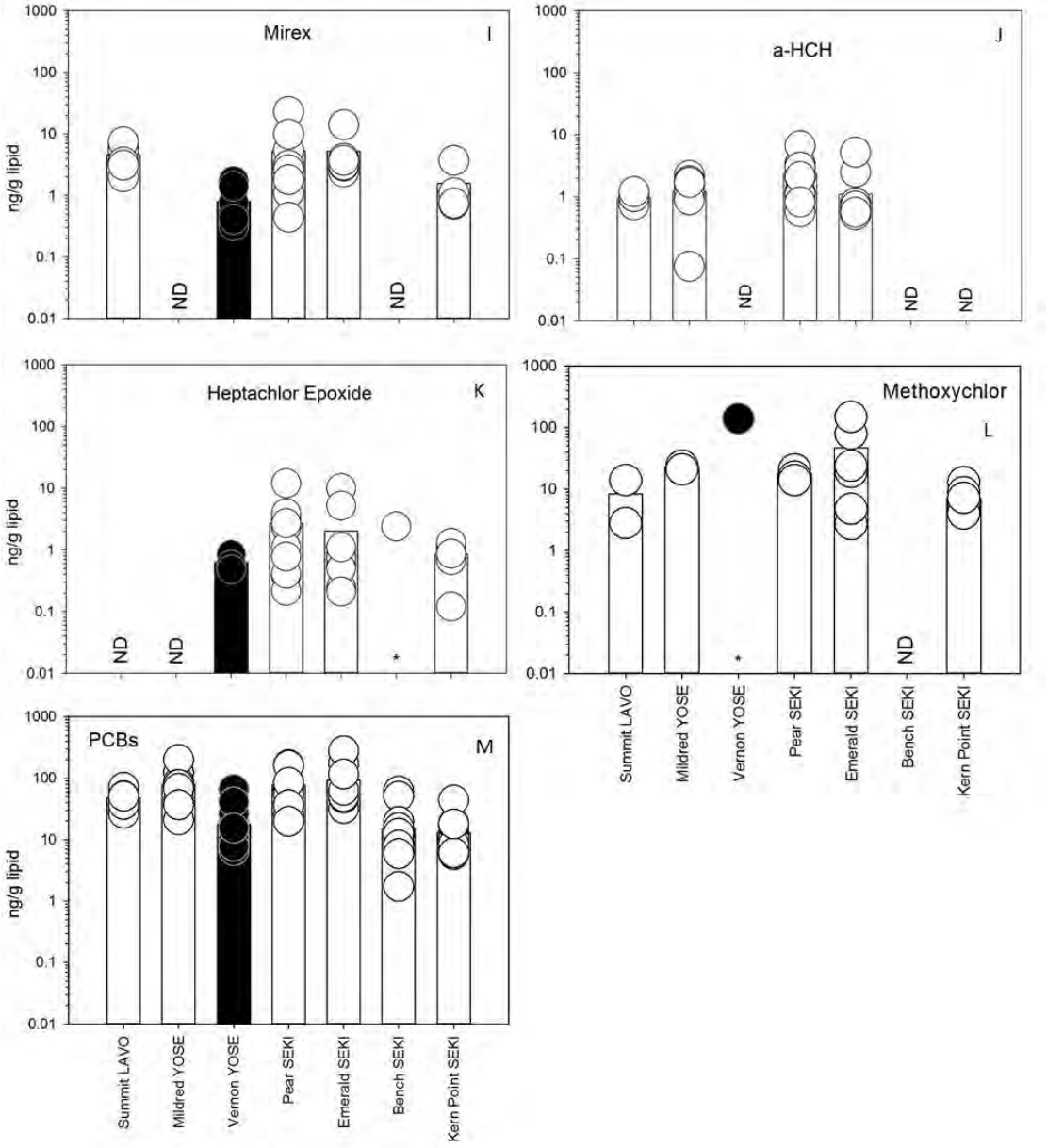


Figure 4 (A-L). Concentrations of SOCs in fish compared to human health consumption thresholds. Top of bar indicates the mean concentration and the circles represent the concentrations of individual fish. The solid line represents the threshold for recreational consumption and the dotted line represents subsistence consumption.

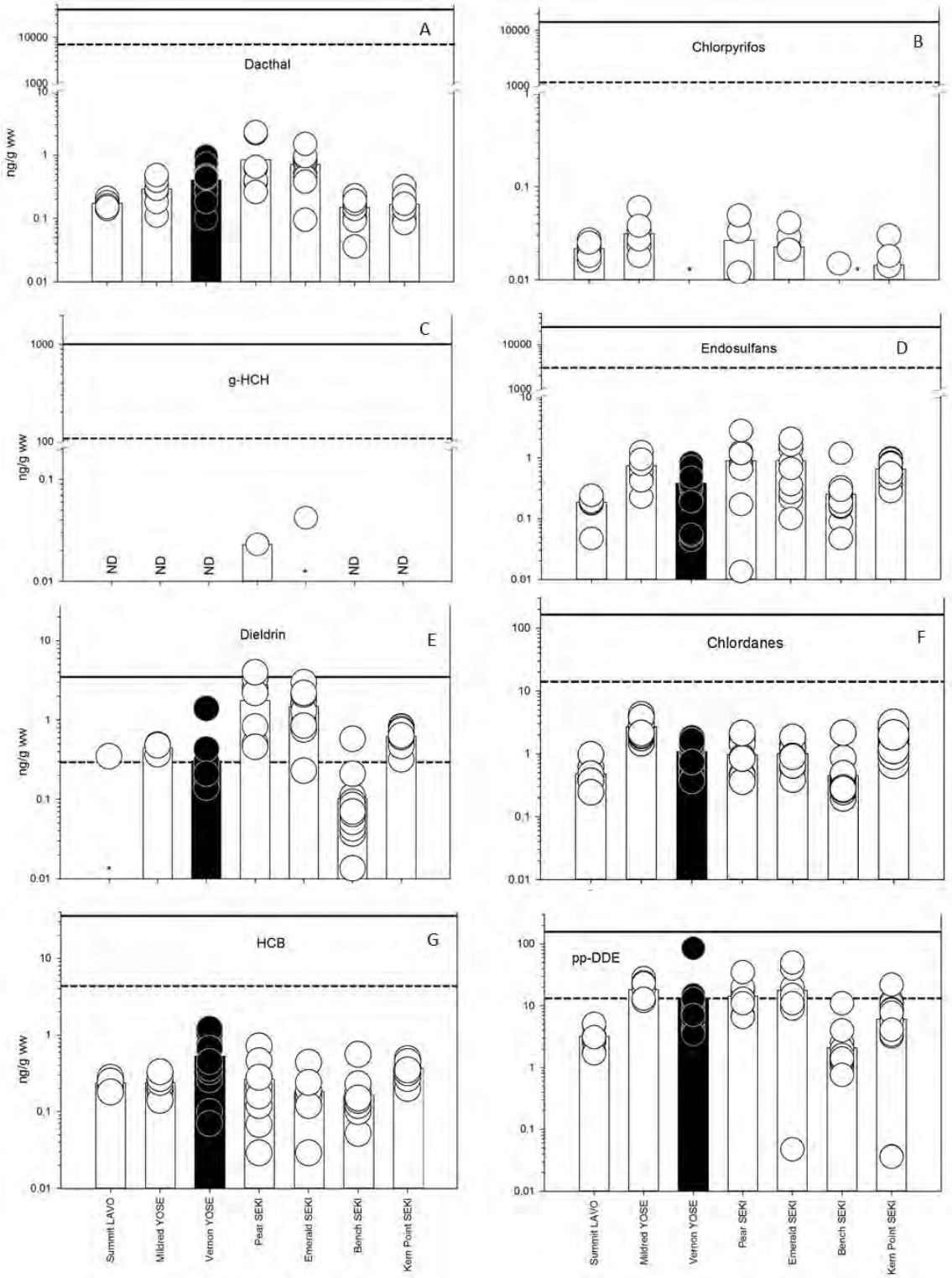
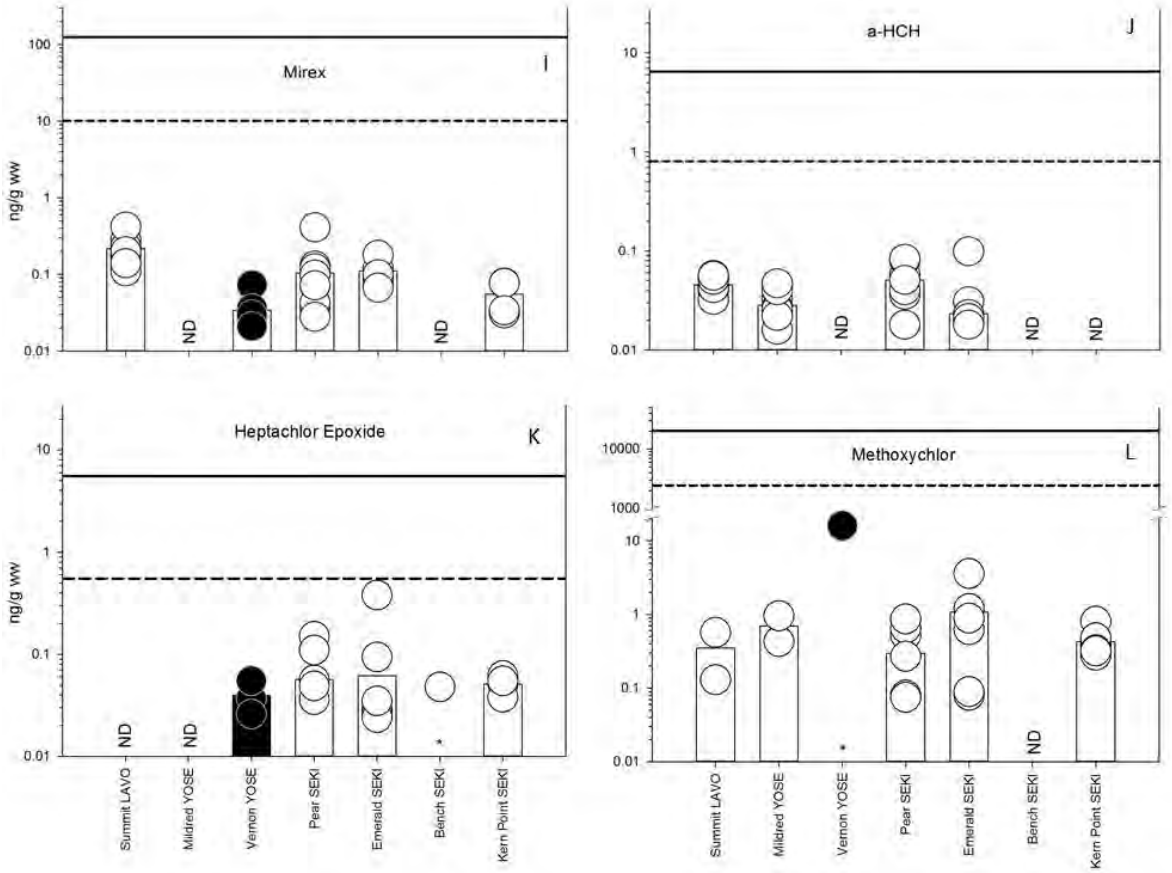


Figure 4 continuted.



Figures 5A–C. Concentrations of historic-use pesticides chlordanes, *p'p*-DDE, and dieldrin in fish (ng/g ww) compared to piscivorous wildlife health thresholds for kingfisher (dotted line), mink (dashed line), and river otter (solid line). Top of bar indicates the mean concentration and the circles represent the concentrations of individual fish. Black bars depict data from current study; white bars depict previously published data from WACAP (Landers et al. 2010; Ackerman et al. 2008). ND, no detect; *, ND > 50% of lake fish.

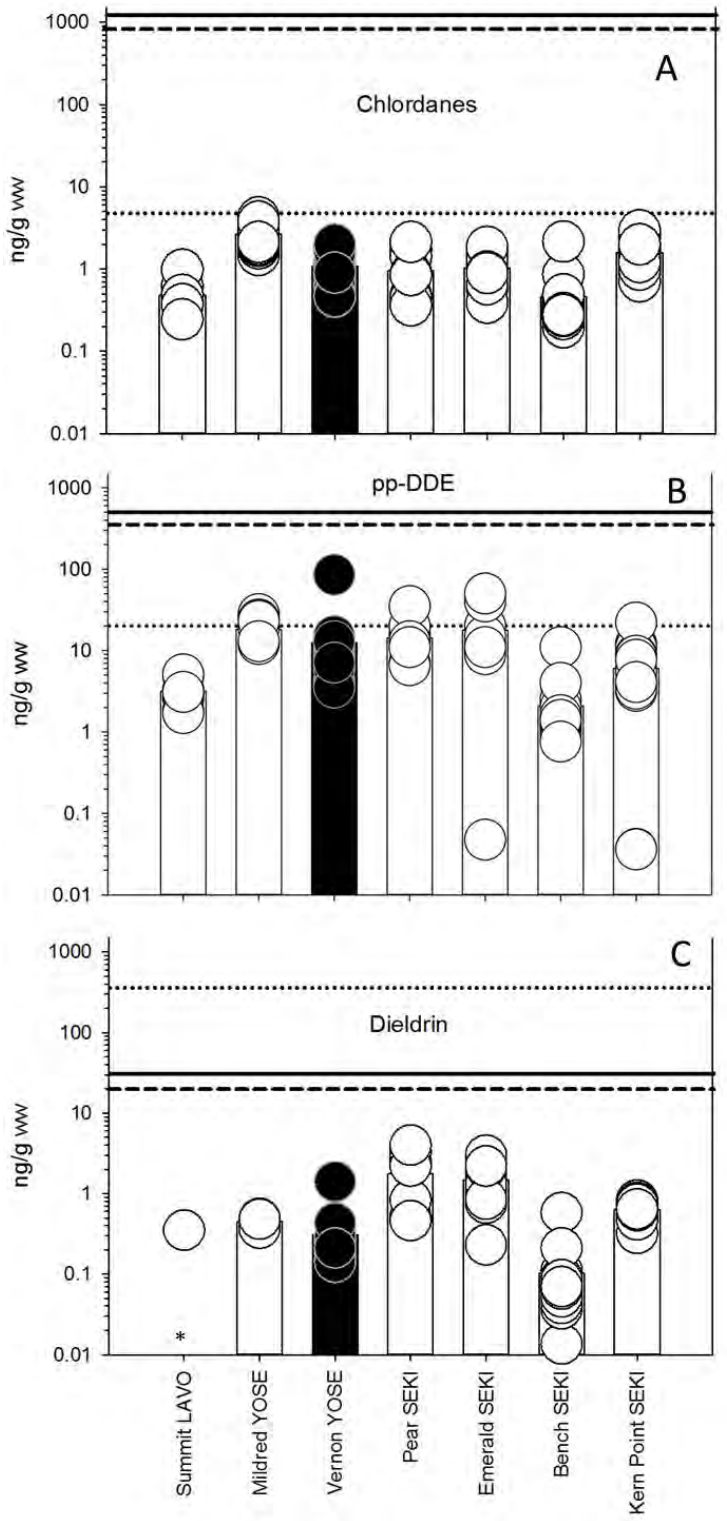


Table 3: Number of fish exceeding subsistence fish consumption threshold established for human health. Numerator indicates number of fish exceeding consumption limit and denominator indicates number of fish analyzed. Shaded cells depict an exceedance. No fish exceeded the recreational fish consumption threshold. Contaminant abbreviations as follows: DCPA, dacthal; CLPRY, chlorpyrifos; γ-HCH, gamma-hexachlorohexane; ENDO, endosulfans; DLDRN, dieldrin; CLDN, chlordanes; HCB, hexachlorobenzene; ppDDE, *p,p'*-dichlorodiphenylethene

Park	**Water Body**	**SOC**							
		DCPA	**CLPYR**	**γ-HCH**	**ENDO**	**DLDRN**	**CLDN**	**HCB**	**ppDDE**
Lassen Volcanic	Summit	0 / 8	0 / 8	0 / 8	0 / 8	1 / 8	0 / 8	0 / 8	0 / 8
Yosemite	Mildred	0 / 10	0 / 10	0 / 10	0 / 10	3 / 10	0 / 10	0 / 10	5 / 10
	Vernon	0 / 19	0 / 19	0 / 19	0 / 19	3 / 19	0 / 19	0 / 19	7 / 19
Sequoia & Kings Canyon	Bench	0 / 18	0 / 18	0 / 18	0 / 18	1 / 17	0 / 18	0 / 18	0 / 18
	Kern Point	0 / 18	0 / 18	0 / 18	0 / 18	12 / 18	0 / 18	0 / 18	1 / 18
	Pear	0 / 10	0 / 10	0 / 10	0 / 10	10 / 10	0 / 10	0 / 10	3 / 10
	Emerald	0 / 10	0 / 10	0 / 10	0 / 10	9 / 10	0 / 10	0 / 10	4 / 10

Table 4: Number of fish exceeding kingfisher health thresholds. Numerator indicates number of fish exceeding consumption limit and denominator indicates number of fish analyzed. Shaded cells depict an exceedance. No fish exceeded the mink or river otter health thresholds. Contaminant abbreviations: DLDRN, dieldrin; CLDN, chlordanes; ppDDE, *p,p'*-dichlorodiphenylethene

Park	**Water Body**	**SOC**		
		DLDRN	**CLDN**	**ppDDE**
Lassen Volcanic	Summit	0 / 8	0 / 8	0 / 8
Yosemite	Mildred	0 / 10	0 / 10	4 / 10
	Vernon	0 / 10	0 / 10	1 / 10
Sequoia & Kings Canyon	Bench	0 / 18	0 / 17	0 / 18
	Kern Point	0 / 18	0 / 18	1 / 18
	Pear	0 / 10	0 / 10	2 / 10
	Emerald	0 / 10	0 / 10	3 / 10

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