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Abstract: Contaminants such as polychlorinated biphenyls and organochlorine pesticides are among the most environmentally persistent pollutants. Although the more problematic of these chemicals are not produced in the United States, the compounds can be transported to Alaskan watersheds from remote locations via winds, currents, and through carcasses of returning salmon. Concentrations of total polychlorinated biphenyls and 23 pesticides eluted from passive samplers deployed for 30 days in the Kenai River were near or below 10 ppb, despite 30-day deployments of the strips. Concentrations of these compounds in both eggs and muscle tissue from returning Chinook salmon were also below 10 ppb and did not differ with respect to ocean residence time. There was no evidence of remote delivery of polychlorinated biphenyls or pesticides in this major salmon producing river.

INTRODUCTION

There is an increasing body of evidence suggesting that the greatest contaminant threat in Alaska comes from atmospheric and marine transport of contaminants from areas quite distant from Alaska. Organochlorines (OC) such as polychlorinated biphenyls (PCB), chlorinated pesticides, and industrial byproducts like dioxins and furans are neurotoxins and potential endocrine disruptors in fish and humans that can persist in the environment for decades. Collectively referred to as Persistent Organic Pollutants (POP), these compounds can be transported atmospherically from remote industrialized sites such as Europe or Asia and find their way via currents and rain to rural locations, especially in the higher latitudes (Simonich and Hites 1995). From trace quantities in the ocean, these chlorinated hydrocarbons can also concentrate to high levels in the lipid-rich tissues of fish such as salmon. These persistent contaminants are returned to the natal stream when the salmon spawn and die, increasing the pollutant loads of the stream sediments by as much as 7-fold (Krummel et al. 2003). Previous studies have noted a reallocation of PCB-laden lipids from muscle to eggs of salmon prior to spawning (Ewald et al. 1998).

The 132-km long Kenai River (60°E 33′N, 151°E 16′W) is one of the world's most productive anadromous salmonid rivers and a popular destination for sport fishers throughout the world (Figure 1). The Kenai River produces large runs of Pacific salmon. In 2004, 1,384,587 sockeye salmon *Oncorhynchus nerka* and 68,640 Chinook salmon *O. tshawytscha* returned to the river. The lower reaches of the river are semi-urbanized and the site of summer boat activity and the upper reaches are very rural. Despite the importance of seafood quality to communities like Kenai, very little research has been done to determine the extent of POP contamination in Alaskan salmon or their watersheds. Analytical costs can make POP surveys prohibitively expensive.

The best way to assess spatial and temporal changes in the concentrations of freely dissolved organic pollutants in water is through the use of passive samplers. These devices mimic uptake of contaminants by living organisms but without the metabolic alteration of compounds or other complicating factors inherent in the use of biological organisms as water quality monitors. The objective of our study was to assess the relative contribution of atmospheric, fish transport, and urban input of POPs to the Kenai River. By documenting POP levels in the river before and after both snowmelt and the return of spawning salmon, we could determine if any of these were important pathways for transporting contaminants to the watershed.

METHODS

In 2002, passive sampling devices were deployed at a variety of locations in the Kenai River to assess spatial and temporal changes in POP input. Eggs and muscle tissues from adult Chinook salmon returning to the

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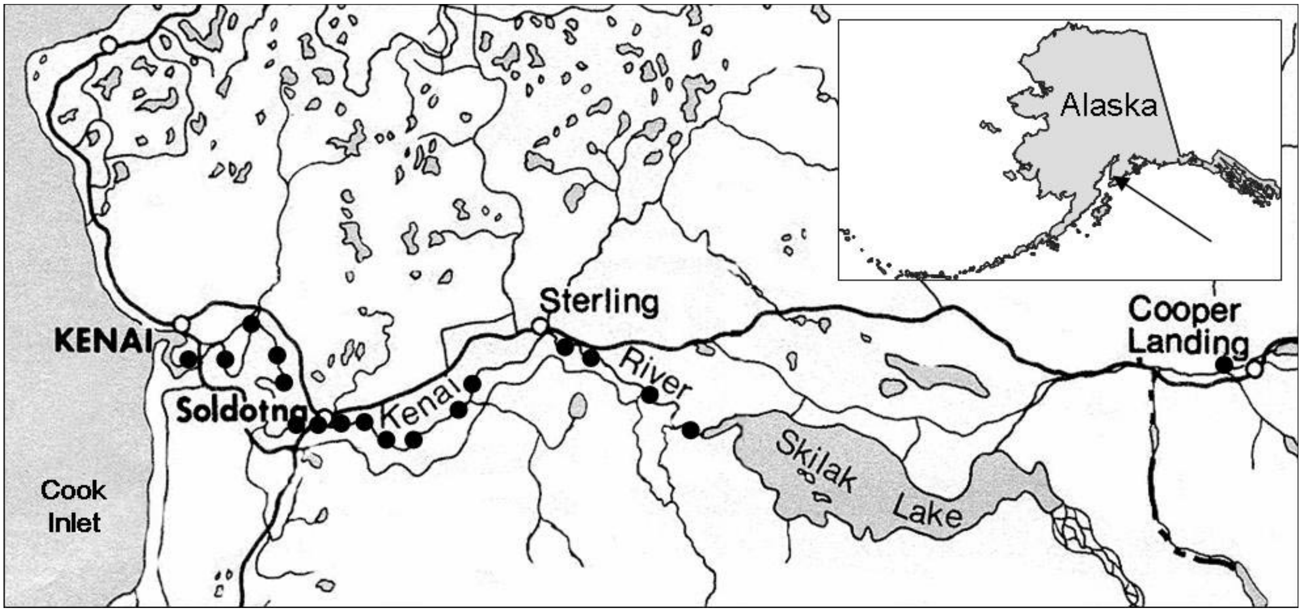

Figure 1. Map of the Kenai River from Kenai Lake to the mouth of the river at Cook Inlet. Sample sites are indicated with dots.

Kenai River were analyzed for OCs to determine if the fish carcasses were a source of these compounds to the river.

The passive samplers were membranes of low density polyethylene measuring 2.6 cm × 50 cm × 88 cm serpentined around aluminum nails in an aluminum pipe (11 cm outside diameter × 6 cm depth) with perforated aluminum end caps that allowed the water to flow freely past the strips. Polycyclic aromatic hydrocarbons were sequestered in the polyethylene matrix (Carls et al. 2004) inside these perforated canisters. These membranes samplers were prepared by sonic extraction in pentane followed by a rinse with pentane during removal from the sonic bath. All canisters, screens, tools, and associated hardware were washed with soap and water and rinsed with chromatography grade methylene chloride prior to use. Some samplers from each batch were retained in the laboratory to serve as laboratory blanks. During each deployment at least one sampler (field blank) was exposed to air for approximately one minute. The passive sampling devices were wrapped in two separate layers of hydrocarbon clean aluminum foil, plus two plastic bags during transport to and from the field to prevent passive sampling of air (Huckins et al. 1996).

A single passive sampler was deployed for 30 days at each of 9 locations along the river during April, July, and August of 2002 to determine the concentrations of an array of pesticides or PCBs present in the river. Replicate samples were not taken because of the large cost of analyzing each membrane. The dates of deployment were chosen to coincide with the beginning and end of runoff from snowmelt (months of April, July, and August). Some samplers were lost, so not every location was sampled each month. Analysis of each monthly set of deployed passive samplers also included one or two field blanks, one laboratory blank, one solvent method blank, one spiked laboratory blank and one spiked solvent method blank. In the laboratory, an internal standard (PCB 103) was added to all samples and a solution containing a suite of chlorinated analytes was added to the two spiked samples. The samples were then extracted in 1:1 methylene chloride:pentane by sonication. The extracts were eluted through silica columns using 1:1 methylene chloride: pentane. The cleaned up extracts were concentrated into 100μL of isooctane, and an instrument internal standard (tetrachloro-m-xylene) was added before the samples were shipped for analysis.

In addition to the passive samplers, 10 adult female chinook salmon were captured upon their return to the river. The fish were taken throughout the month of July to ensure maximal variation in the analytical results. Each of the 10 fish was of a different size to ensure a wide selection of ages. Upon capture, eggs and 2 grams of flesh were taken from each fish for chlorinated hydrocarbon analysis. Gloves and hydrocarbon-free tools were used to avoid contamination of the samples. Each fish was aged using scale analysis to determine if the length of ocean residency increased the concentration of OCs in either tissue. The passive sampler membranes and frozen tissue samples were sent to the Northwest Fisheries Science Center in Seattle, Washington for analysis using the gas chromatography/mass spectrometry techniques described in detail in Sloan et al. (2004). Units are ng of analyte per gram of membrane for the passive samplers and ng/g of tissue for the egg and muscle samples. The PCB congeners and pesticides measured are identified in Table 1.

RESULTS

The POP concentrations in the passive samplers from the river and in salmon tissue extracts were very low, often near the detection limits of the instruments (Table 2). Pesticides such as hexachlorohexanes (HCH), dieldrin, and mirex were not detected in the passive samplers from the river and total endosulfans, aldrin, and chlordanes were present at concentrations below 1 ng/g. The two pesticides present at higher concentrations were hexachlorobenzene (mean concentration of 0.87 ppb) and total DDTs (mean concentration of 0.95). The only pesticide levels that exceeded 1 ng/g were the July and August samples collected from a tributary draining from the local airport near the mouth of Cook Inlet and the July sample from the area of a commercial boat dock. Levels of PCBs ranged from 3 ng/g to 10 ng/g in the river. Concentrations of PCBs on samplers from the river were not related to month sampled or to location.

In the tissue samples, some POPs were not present (aldrin, endosulfans, and mirex) and others were low. Other non-DDT pesticides were present at <5 ng/g. Mean total DDT concentrations were 9.5 ng/g wet weight for eggs and 9.8 ng/g for muscle tissue. Mean total PCB concentrations were 9.8 n/g wet weight for eggs and 9.1 ng/g for muscle. The POPs did not increase with greater length of time at sea; low concentrations of OCs were detected in Chinook salmon that spent 2, 3 or 4 years at sea. Their eggs and muscle tissues had comparably low levels of OCs.

Table 1. List of organochlorine compounds analyzed from the Kenai River

Polychlorobiphenyl congeners	PCBs
17, 18, 28, 31. 33, 44, 49, 52, 66, 70	
74, 82, 87, 90, 95, 99, 101, 105, 110	
118, 128, 132, 138, 149, 151, 153	
156, 158, 159, 163, 164, 170, 171	
177, 180, 182, 183, 187, 190, 191	
194, 195, 199, 205, 206, 208, 209	
hexachlorobenzene	HCB
alpha hexachlorohexane	HCH
beta hexachlorohexane	
lindane	
aldrin	aldrin
dieldrin	dieldrin
endosulfane I	endosulfans
endosulfan II	
endosulfan sulfate	
mirex	mirex
heptachlor	chlordanes
heptachlor epoxide	
oxy-chlordane	
gamma chlordane	
alpha chlordane	
trans-nonachlor	
cis-nonachlor	
nonachlor III	
o,p’-DDE	DDT
p,p’-DDE	
p,p’-DDD	
o,p’-DDT	
p,p’-DDT	

DISCUSSION

The low concentrations of OCs in the Kenai watershed and in adult fish returning to the watershed suggest that there is no remote or significant local source of these compounds in the watershed. Even though PCBs and DDT have not been manufactured in North America for decades, these pollutants have been distributed by winds and currents throughout the world and are present in low concentrations in nearly every animal product. The concentrations in the river were the same before and after snowmelt, and the return of large numbers of salmon to the river did not result in any increased levels of OCs. This indicates neither atmospheric nor carcass deposition are a major source of these pesticides and PCBs to the river. Chlorinated hydrocarbons are present at low levels in virtually every living tissue, so it was not surprising to find background concentrations of a few compounds such as PCBs, HCBs, and DDTs.

Semipermeable membrane devices mimic the uptake and bioaccumulation of these contaminants by resident organisms (Vinturella et al. 2004). Membrane devices such as the polyethylene samplers concentrate trace quantities from the water, permitting the capture of intermittent pulses of contaminants (Huckins et al 1996). In the process, the devices provide a time-integrated average measure of freely-dissolved organic compounds that cannot be easily duplicated with conventional sampling procedures. The concentrations of OCs accumulated on the membranes are much lower than values reported for urban rivers. Semipermeable membrane devices suspended in sites around Amsterdam sequestered total PCBs ranging from 4–40 ng/g

Table 2. Concentrations (ng/g) of PCBs and OC pesticides in passive samplers and in eggs and muscle tissue from adult chinook salmon (ND=non-detectable concentration)

Month	River Km	Σ PCB	HCB	HCH	Aldrin	Dieldrin	Endosulfan	Mirex	Chlordanes	DDT
April										
	1	8.6	0.81	ND	0.26	ND	ND	ND	ND	0.81
	3	7.24	1.27	ND	ND	ND	ND	ND	ND	0.22
	19	3.76	0.24	ND	ND	ND	0.21	ND	ND	0.25
	32									
	57	4.53	0.15	ND	ND	ND	ND	ND	ND	ND
	62	3.89	0.59	ND	ND	ND	0.15	ND	0.1	0.17
	71	7.24	0.63	ND	ND	ND	0.07	ND	0.12	0.19
	104	3.3	0.4	ND	ND	ND	0.14	ND	ND	0.17
	132									
July										
	1	9.05	0.63	ND	0.25	ND	ND	ND	0.06	3.94
	3	10.41	1.72	ND	0.21	ND	1.77	ND	2.3	2.81
	19	7.69	1.22	ND	ND	ND	1	ND	0.29	0.63
	32	9.5	1.45	ND	ND	ND	ND	ND	0.35	0.55
	57	6.34	0.25	ND	ND	ND	0.5	ND	ND	ND
	62									
	71									
	104	8.15	0.91	ND	ND	ND	1.72	ND	0.21	0.71
	132	6.79	1.09	ND	ND	ND	1.22	ND	0.17	ND
August										
	1	9.5	0.54	ND	0.23	ND	1.72	ND	0.06	4.53
	3	7.69	1.58	ND	0.4	ND	ND	ND	0.83	0.99
	19									
	32	6.34	1.09	ND	ND	ND	ND	ND	0.3	0.15
	57									
	62									
	71									
	104									
	132	7.69	1.04	ND	ND	ND	0.11	ND	0.26	0.18
	Tissue									
Age 2										
n=2	Eggs	9.4	2.9	3.51	ND	1.15	ND	ND	4.03	9.38
	Muscle	9.5	3.5	3.17	ND	1.35	ND	ND	7.29	13.93
Age 3										
n=4	Eggs	10.7	3.2	4.11	ND	1.2	ND	ND	4.95	12.1
	Muscle	7.35	1.67	1.58	ND	0.61	ND	ND	2.75	7.74
Age 4										
n=4	Eggs	9.38	2.74	3.47	ND	0.98	ND	ND	2.98	7.93
	Muscle	10.63	2.6	2.23	ND	0.96	ND	ND	4.57	9.84

and total DDT ranging from 1–22 ng/g, depending on the sampling site (Verweij et al. 2004).

The wild salmon had concentrations of OCs in their tissues similar to or lower than those reported for other Pacific Coast wild salmon. Hites et al. (2004) reported mean PCB and total DDT concentrations of 3–10 ng/g wet weight for several stocks of wild Alaskan salmon, with the highest levels found in spawning Chinook salmon. These PCB concentrations are far below the 49 ng/g reported for Puget Sound Chinook (O'Neill et al. 1998) and the 221 ng/g wet weight threshold (assuming 9% lipid) considered protective against adverse effects in salmonids (Meador et al. 2002). The levels from the tissue samples in our study were too low to make any statement about the possible effects of fish age or tissue type on the results.

There is no evidence for remote delivery of either PCBs or chlorinated pesticides to this productive salmon river, either through atmospheric deposition or via carcasses of returning Chinook salmon. Although these toxic and persistent contaminants may be present at sufficiently high concentrations in a variety of Arctic habitats and wildlife to pose a potential threat to consumers (AMAP 2002), our study found only trace amounts of these contaminants in the Kenai River or in Chinook salmon.

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