



Characterization of organic contaminants in fjords and bays on the Kenai Peninsula Alaska

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Abstract A baseline environmental characterization of Seldovia Bay and harbor on the Kenai Peninsula, Alaska, was conducted using a sediment quality approach. The data was derived from a larger study that assessed seven distinct water bodies on the Kenai Peninsula's north side, draining into Kachemak Bay or into Lower Cook Inlet. Sampling sites for water quality measurements, sediment chemistry, and benthos were randomized within each embayment. Concentrations of 140 organic and elemental contaminants were analyzed. Habitat parameters (depth, salinity, grain size, organic carbon, etc.) that influence species and contaminant distribution were also measured at each sampling site. Concentrations of chlorinated pesticides and PCBs were uniformly low, with the exception of Seldovia Harbor, where total DDT and PCBs exceeded the lower sediment quality guidelines. Concentrations of PAHs were relatively low, except in Seldovia Harbor where concentrations exceeded lower sediment quality guidelines for PAHs, and in one location approached the upper limit. That concentration of PAHs exceeded all

other measurements in the NOAA National Status & Trends database for the entire State of Alaska. Characteristics of the PAH compounds present indicate large contributions of pyrogenic sources (burned fuel and/or other organic matter). Seldovia Bay had much lower PAH concentrations than the harbor.

Keywords Kenai peninsula, AK · Organic contaminants · PAHs · PCBs · Pesticides

Introduction

Alaska has an extensive coastline of 49,700 mi, greater than the contiguous US (U.S. EPA 2005; Shorezone 2016), and vast natural marine and coastal resources. However, due to a small population and lack of infrastructure, Alaska lacks adequate data to provide baseline information necessary to assess future trends. Historically, assessment in Alaska has been either limited or focused on areas of known impairment. Contaminants can biomagnify in the coastal food chain with increasing concentration in predatory wildlife and humans. Thus, characterizing and delineating areas of sediment contamination and toxicity are viewed as important goals of coastal resource management. This is particularly important in Alaska, where subsistence food contamination is an emerging health concern, especially in rural areas where large amounts of these foods are consumed as a primary source of protein (Wolfe 1996).

As part of the National Status and Trends (NS&T) Program, NOAA conducts bioeffects studies to

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determine the spatial extent and severity of chemical contamination and associated adverse biological effects in coastal bays and estuaries of the United States. Results from previous sediment bioeffects studies in over 20 coastal water bodies and estuaries have been published (Long et al. 1996; Turgeon et al. 1998; Long 2000; Hartwell et al. 2001, 2009, 2016, 2017; Hartwell and Hameedi 2006, 2007; Pait et al. 2006). The State of Alaska Department of Environmental Conservation (ADEC) Division of Water is responsible for protecting the quality of all Alaskan waters and under the Clean Water Act (CWA) and to report and identify causes and sources of water quality impairment.

Sediment chemistry, toxicity, and benthos assessments were conducted on the north side of Kachemak Bay in 2007 and in the deep central portions of the Bay in 2008, in collaboration with the North Pacific Research Board (Hartwell et al. 2009) and the Cook Inlet Regional Citizens Advisory Council (CIRCAC). This paper summarizes the results of organic contaminants in a joint NOAA, ADEC, and the University of Alaska Fairbanks (UAF) project to assess chemistry, benthic community, and sediment toxicity studies in the embayments on the south side of Kachemak Bay and bays on the Kenai Peninsula (Hartwell et al. 2017). A companion paper summarizes the results of heavy metals and metalloids (Hartwell et al. 2019).

The NS&T Program has analyzed contaminants in sediment and mussels collected from selected sites in the Gulf of Alaska (O'Connor 2002). The Prince William Sound Regional Citizens Advisory Council (PWSRCAC) has been assessing PAHs and other petroleum-related compounds in Prince William Sound since the Exxon Valdez Oil Spill in 1989 (EVOS) (Page et al. 2001). In collaboration with the U.S. EPA National Aquatic Resource Survey, ADEC undertook a state-wide coastal ecological condition study (AKMAP) that encompasses assessment of contaminants and benthic assemblage in sediment along the Gulf of Alaska and the Aleutian Islands (Saupe et al. 2005). The Cook Inlet Regional Citizens Advisory Council (CIRCAC) assesses the impacts of oil and gas operations in Cook Inlet, including chemical and benthic community assessment, and undertook a comprehensive sediment and water quality survey of Cook Inlet in 2008. The study reported here augments these efforts to provide detailed data on sediment quality on the Kenai Peninsula, where data is sparse.

Cook Inlet is a major estuary in South Central Alaska. The watershed covers 102,000 km² and is home to

482,166 people or 65% of Alaska's population, including the state's largest city Anchorage (Brabets et al. 1999; Alaska Department of Labor 2019). Pollutants from human activities within the watershed are delivered to the estuary from both non-point and point sources. These sources may include wastewater discharge, marine activities associated with commercial and recreational fishing, commercial shipping, oil rig maintenance, storm water runoff, and short- and long-range atmospheric transport (Saupe et al. 2005; Norman 2011). Historically, seafood canning operations and the mining and export of coal and minerals in the region have generated shoreline and watershed contaminant inputs in the region. Oil from the Exxon Valdez oil spill was carried by currents from the Prince William Sound into lower Cook Inlet, including into Kachemack Bay (Saupe et al. 2005). Cook Inlet estuary hosts a major salmon fishery, an endangered beluga whale population, and provides a major recreational/subsistence resource to Alaskans.

Kachemak Bay is a 64-km-long glacial fjord on the east side of lower Cook Inlet located in south central Alaska (Fig. 1). The south shore is bounded by the Kenai Peninsula, which has numerous smaller fjords and embayments cut into steep terrain that rises to glaciated valleys and uplifted mountain peaks composed of a jumble of volcanic rock and upthrust marine sedimentary deposits. Glaciers have covered and retreated from Kachemak Bay repeatedly over the past 25,000 years. The Kenai Peninsula is a tectonic rupture zone and is subject to violent earthquakes, including the largest ever recorded in North America in modern times (Good Friday earthquake 1964). The earthquake and subsequent tsunami nearly destroyed the City of Seldovia, and ended the canning industry that was there. It also caused a land subsidence of 4 ft. in the Kachemak Bay area. This sudden change in elevation has resulted in dynamic changes in local sedimentation and erosional patterns. There are five active volcanoes on the western side of Cook Inlet. These periodically contribute volcanic ash to the region and have produced tsunamis that impact Kachemak Bay.

With no known industrial point sources of contamination, current sources of pollution on the Kenai Peninsula may include domestic wastewater discharge, marine activities associated with commercial and recreational fishing, commercial shipping, oil rig maintenance, storm water runoff, and long-range atmospheric transport. Historically, seafood canning operations and the mining and export of coal and minerals in the region have generated shoreline and watershed contaminant inputs in the region.

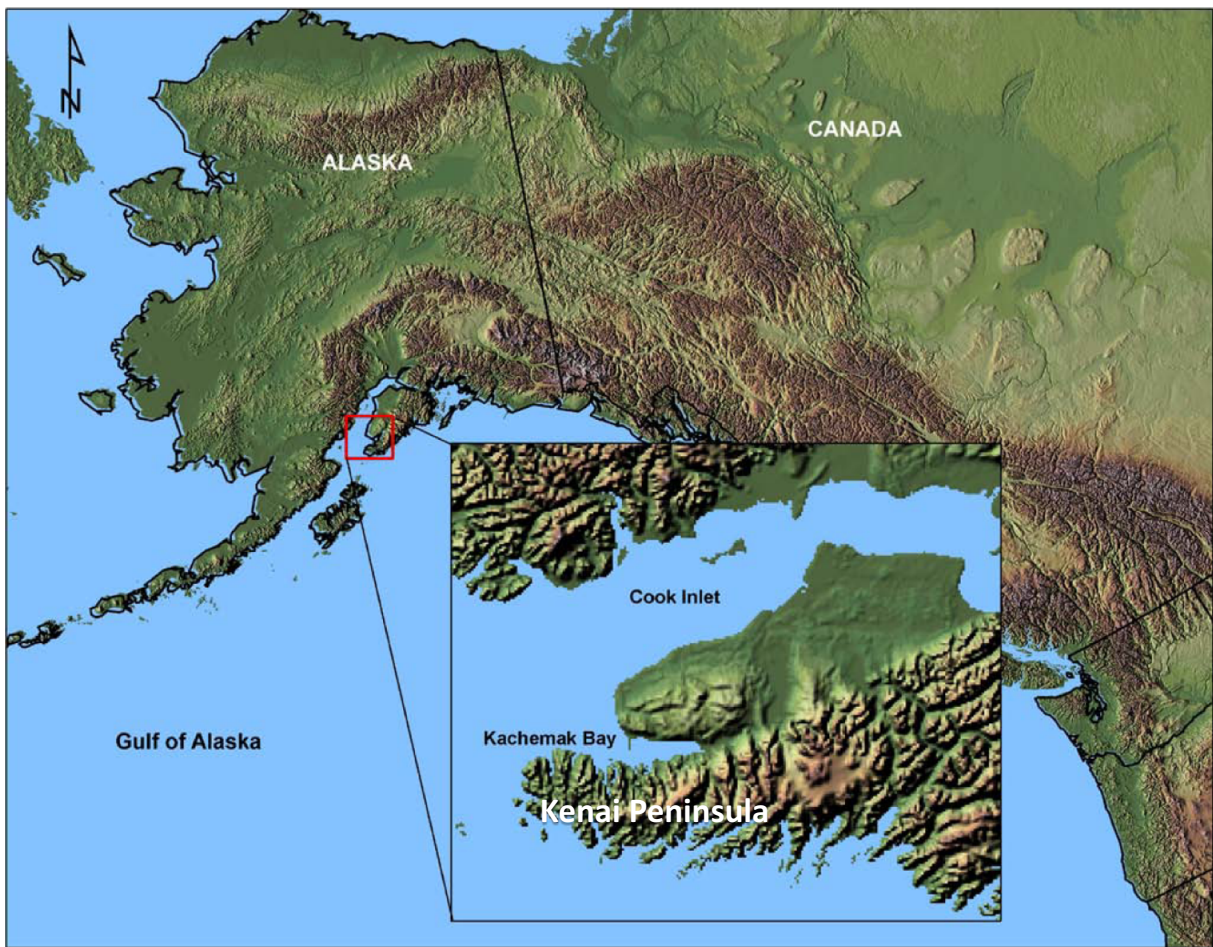


Fig. 1 Kachemak Bay on the east side of lower Cook Inlet located in south central Alaska

Since Kachemak Bay lies between Cook Inlet and Prince William Sound oil operations traffic, its deep water anchorage is being proposed as one of several repair sites and safe refuges for distressed and disabled vessels (ADEC 2006). The risk of using the bay as shelter for vessels would be pollution from oil leaks and release of other hazardous substance that can impact marine resources. The bay was impacted by the Exxon Valdez Oil Spill (EVOS) of 1989. Fourteen days after the spill, the oil slick traveled westward then northward through the Kennedy Entrance to cover part of the lower Cook Inlet and Kenai Peninsula (www.evostc.state.ak.us/History/PWSmap.cfm). Kachemak Bay, being further removed from the spill epicenter in Prince William Sound, suffered relatively minimal ecological damages (Kuletz 1994), which nevertheless injured marine and coastal resources. It is anticipated that results of this study will serve as baseline data for unforeseen events and future reference.

Seldovia Bay is a 1 × 6-km-long bay/fjord southwest of Homer that opens into the mouth of Kachemak Bay. The city of Seldovia sits on the eastern side of the mouth of the Bay. The Bay and the harbor at Seldovia were both sampled. Other bays/fjords that were sampled in the larger study included Port Graham Bay, Jakolof Bay, Sadie Cove, Tutka Bay, China Poot Bay, and Halibut Cove Lagoon (Fig. 2; Hartwell et al. 2017).

Methods

The NS&T Program and AKMAP use a stratified-random design for selection of sampling sites to determine the spatial extent of sediment toxicity in US coastal waters. Three sampling sites were located on a random basis within each bay except Sadie Cove and Tutka Bay (Fig. 2). This approach combines the strengths of a

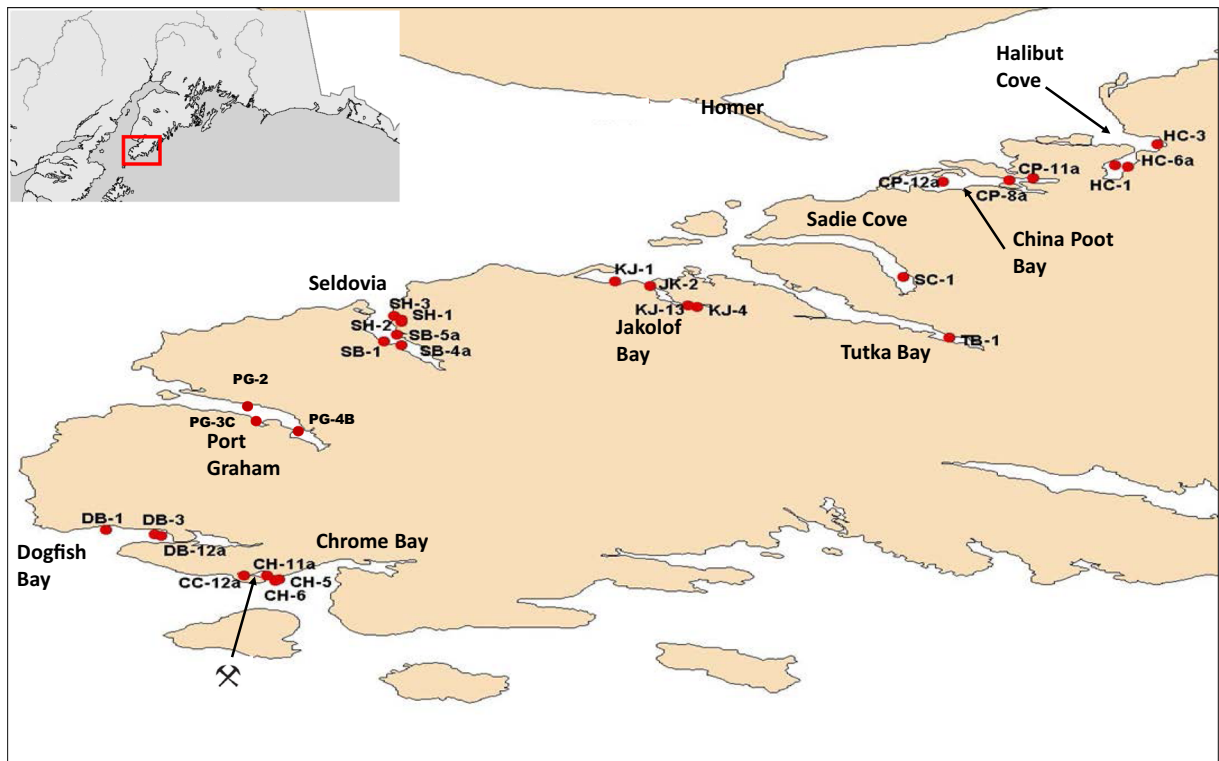


Fig. 2 Other bays/fjords that were sampled in the larger study

stratified design with the random-probabilistic selection of sampling locations.

Sediment samples were taken at each site in addition to water quality measurements with YSI meter readings at the surface and bottom of the water column. Samples were collected with a stainless steel 0.04 m² PONAR grab sampler. Sampling methods followed standard NS&T field methods (Apeti et al. 2012) that ensure QA/QC and minimize cross contamination. Only the upper 2–3 cm of the sediment was retained in order to assure collection of recently deposited materials.

The sediment samples were thoroughly homogenized in the field with an acetone-rinsed, stainless steel mixer attachment on an electric drill. This composite sample was subdivided for distribution to various testing laboratories. Subsamples were collected for grain size characterization. Samples for chemical analyses were stored in pre-cleaned glass jars with Teflon® liners and frozen.

Chemical analyses followed procedures routinely used in the NOAA NS&T Program (Kimbrough and Lauenstein 2006; ASTM 2004). A broad suite of sediment contaminants were analyzed at each station, including 51 PAHs, 25 aliphatics from C10-C34 plus

pristane and phytane, 30 chlorinated pesticides, including DDT and its metabolites, and 54 polychlorinated biphenyls (PCBs) (Tables 1, 2, and 3). In addition to organic contaminants, other parameters included 15 major and trace elements (reported elsewhere, Hartwell et al. 2017), grain size analysis, total organic/inorganic carbon (TOC/TIC), and percent solids. Mono-, di-, and tributyltins were analyzed in sediments collected in Seldovia Harbor.

Samples were shipped frozen to the laboratory and stored at –20 °C until analysis. Quantitation of PAHs and their alkylated homologs was performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. Chlorinated hydrocarbons (chlorinated pesticides and PCBs) were quantitatively determined by capillary gas chromatography with an electron capture detector (ECD). For the butyl-tin analyses, samples were extracted three times by agitation with tropolone in dichloromethane. Hexylmagnesium bromide (2 M; Grignard reagent) was added to the sample extract under nitrogen and heated to hexylate the sample. The hexylated extract was dried by addition of anhydrous Na₂SO₄ and then concentrated. The extract was purified using silica gel/

Table 1 Polycyclic aromatic hydrocarbons (PAHs) measured in Kenai Peninsula samples

Compound		
Naphthalene	Carbazole	Naphthobenzothiophene
C1-Naphthalenes	Anthracene	C1-Naphthobenzothiophenes
C2-Naphthalenes	Phenanthrene	C2-Naphthobenzothiophenes
C3-Naphthalenes	C1-Phenanthrene/anthracenes	C3-Naphthobenzothiophenes
C4-Naphthalenes	C2-Phenanthrene/anthracenes	Benz(a)anthracene
Benzothiophene	C3-Phenanthrene/anthracenes	Chrysene
C1-Benzothiophenes	C4-Phenanthrene/anthracenes	C1-Chrysenes
C2-Benzothiophenes	Dibenzothiophene	C2-Chrysenes
C3-Benzothiophenes	C1-Dibenzothiophene	C3-Chrysenes
Biphenyl	C2-Dibenzothiophene	C4-Chrysenes
Acenaphthylene	C3-Dibenzothiophene	Benzo(b)fluoranthene
Acenaphthene	Fluoranthene	Benzo(k)fluoranthene
Dibenzofuran	Pyrene	Benzo(e)pyrene
Fluorene	C1-Fluoranthenes/pyrenes	Benzo(a)pyrene
C1-Fluorenes	C2-Fluoranthenes/pyrenes	Perylene
C2-Fluorenes	C3-Fluoranthenes/pyrenes	Indeno(1,2,3-c,d)pyrene
C3-Fluorenes	Dibenzo(a,h)anthracene	Benzo(g,h,i)perylene

alumina column chromatography. The quantitative method was based on high resolution, capillary gas chromatography using flame photometric detection (GC/FPD). This method quantitatively determined tributyltin (TBT), dibutyltin (DBT), and monobutyltin

(MBT). QA/QC controls for all analyses included standard reference materials, matrix spikes, duplicate analyses, internal standards, and blanks. Method detection limits for all analyses were determined following the procedures outlined in CFR 40, part 136 (1999).

Table 2 Chlorinated pesticides measured in Kachemak Bay sediments

Compound class	Compound	Compound class	Compound
Cyclodienes	Aldrin	DDT and metabolites	2,4'-DDD
	Dieldrin		4,4'-DDD
	Endrin		2,4'-DDE
	Heptachlor		4,4'-DDE
	Heptachlor-epoxide		2,4'-DDT
	Oxychlordane		4,4'-DDT
Hexachlorocyclohexanes	Alpha-chlordane	Chlorinated benzenes	1,2,3,4-Tetrachlorobenzene
	Gamma-chlordane		1,2,4,5-Tetrachlorobenzene
	Trans-nonachlor		Hexachlorobenzene
	Cis-nonachlor		Pentachloroanisole
	Alpha-HCH	Other	Pentachlorobenzene
	Beta-HCH		Endosulfan II
	Delta-HCH		Endosulfan I
Gamma-HCH		Endosulfan sulfate	
		Mirex	
		Chlorpyrifos	

Table 3 Polychlorinated biphenyls (PCBs) measured in Kenai Peninsula samples. (Co-eluting congeners are shown together)

Congener (s)	
PCB8/5	PCB128
PCB18	PCB138/160
PCB28	PCB146
PCB29	PCB149/123
PCB31	PCB151
PCB44	PCB153/132
PCB45	PCB156/171/202
PCB49	PCB158
PCB52	PCB170/190
PCB56/60	PCB174
PCB66	PCB180
PCB70	PCB183
PCB74/61	PCB187
PCB87/115	PCB194
PCB95	PCB195/208
PCB99	PCB199
PCB101/90	PCB201/157/173
PCB105	PCB206
PCB110/77	PCB209
PCB118	

Results were compared to numerical sediment quality guidelines (SQG) developed by Long and Morgan (1990) and Long et al. (1995) known as ERM and ERL (effects range-median, effects range-low), which express statistically derived levels of contamination, above which toxic effects would be expected to be observed with at least a 50% frequency (ERM), and below which effects were rarely (< 10%) expected (ERL). Spearman

rank correlation coefficients were calculated for each chemical class and sediment physical characteristics.

Results and discussion

Physical parameters of the water column and sediment are shown in Table 4. Seldovia Bay does not receive turbid drainage from existing glaciers. All water input is from rain, snowmelt, and groundwater. Water clarity as measured by Secchi disk averaged 4.4 and 3.3 m in the harbor and Bay, respectively, the harbor area being closer to the mouth which opens to outer Kachemak Bay. Seldovia Bay is 18 m deep at its deepest point and the sampling stations ranged from 2 to 10.5 m. The harbor and approach to the ferry dock is dredged. Harbor sample site depths ranged from 3.4 to 7.5 m. The grain size distributions reflect the effect of dredging in the harbor as opposed to the predominately fine-grained material in the bay with higher total organic carbon (TOC). The tidal range is 6+ meters so the water column is well mixed by tidal flushing. The percent composition of fine-grained sediment was strongly correlated with organic carbon content (Spearman's $\rho = 0.7537$, $p < 0.0001$).

Mirex and chlorpyrifos were below detection limits at all stations. Endosulfan sulfate was found in Seldovia Harbor and Bay, but the highest concentration was only 5 ng/g (parts per billion). Endosulfan is hydrophobic and would be expected to be found in sediment preferentially over water. The updated EPA water quality criteria for human consumption of drinking water and fish consumption is 20 $\mu\text{g/l}$ (U.S. EPA 2015). There are no sediment standards. Endosulfan I and II were below

Table 4 Physical parameters of the water column and sediment in Seldovia Bay and harbor

Bay site	Depth m	Secchi depth (m)	Bottom temp. (°C)	Surface temp. (°C)	Bottom Salinity (ppt)	Surface Salinity (ppt)	Bottom DO mg/L	Surface DO mg/L	%Gravel	%Sand	%Silt	%Clay	% fine grained	TOC %
SB-1	10.5	2.7	11	11.8	27.8	27	7.85	8.15	1.32	16.78	62.03	19.87	81.90	1.88
SB-4a	8.5	3.8	11.2	12	28.1	24.7	7.88	8.28	1.01	19.06	58.57	21.36	79.93	2.74
SB-5a	2	3.2	11.3	11.3	27.9	27.9	8.5	8.5	12.97	22.72	48.09	16.22	64.31	2.19
Harbor site														
SH-1	5.5	4.9	11.5	13.6	27.8	24.8	8.12	8.23	8.98	40.57	30.73	19.72	50.45	1.90
SH-2	3.4	3.4	11.6	11.9	27.7	27.2	8.47	7.94	1.93	66.41	20.11	11.55	31.66	1.71
SH-3	7.5	4.9	11.3	12.5	27.8	26.3	8.1	8.22	3.11	81.36	9.14	6.39	15.53	0.73

detection limits at all stations. Hexachlorohexane (HCH) was detected in several locations, but always less than 1 ppb. The gamma isomer (lindane) was not detected at any station. Chlorinated benzenes were also detected in most bays, but the highest concentration was 0.46 ppb. DDT and its breakdown products were found at isolated stations in Seldovia Harbor and Bay (Table 5). For comparative purposes, values from the other bays in the larger study on the peninsula (Hartwell et al. 2017), and Homer Harbor (Hartwell et al. 2009) are shown for comparison. One station in Seldovia Harbor (SH3) and one in Seldovia Bay (SB1) had total concentrations of 9.75 and 4.09 ppb, respectively, which

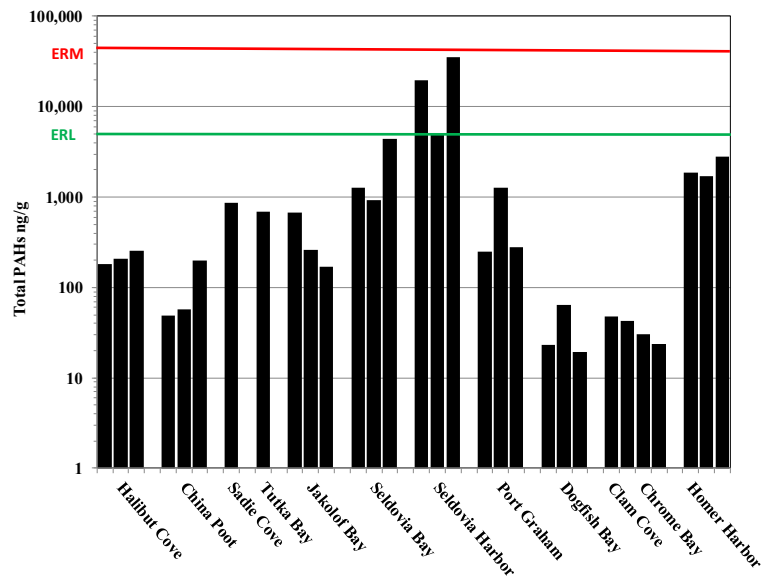
exceed the ERL for total DDTs of 1.58 ppb. No other station exceeded the ERL. The ERM for total DDTs is 46.1 ng/g. Chlordanes and related cyclodienes (e.g., Aldrin) were found at low levels. Only 2 stations in Seldovia Harbor exceeded 1.0 ppb.

There are no reliable records of pesticide use in the Kachemak Bay area and it is unknown if DDT and the other pesticides detected there were of local origin or not. The presence of these chemicals at concentrations above detection limits in a relatively remote and sparsely populated area like the Kenai Peninsula highlight their environmental persistence and the possible contribution of long-range atmospheric transports, or global distillation

Table 5 Sediment concentrations (ng/g) of organic chemicals in fjords and bays on the Kenai Peninsula

Water body	Site	PAHs	Perylene	Cyclodienes	HCH	DDT	PCBs
Halibut Cove	HC-3	183.1	26.8	0.09	0.21	0.00	0.30
	HC-1	209.3	26.4	0.16	0.21	0.00	0.23
	HC-6a	256.1	37.2	0.21	0.26	0.00	0.49
China Poot	CP-11a	48.4	4.8	0.08	0.00	0.00	0.04
	CP-12a	57.9	3.4	0.26	0.00	0.11	0.09
	CP-8a	200.4	15.4	0.26	0.07	0.00	0.02
Sadie Cove	SC-1	871.9	151.0	0.14	0.38	0.00	0.37
Tutka Bay	TB-1	682.1	135.0	0.19	0.25	0.02	0.43
Jakolof Bay	KJ-1	670.1	109.0	0.09	0.00	0.04	0.64
	KJ-13	263.5	63.7	0.09	0.05	0.00	0.13
	KJ-4	170.7	23.0	0.20	0.00	0.00	0.34
Seldovia Bay	SB-1	1268.4	83.5	0.10	0.00	4.09	3.60
	SB-4a	919.6	80.3	0.12	0.09	0.90	2.48
	SB-5a	4450.0	94.3	0.20	0.10	0.49	5.40
Seldovia Harbor	SH-1	19,500.9	398.0	1.11	0.00	1.06	45.95
	SH-2	5058.5	95.9	0.61	0.00	0.35	28.43
	SH-3	35,259.8	118.0	2.40	0.00	9.75	13.20
Port Graham	PG2	249.2	37.9	0.21	0.00	0.02	0.67
	PG3C	1264.1	64.0	0.16	0.06	0.91	2.86
	PG4B	279.6	60.2	0.14	0.00	0.55	1.26
Dogfish Bay	DB-1	23.2	0.2	0.00	0.00	0.01	0.03
	DB-12a	63.6	0.8	0.04	0.05	0.00	0.02
	DB-3	19.3	0.2	0.01	0.00	0.00	0.05
Clam Cove	CC-12a	47.3	0.9	0.06	0.05	0.00	0.52
	CH-11a	42.5	1.5	0.04	0.05	0.01	0.08
Chrome Bay	CH-5	30.3	0.8	0.01	0.00	0.20	0.01
	CH-6	23.7	0.6	0.02	0.00	0.01	0.02
Homer Harbor	HH-1	1882.4	167	0.07	0.00	0.47	2.95
	HH-2	1689.3	209	0.46	0.00	0.54	4.64
	HH-3	2802.9	230	0.70	0.00	0.73	3.56

Fig. 3 Sediment concentration of total PAHs in fjords and bays on the Kenai Peninsula



processes (Wania and Mackay 1995) whereby pesticides circulate from warm areas and collect in colder areas, such as the poles, where they have never been used. Chlordane and the related cyclodienes, and DDT have accumulated in the fine grained, organically enriched sediments in Seldovia.

Total PAH concentrations were highly variable between embayments. Seldovia harbor had the highest concentrations by far (Fig. 3). All three stations exceeded the ERL for total PAHs and one approaches the ERM (note the log scale). Seldovia Bay did not exhibit such high concentrations, but were still on the

same order of magnitude as inside Homer Harbor, which is also included in this graph from data collected in 2007 (Hartwell et al. 2009). Perylene is a natural by-product of the breakdown of terrestrial plant material (NRC 1985). Perylene concentrations varied from negligible to 24% of total PAHs (0–400 ppb), but removing this compound from the total PAH values did not alter the overall PAH pattern. The Seldovia harbor watershed is very small and includes the town of Seldovia. Outside of the harbor areas, the watersheds of the bays are sparsely populated and forest covered. It is unclear why there is such a wide spread in the perylene concentrations.

Fig. 4 Mean, high, and low concentrations of PAHs from locations around Alaska, without Seldovia Harbor. (Data from NS&T)

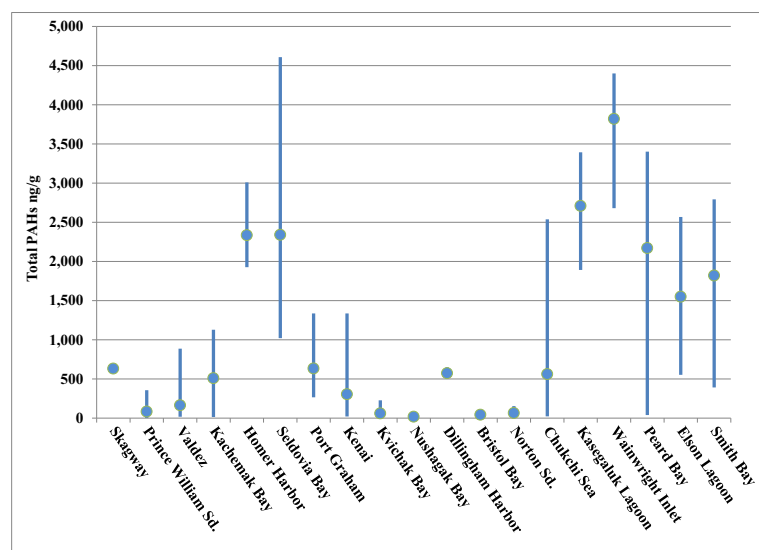
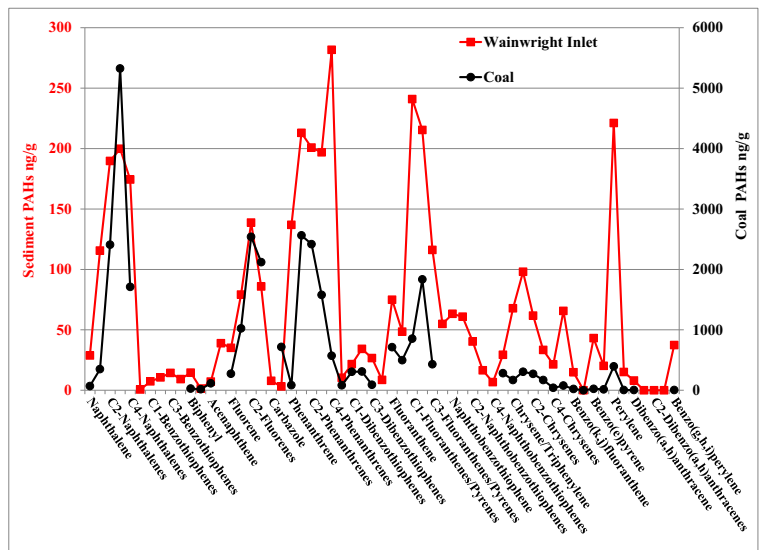


Fig. 5 Individual PAH concentrations in sediment from Wainwright Inlet and coal chips in the Chukchi Sea. (For clarity, every other PAH compound is listed on the X-axis)

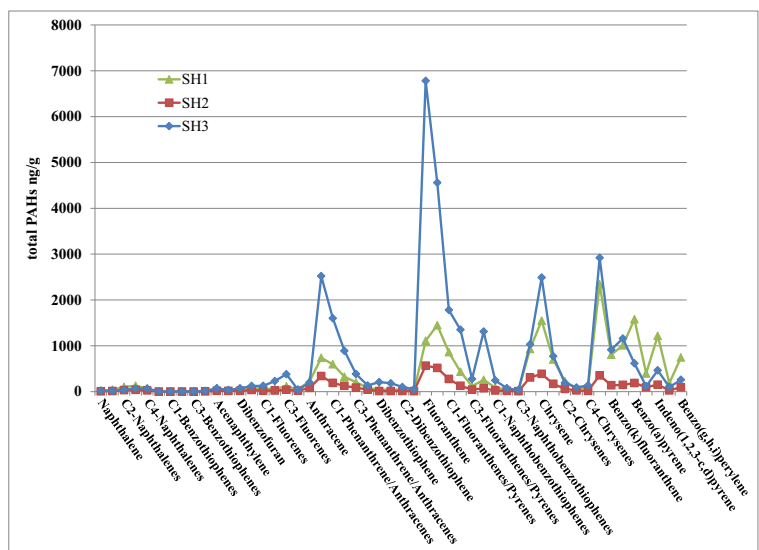


Comparing the current PAH data to sediment concentrations throughout the rest of Alaska in the NS&T data base, Seldovia Harbor has higher concentrations than anywhere else. Figure 4 shows the mean and range of PAH concentrations on all three Alaskan coasts, in harbors and open water, excluding Seldovia Harbor. The lowest Seldovia Harbor concentration (5221.8 ng/g) is greater than all other locations.

The Arctic estuary concentrations are higher than most locations. This is the result of abundant natural coal and peat deposited in the estuarine sediments. For example, Fig. 5 shows the pattern of individual PAH concentrations in sediment from Wainwright Inlet and

coal chips collected in the same vicinity in the Chukchi Sea. Note the large peak for perylene. In contrast, PAH concentrations in sediments from Seldovia Harbor demonstrate an entirely different pattern (Fig. 6). In this case, there are few low molecular weight compounds (three carbon rings or less, e.g., anthracene), and few alkylated homologs of the higher weight compounds. This would not indicate a fuel spill or a natural source, but more likely highly weathered oil, or a burned fuel source. Also, note that station SH3 has higher concentrations of all constituents, particularly fluoranthene and pyrene, typical of combustion products. The specific locations of the Seldovia sampling stations are shown in Fig. 7.

Fig. 6 Individual PAH concentrations in sediment samples from Seldovia Harbor. (For clarity, every other PAH compound is listed on the X-axis)



Stations SH1 and SH2 were located in the boat slip area while SH3 is behind the ferry dock. The history of spills and/or disposal or other potential sources, possibly going back to the 1964 Good Friday earthquake when Seldovia was a much larger industrial center, has not been documented. The PAH pattern in the Seldovia Bay samples mirrored the harbor samples, but at lower concentrations.

Distribution of measured PCBs in the study area is illustrated in Fig. 8. PCBs were detected throughout the study area and their spatial distributions were similar to those of PAHs. Relative to other sites, Seldovia Harbor and Bay, and Homer Harbor had elevated PCB concentrations. Two sites in Seldovia Harbor exceeded the

ERL, but no site approached the ERM (180 ng/g). In this case, the two highest values were in the boat slip area as opposed to the ferry dock.

Spearman rank correlations between physical factors and organic contaminants from all the bays in the larger study are shown in Table 6. As expected, most organic contaminants were significantly positively correlated with fine-grained sediment and percent TOC and negatively correlated with coarse-grained sediment. The pattern of correlation generally followed that of the percentage fines, as TOC and percentage fines would be expected to be confounded. The total DDTs, which were rarely found at elevated levels, did not correlate with any physical parameter. These relationships did not change

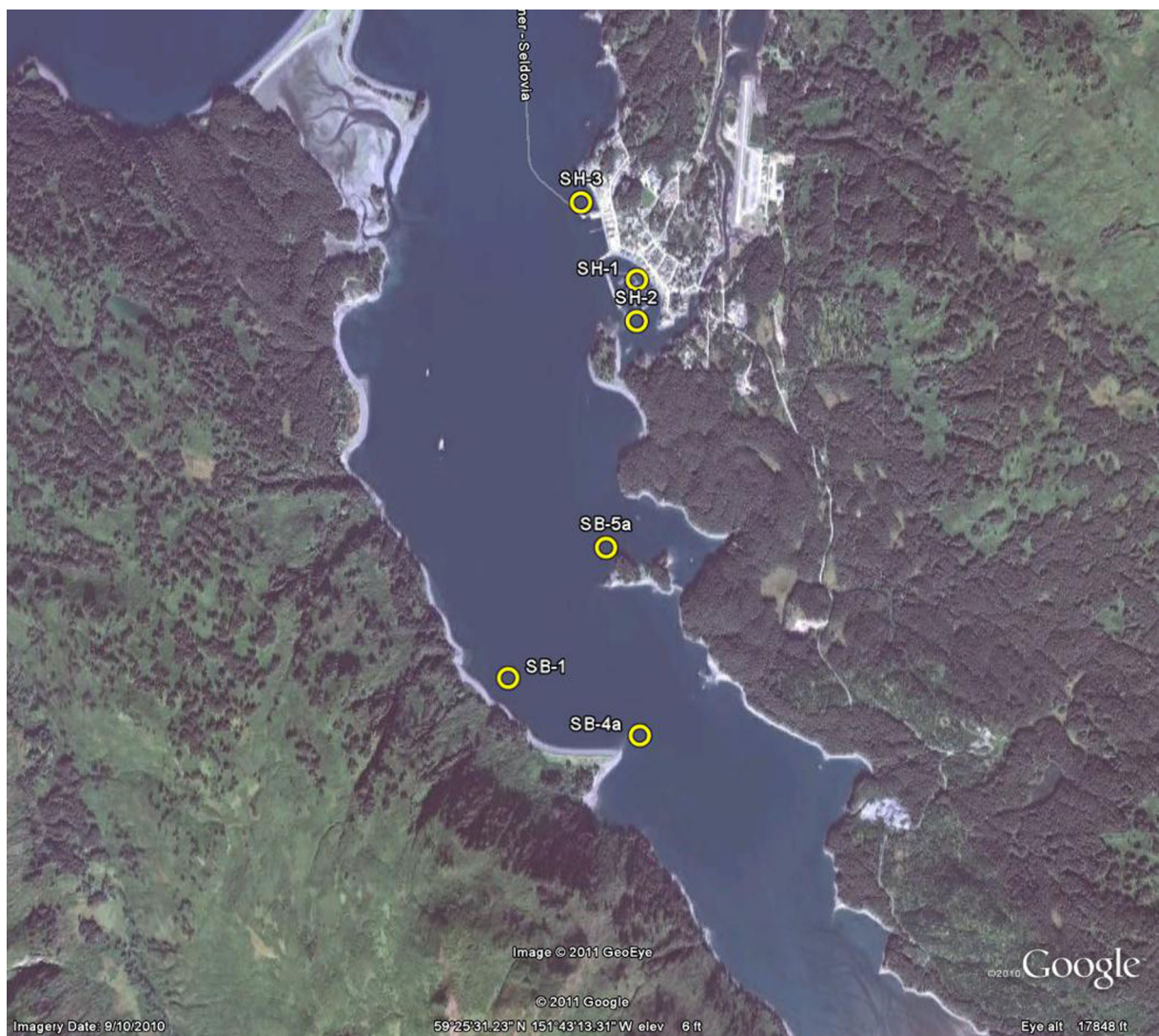
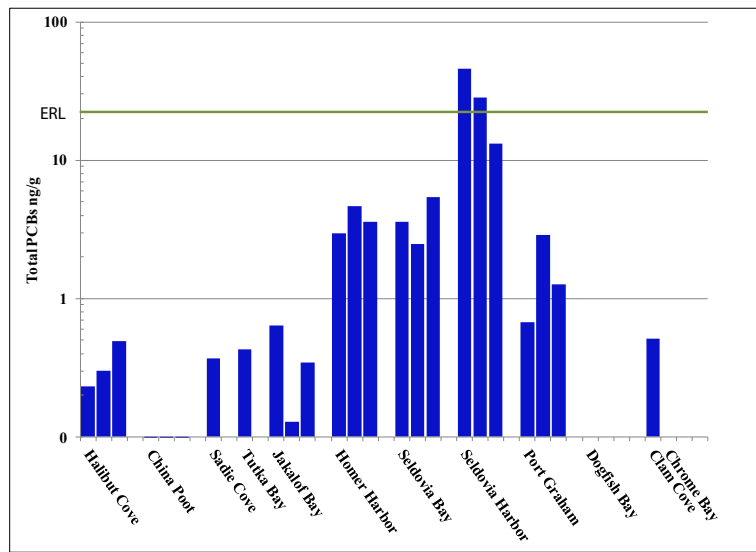


Fig. 7 Specific sampling locations in Seldovia Harbor and Bay

Fig. 8 Sediment concentration of total PCBs in fjords and bays on the Kenai Peninsula



when the extreme values from Seldovia Harbor were excluded from the data set.

Aliphatic and total petroleum hydrocarbon concentrations are shown in Table 7, along with descriptive ratios. Consistent with the PAH data, Seldovia Harbor had the highest petroleum hydrocarbon concentrations among the other Kenai locations. Homer Harbor did have higher concentrations than Seldovia however. The ratio of odd to even alkanes was greater than 1 in almost all cases. The carbon chains from biogenic sources tend to have more odd-numbered alkanes. Long-term degradation tends to increase the number of even numbered alkanes as the chains break down, and

the ratio approaches 1. Degradation also produces increasingly higher proportions of lower weight alkanes. The ratio of low weight ($n-C < 20$) to high weight ($n-C > 21$) alkanes is also an indicator of biogenic vs petroleum sources. In all cases, this ratio is less than 1. Both of these ratios indicate primarily biogenic sources predominate, including Seldovia Harbor. The values in Dogfish Bay are contradictory. However, the overall concentrations of alkanes in this location were so low, with many zero values, the ratios may be meaningless. The dominant alkane at most sites was $n-C 27$ or 29 , which is typically associated with vascular plant sources (Colombo et al. 1989). The major alkane at Seldovia

Table 6 Spearman Rank correlation coefficients (above) and probabilities (below) between organic constituents and sediment characteristics. (totCyclo = total chlordanes and cyclodienes)

Variable	% SiCl	TOC	Total PAH	Total PCB	Tot Cyclo	Tot DDT
SAND	-0.95726	-0.69171	-0.54151	-0.57802	-0.35469	0.0718
	< .0001	< .0001	0.0035	0.0016	0.0695	0.7219
% SiCl		0.7537	0.65934	0.64374	0.47424	0.02372
		< .0001	0.0002	0.0003	0.0124	0.9065
TOC			0.82119	0.70122	0.51422	0.33892
			< .0001	< .0001	0.0061	0.0837
Total PAH				0.79933	0.70387	0.60826
				< .0001	< .0001	0.0008
Total PCB					0.52939	0.42697
					0.0045	0.0263
Tot Cyclo						0.34393
						0.079

Table 7 Alkane and petroleum hydrocarbon concentrations ($\mu\text{g/g}$) in sediments in embayments on the Kenai Peninsula. (N/A, cannot calculate due to zeros)

	Site	Total alkanes	Pristane	Phytane	Petroleum hydrocarbons	Odd/even	CPI	Dominant n-C	Low wt/high wt	pris+phyt/n-C17
Halibut Cove	HC 1	3.43	0.01	0.00	23.51	3.81	11.83	27	0.25	0.11
	HC 3	2.33	0.00	0.00	14.16	4.14	14.77	27	0.17	N/A
	HC 6a	3.01	0.02	0.00	21.84	2.76	7.98	27	0.27	0.19
China Poot	CP 11a	0.33	0.00	0.00	5.32	1.81	N/A	27	0.84	0.00
	CP 12a	0.44	0.00	0.00	6.82	3.02	N/A	27	0.53	0.00
	CP 8a	2.18	0.01	0.03	22.81	2.44	5.85	27	0.52	0.27
Sadie Cove	SC 1	8.95	0.13	0.19	89.36	4.88	9.35	27	0.17	1.08
Tutka Bay	TB 1	6.03	0.03	0.02	43.64	3.99	8.31	27	0.14	0.41
Jakolof Bay	KJ 1	3.54	0.04	0.02	33.60	2.47	4.14	27	0.18	0.80
	KJ 13a	7.10	0.01	0.01	53.65	4.99	8.43	27	0.09	0.32
	KJ 4	4.18	0.02	0.01	46.77	3.52	4.70	27	0.11	0.73
Homer	HH-3	10.67	0.32	0.18	212.85	3.59	7.22	29	0.23	1.74
Seldovia Harbor	SH 1	6.40	0.09	0.06	113.68	3.49	13.83	27	0.21	1.07
	SH 2	5.83	0.04	0.02	76.92	4.62	11.89	27	0.16	0.48
	SH 3	3.81	0.08	0.05	93.90	1.94	2.87	21	0.44	1.65
Seldovia Bay	SB1	7.67	0.07	0.02	59.78	3.63	8.35	27	0.18	0.69
	SB 4a	9.72	0.05	0.02	71.42	4.11	9.88	27	0.14	0.46
	SB 5a	6.29	0.06	0.02	72.03	3.01	7.06	27	0.18	0.53
Port Graham	PG-3c	4.12	0.03	0.02	67.72	3.36	5.85	29	0.25	0.63
Dogfish Bay	DB 1	0.06	0.00	0.00	1.43	0.28	N/A	16	3.64	N/A
	DB 12a	0.71	0.00	0.00	5.41	1.40	N/A	27	1.27	0.00
	DB 3	0.18	0.00	0.00	9.01	0.43	N/A	18	3.82	0.00
Clam Cove	CC 12a	0.91	0.02	0.00	12.10	4.53	N/A	27	0.33	1.23
Chrome Bay	CH 11a	0.39	0.00	0.00	5.18	1.16	2.42	Multiple	0.51	0.00
	CH 5	0.26	0.00	0.00	3.23	0.71	1.59	Multiple	0.60	N/A
	CH 6	0.22	0.00	0.00	7.52	0.75	1.95	16	0.78	0.00

Harbor site SH-3 was 21, which is much closer to typical petroleum values. The carbon preference index ($\text{CPI} = 2(\text{C}27 + \text{C}29)/(\text{C}26 + 2\text{C}28 + \text{C}30)$) (Boehm et al. 1984) was greater than 3 in all cases, except Seldovia Harbor site SH-3, which is another indicator of biogenic sources. Again, the values in Chrome and Dogfish Bays are unreliable due to so many zero values. A ratio of pristane + phytane/n-C17 much greater than 1 indicates contamination by degraded oil (Gill and Robotham 1989). The two highest values of this ratio were seen at Seldovia and Homer Harbors.

Butyltins were analyzed only in samples from Seldovia Harbor to contrast with the 2007 data from Homer Harbor. Tributyltin was the active ingredient in a popular boat bottom paint, which has been banned in most countries

due to side effects on non-target organisms, especially mollusks (Bray and Langston 2006). Homer Harbor was the only location where butyltins were detected in all of Kachemak Bay in 2007 (Hartwell et al. 2009). In Seldovia Harbor only one sample had detectable dibutyltin (a breakdown product of the original tributyltin) at a relatively low level of 4 ng/g Sn. Homer Harbor concentrations ranged between 7 and 11 ng/g Sn, probably due to boat hull cleaning in unconfined facilities.

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