

## Preassessment Data Report #3

### *Selendang Ayu* oil risk to early life stage salmon

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#### Abstract

Polynuclear aromatic hydrocarbons (PAH) from the *Selendang Ayu* oil spill were biologically available at detrimental concentrations in 1 of 14 streams examined, likely placing resident juvenile fish and possibly embryos at risk. Assessment began several months after the spill; aqueous total PAH (TPAH) concentrations were likely higher before sampling commenced. Estimated aqueous TPAH concentrations in that stream (SKN14) were high enough to have negative impacts on survival and growth but pink salmon embryos were generally absent in the affected river area and we conclude this was due to marginal habitat quality (too much sand and mud) rather than oil related mortality. Species that reared in oiled reaches of the main channel (Dolly Varden and coho) were also at risk; analysis of tissues for hydrocarbon exposure can be conducted if warranted. Although bioavailable PAH in bays was widely distributed, only the water of Skan Bay posed a potential risk to emigrant juvenile pink salmon during the sampling period. Although bioavailable TPAH concentrations in Skan Bay were significant, several unknowns precluded definitive assessment of risk in marine water, including the residence time of juvenile pink salmon, their dependence on potentially oiled prey, and true aqueous TPAH concentrations. Overall, we conclude that the *Selendang Ayu* spill placed a relatively small number of pink salmon embryos and fry at lethal and sublethal risk in stream habitat.

#### Introduction

Oil spilled by the freighter *Selendang Ayu* on December 8, 2004 (approximately 321,000 gallons of IFO 380 intermediate fuel oil and 15,000 gallons of Marine diesel fuel) spread into adjoining bays of Unalaska Island, along an estimated 70 miles of shoreline (Fig. 1). The impacted area contained 19 streams utilized by pink salmon (*Oncorhynchus gorbuscha*) and other species as spawning and rearing habitat (from Kashega Bay through Volcano Bay; ADF&G), raising concerns that incubating eggs, alevins, and fry could be damaged by oil exposure. These concerns were based on prior field experience, where toxic effects of *Exxon Valdez* oil on pink salmon were observed for up to four years after the spill (Bue et al. 1996,1998; Wertheimer et al.1996; Willete et al. 1996). Long term follow-up studies demonstrated that low part per billion level exposures [1 to 18 µg/L total polynuclear aromatic hydrocarbons (TPAHs)] were effective in causing both short term (Marty et al 1997, and long term effects, including reductions in adult returns after embryonic exposures (Heintz et al. 1999, 2000; Carls et al. 2005).

*Selendang Ayu* oil was deposited primarily on gravel beaches, including storm-created berms adjacent to the intertidal reaches of salmon streams, but also inland on banks along two streams (SCAT data). Areas surrounding low-gradient stream mouths were often oiled. This caused considerable concern because the *Exxon Valdez* experience demonstrated significant multi-year negative effects in pink salmon when banks of streams were contaminated with oil. Dye studies in Prince William Sound (PWS) after the *Exxon Valdez* oil spill demonstrated gravity-driven groundwater flow from contaminated intertidal substrate into stream channels,

including the hyporheic zone utilized by developing pink salmon embryos (Carls et al. 2003). Sensitive passive samplers (low-density polyethylene membrane devices (PEMDs) detected a PAH concentration gradient in at least one affected stream a decade after the *Exxon Valdez* spill, demonstration of the long, slow release from stranded intertidal crude oil (Carls et al. 2004a). Consistent with drainage of PAH into stream systems, cytochrome P4501A (CYP1A) was induced in pink salmon alevins (1989 to 1991; Wiedmer et al. 1996). All of these observations in PWS explain the elevated pink salmon egg mortality that persisted for 4 years in oiled PWS streams (Bue et al. 1998).

Experience and sampling strategy developed in the study of the *Exxon Valdez* spill was applied to the *Selendang Ayu* spill, including division of streams into zones with oil contamination plus upstream zones above oil to act as stream-specific reference sites. Deployment of passive samplers (PEMDs) to detect oil began 3 months after the *Selendang Ayu* spill, a technology developed after the *Exxon Valdez* oil spill (Huckins et al. 1990; Carls et al. 2004b). Advantages of PEMDs are high sensitivity; hydrocarbons are concentrated by  $10^4$  to  $10^5$  times above those in surrounding water, hydrocarbon analysis requires fewer cleanup steps than tissue, PAH are not metabolized by passive samplers, samplers can be placed and retrieved at known times, and they capture intermittent exposures such as those driven by tidal pumping and surface runoff. Stream and bank sediment was also collected to quantify oil concentrations within and around the streams and to confirm PAH composition and source. Alevins (hatched embryos, but still with yolk and resident within the spawning gravels) were hydraulically pumped from stream sediment to examine the CYP1A biomarker and for direct analysis of hydrocarbon burdens. This sampling would also confirm whether a stream reach was a spawning habitat or not. CYP1A is induced by planar hydrocarbons such as PAH; induction provides evidence of recent or ongoing exposure.

Our specific objectives were to: 1) determine if oil was visible on stream banks in pink salmon spawning habitat for streams designated as priority by preliminary NOAA surveys ( $n = 15$ ), 2) determine the potential for early life stage salmon exposure in 3 oiled and 2 reference streams using PEMDs as surrogate accumulators of biologically available oil, 3) determine PAH exposure in pink salmon alevins using direct hydrocarbon analyses and cytochrome P4501A (CYP1A) induction techniques, 4) determine bioavailability in marine waters near the mouths of salmon streams where out-migrating fry might first feed and reside using PEMDs, 5) determine concentration and PAH composition in stream and bank sediment to augment PEMD measurements and aid in interpretation, and finally, 6) evaluate the risk to salmonids in oil-affected streams and marine water. To date, CYP1A analyses not been completed; these samples may be analyzed, if warranted in the Assessment Phase.

## Methods

### Stream sampling

Preliminary identification of oiled salmon streams was based on Shoreline Cleanup Assessment Team (SCAT) data collected after the *Selendang* spill and on Alaska Department of Fish and Game (ADF&G) salmon data. Oiling conditions were verified visually at each of 14 streams identified by NOS as important and classified as no oil, light, moderate or heavy oil. The fifteenth priority stream (Spray Cape<sup>1</sup>) could not be sampled due to weather. The suitability

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<sup>1</sup> No salmon escapement data are available for this stream.

of habitat for spawning in oiled areas was assessed visually (based on substrate type) and confirmed by hydraulic pumping for alevins. Results of these subjective measures were used to define a subset of streams for objective, quantitative chemical and biological sampling including both oiled and non-oiled streams. All data were collected in 2005, beginning in March (approximately 4 months after the spill) and prior to alevin swim up from the spawning gravels and emigration from the streams.

Streams were subdivided into two zones: oiled (downstream) and non-oiled (upstream) sections based on visual observation oil. Three streams with oil (SKN4, SKN14, and MKS5) and two non-oiled reference streams (PMS16 and PMN20) were sampled. A tributary in one of the oiled streams (SKN14) was also examined. To estimate the potential bioavailability of dissolved PAH, PEMDs were placed at 3 oiled sites and 1 non-oiled site in each stream in March and collected about 1 month later (1 device per site). Non-oiled sites were located above the oiled zones and served as stream-specific references. Stream gradients varied considerably, thus site elevations and spacing between sites varied from stream-to-stream. Observation by PEMD of two oiled streams with overlap between spawning habitat and oil (SKN14 and MKS5) and the tributary (of SKN14) continued monthly through September, an extension of the original study design.

*Assessment of spawning habitat suitability.* Field determination of the suitability of habitat for salmon spawning was based on observation of stream sediment, water flow, and exploratory hydraulic pumping to determine the presence or absence of eggs and alevins.

*Alevin and fish sampling.* To confirm oil exposure, pre-emergent alevins collected by hydraulic pumping were either frozen in glass jars for hydrocarbon analysis or fixed in 10% phosphate-buffered formalin to estimate CYP1A induction. In August, additional resident Dolly Varden char (*Salvelinus malma*) and coho salmon (*O. kisutch*) smolts were collected for CYP1A induction and PAH analysis from two oiled streams (SKN14 and MKS5). Analysis of these samples could be conducted in the Assessment Phase, if warranted.

*Sediment sampling.* Sediment samples were collected from stream channels at each site and sediment from adjacent banks was collected and frozen in certified hydrocarbon-free jars. These samples are pending analysis. Blank jars were included in the collection for quality control.

### **Assessment of nearshore marine habitat**

Additional PEMDs were deployed in the nearshore marine environment and remained approximately 1 m below the surface on anchored buoys in bays adjacent to stream mouths for 1 month intervals (Appendix 1). These PEMDs were deployed in March, April, May, and August 2005; sampler loss in this high energy environment was relatively frequent, resulting in discontinuous sampling. Lack of vessel support precluded sampler replacement in June. In total, 17 marine PEMDs were retrieved and analyzed.

### **PEMD preparation and quality assurance**

The PEMDs were prepared according to Carls et al. (2004b). In brief, low-density polyethylene tubing (98  $\mu\text{m}$   $\times$  4.9 cm  $\times$  50 cm) was sonicated twice in pentane to remove hydrocarbons, placed in aluminum samplers (11.5 mm diameter  $\times$  6.6 cm with perforated endplates, 3 mm holes spaced 4.8 mm apart, precleaned in dichloromethane), wrapped with two layers of aluminum foil, heat-sealed in two plastic bags, and frozen until shipment to Dutch Harbor. Laboratory and field blanks were included in each sampling event for quality control.

The field blanks were used as transportation and handling blanks; they were transported to the field with all other PEMDs, opened briefly (1 per stream), then repackaged and as handled as all other samples. Deployed PEMDs were tethered to solvent-cleaned Duckbill<sup>®</sup> anchors with solvent-cleaned steel cable and zip ties or to nylon line fastened to rock-filled polypropylene mesh bags. The PEMDs were buried about 3 to 6 cm below the stream bed during the first installation. Because many were excavated by stream activity, subsequent devices were not buried. Additional anchors were often placed a meter or two downstream to secure small marker floats. Retrieved PEMDs were rinsed in place as they were retrieved to remove accumulated sediment, double-wrapped in aluminum foil, placed inside two Ziplock<sup>®</sup> bags, and frozen as soon as possible.

### PAH Analyses

All hydrocarbon samples were extracted with organic solvent. The PEMDs were wiped to remove gross surface contamination, placed in centrifuge tubes and spiked with 6 deuterated PAH standards (naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub>, and benzo[a]pyrene-d<sub>12</sub>). Spike solvent (hexane) was allowed to evaporate, then the tubes were placed in a sonic bath, and extracted in 80:20 ml pentane/dichloromethane for 130 min. The sonicator was on for the first 20 min of each 50 min period. The PEMDs were rinsed without delay with pentane as they were removed after the final sonication; extracts were concentrated to 20 to 30 ml, dried with 2 to 4 g of sodium sulfate, concentrated to 1 to 2 ml in hexane, and passed through 1.5 g silica gel columns. All extracts were spiked with an internal standard (hexamethyl benzene) and frozen pending analysis. Sediment and tissue samples were analyzed using the methods of Short et al. (1996). Samples were extracted twice with dichloromethane after addition of previously identified 6 internal standards. Extracts were reduced in volume, exchanged with hexane over a steam bath, and fractionated and purified by alumina/silica gel chromatography.

Extracts were analyzed by gas chromatography equipped with a mass selective detector and PAH concentrations were determined by the internal standard method (Short et al. 1996). Experimentally determined method detection limits (MDL) were generally 0.18 to 3.94 ng/g in PEMDs, about 1 ng/g in tissue, and <2 ng/g in sediment; concentrations below MDL were considered equivalent to zero and are not reported. The accuracy of the hydrocarbon analyses was within 15% (i.e., ± 15%) based on comparison with National Institute of Standards and Technology values, and precision expressed as coefficient of variation was usually less than about 20%, depending on the PAH. All internal standard recoveries were within acceptable limits (32 to 136%; mean 93%). Internal standard recoveries in PEMDs increased from naphthalenes (87 ∓ 10%) to phenanthrenes (99.7 ∓ 8%) and declined toward higher molecular mass PAH (90 ∓ 19% for perylene).

Total PAH concentrations were calculated by summing concentrations of 44 individual PAH, ranging from 2 to 5 rings (naphthalenes (N0 to N4), fluorenes (F0 to F4), dibenzothiophenes (D0 to D4), phenanthrenes (P0 to P4), anthracene (AN), fluoranthene (FL), pyrene (PY), substituted fluoranthenes/pyrenes (A1 to A4), chrysenes (C0 to C4), benzo(b)fluoranthene (BB), benzo(k)fluoranthene (BK), benzo(e)pyrene (BE), benzo(a)pyrene (BA), perylene (PE), indeno(1,2,3-cd)pyrene (IC), benzo(a,h)anthracene (DB), and benzo(ghi)perylene (BZ).

*Interpreting PAH concentrations in PEMDs.* Passive samplers accumulate PAH over time and higher concentrations indicate substantially greater exposure during the period of

deployment. The relationship between deployment time and PAH concentration in PEMDs is inexact because PEMDs might capture transient high concentrations or measure a more stable concentration, different situations that cannot be distinguished with multi-day deployments. In a laboratory study (Carls et al. 2004), TPAH concentrations in PEMDs in contact for 52 d with exponentially declining aqueous TPAH concentrations were 94% of those deployed for 26 d, demonstrating good retention capacity. PEMDs are very sensitive to all water or airborne organics, hence laboratory and field blanks are required for interpretation. Laboratory and field blanks often have TPAH concentrations between zero and 100 ng/g. Concentrations between 100 and 500 ng/g usually indicate low exposures.

A summary oil-identification model comprised of multiple oil-identification models was used to determine if PAH composition in PEMDs, sediment, and tissue was consistent with a petrogenic source, presumptively *Selendang Ayu* oil, the only known and largest potential source of oil (Carls 2006). Contributing models were authored by Short and Heintz (1997), Bence and Burns (1995), and Carls (2006). Summary scores range from 0 to 6; a score of 4 is considered probably petrogenic, hence probably *Selendang Ayu* oil, and scores greater than 5 are considered definite evidence of oil. Oil was considered fresh when PAH composition was dominated by naphthalenes and weathered when higher molecular weight PAH were dominant.

**CYP1A analyses.** Samples were collected and will be analyzed if warranted in the Assessment Phase.

### Study area

The *Selendang Ayu* grounded on the western coast of Unalaska Island, near Spray Cape (53.6297°N, 167.1392°W). The reference streams were located south of the wreckage along the outer coastline (Outer Pumicestone) or near the head of the long, narrow Pumicestone Bay (Fig. 1). Oiled streams were located to the north or northwest in Skan Bay (two streams) and Makushin Bay (Fig. 1).

#### Oiled area.

Stream SKN4 in Skan Bay was lightly oiled; oil was observed only near the mouth and in the intertidal berm, consistent with SCAT observations (Fig. 1). The stream did not discharge directly into the bay, when the PEMDs were placed (March 2005) and retrieved (April), rather it percolated through the rocky beach berm. The stream broke through the berm a few days after samplers were placed but the berm reformed before the PEMDs were retrieved. The lowest sample elevation was 1.04 m above mean lower low water (MLLW) and water was fresh (0 ppt) throughout. The stream was deep, broad (23 m near site 2), and had a low gradient (0.1 cm/m). Sampling extended about 475 m upstream; this reach was almost lake-like, with a slow flow rate (mean less than 0.1 m/s). The stream substrate was gravel-cobble. Alevins were encountered above site 3 (greater than 380 m stream distance) and collected only from the uppermost elevation (site 4; about 500 m stream distance). A few dead eggs were discovered near site 3; no eggs or alevins were encountered in lower zones. The mean pink salmon run in SKN4 is 6000 fish (Appendix 2). Samplers, including two in the bay, were placed in March and retrieved in April (26 d).

Stream SKN14 in northern Skan Bay was heavily oiled, consistent with SCAT observations (Fig. 1). This was a wide, generally shallow, low-gradient stream with generally

low water velocities (mean 0.1 m/s, excluding one apparent measurement error;  $n = 14$ ). The first 300 m of streambed consisted of 75% sand and 25% gravel/cobble substrate. Above this point the stream widened (about 100 m) into a shallow lake primarily consisting of sand and mudflats. In June 2005, numerous adult salmon carcasses, apparently pink salmon, were observed partially buried in fine bottom sediments in this area. The channel narrowed near site 3 but was similarly broad in places between sites 3 and 4. The river bank and adjacent vegetation was oiled for about 1.7 km and a boom was located 40 m upstream of this point. Surveying over these distances was not feasible and gradient was not determined. Water was fresh throughout (0.0 ppt); temperatures declined from 6.2 °C (site 1) to 2.9 °C (site 4) in March. Habitat in vicinity of sites 1, 2, and 4 was apparently not suitable for salmon spawning; dead eggs but no alevins were discovered at site 3 (about 400 m stream distance and adjacent to the tributary). However, pink salmon spawning between sites 3 and 4 was observed in August. Site 4 was the above-oil reference in this stream. Stream samplers were first placed in March 2005 then retrieved and replaced at roughly 1 month intervals (24 to 41 d; Appendix 3). Two to three PEMDs were placed in the bay in March, April, and August and retrieved 24 to 33 d later (Appendix 3). The lower portion of SKN14 had been cleaned in the vicinity of site 1 before sampling began; the remainder was cleaned during the April-May deployment. Stream SKN14 supports a pink salmon run (mean 12,000 fish,  $n = 3$ ; Appendix 2).

A partially oiled tributary that entered SKN14 near site 3 and rose to the north was also sampled (Fig. 1). The tributary had several channels; the main channel was always filled with water, side channels were sometimes filled. The channel was relatively narrow (6.6 m at the delta where it entered SKN14), rose quickly (3.5 cm/m), and extended above the oiled zone within 36 m. Flow was rapid (mean 0.7 m/s) and the water was fresh (0.0 ppt). The substrate was gravel-cobble. Alevins were collected from the gravel at both below and above oil sites. Samplers were first placed in March 2005, then retrieved and replaced at roughly 1 month intervals (22 to 41 d; Appendix 3).

A braided, glacially turbid stream (MKS5) in Makushin Bay was lightly or moderately oiled to about 350 m stream distance, consistent with SCAT observations (Fig. 1). In June and August, high densities of juvenile coho and Dolly Varden were observed in turbid main channels, clear side-channels, and isolated pools. Water velocity was low in an eastern channel and orange clay coated the rocky substrate, though in September when flow rates increased, adult fish were observed in this channel. Mean flow in the braided portions of the stream was 0.9 m/s and the mean gradient was 1.0 cm/m. The first section of the river paralleled the bay and was separated from it by a rocky berm in the spring. The stream broke through the berm in the fall as apparent flow volumes increased. Some oil was evident on the berm. A boom was located along this stretch, about where the river turned uphill. Sediment and plants inland were oiled up to an elevation of 2.8 m above MLLW. Salinity was consistently 0.1 ppt. Water temperature ranged from 7.2 to 7.6°C in March with no obvious elevation-related pattern. The lowest site (1) was 1.25 m above MLLW and the highest (4) was 3.71 m above MLLW. Site 4 was the above-oil reference in this stream (430 m stream distance). The substrate was gravel-cobble. Pink salmon alevins were collected near sites 2 (270 m stream distance), 3, and 4. Samplers, including two in the bay, were first placed in March 2005, then retrieved and replaced at roughly 1 month intervals (24 to 41 d; Appendix 3). Beginning in April, Makushin Bay samplers were relocated to the ends of the straight beach section, about 2 km apart. Stream MKS5 supports a salmon run (mean 22,000; Appendix 2). Stream MKS5 was cleaned in July.

### **Reference area.**

The reference stream in Outer Pumicestone Bay (PMN20) was broad (nearly 60 m at the widest point near site 2) with a low gradient (about 0.6 cm/m; Fig. 1). No oil was observed, consistent with SCAT observations. Salinity ranged from 0.9 ppt at site 1 (near mouth) to 0.1 ppt at site 4 (about 600 m upstream). The elevation at site 1 was less than 0.9 meters above MLLW and the mean flow rate was 0.4 m/s. The stream channel habitat, primarily sand and mud, was unsuitable as pink salmon spawning habitat; no eggs or alevins were found during exploratory pumping. Stream PMN20 supports a pink salmon run (mean 9,000,  $n = 19$ ; Appendix 2); presumably the primary spawning habitat is upstream of the area sampled. Samplers, including two in the bay, were placed in March 2005 and retrieved in April (25 d).

The mouth of stream PMS16 consisted of three channel braids flowing into Pumicestone Bay over a broad alluvial fan. No oil was observed, consistent with SCAT observations. Stream gradient (greater than 1.4 cm/m), water velocities were high (mean = 1.2 m/s), and the central channel was often too deep to sample (Fig. 1). The streambed substrate was dominated by cobbles and small boulders. Water was fresh (0.0 ppt) and cold (2.9 °C) throughout. The alluvial fan and other areas around this stream have been used as a cattle pasture; no cattle were observed during sampling. Site 1 was 0.75 m above MLLW; the uppermost site (4) was greater than 2.66 m above MLLW and was 166 m upstream. The sampled habitat was suitable for spawning and alevins were present in stream gravel. The stream supports a pink salmon run (mean 31,000; Appendix 2). Samplers, including two in the bay were placed in March 2005 and retrieved in April (24 d).

## **Results**

All PEMD samples (105) have been analyzed. Hydrocarbons in sediment and tissue and CYP1A induction will be analyzed if warranted in the Assessment Phase.

### **Oil and spawning habitat distributions**

There was little overlap between oiled habitat and pink salmon spawning habitat in most streams. Of the 14 streams visually surveyed for pink salmon alevins and the presence of oil, alevins were potentially exposed to oil in 2 (SKN14 and MKS5) but not in the remaining 12 (Appendix 2). [This assessment was based on visual evidence of oil contamination on the stream banks and surrounding vegetation and the presence of spawning gravel (not mud or sand), plus confirmation of spawning habitat through the hydraulic pumping for embryos and alevins]. Chemical confirmation of biological availability of oil in these streams is reported in the next section. All visual assessments were consistent with SCAT data. There was no evidence of intertidal spawning at any stream (examined with hydraulic pumping); the habitat in the Aleutians was not similar to the intertidal habitat in PWS. Tides are significantly smaller in the Aleutians and beaches and stream mouths are typically subjected to higher energy surf. In addition, stream gradients in the lower reaches above the surf zone are often too low to provide spawning gravels. Observed oiling was generally confined to beach areas and usually did not extend upstream to spawning habitat.

*MKS5 stream.* Salmon habitat and oil overlapped in the lightly or moderately oiled braided portion of the MKS5 stream. Bank sediment and terrestrial plants were oiled inland up to 2.8 m above MLLW (about 350 m stream distance). Pink salmon alevins were discovered by hydraulic pumping within the oiled zone (270 and 315 m stream distance) and above it (430 m).

Juvenile coho and Dolly Varden also utilized this habitat and were sampled in August for potential hydrocarbon and CYP1A analyses.

*SKN14 stream.* Salmon habitat and oil overlapped in the heavily oiled SKN14 stream. The stream banks and surrounding vegetation were heavily oiled for at least 900 m and oiling extended to about 1.7 km upstream. Suitability of the main stream channel was questionable as pink salmon spawning habitat; the only main channel location where evidence of spawning was discovered in the spring was site 3, adjacent to a tributary with suitable spawning habitat. Thus, oil and spawning habitat overlapped in less than 1% of the study area. However, some spawning activity was observed in the main channel in the fall. A tributary in the vicinity of site 3 was prime spawning habitat; alevins were abundant both above and below oiled area. The lower portion of this tributary was oiled for about 35 m. Juvenile coho and Dolly Varden were abundant along the margins of the main channel and were observed in areas covered with oil sheen. Both species were sampled in August.

### **Potential biological availability of PAH, measured in PEMD surrogates.**

*Oiled streams. SKN14.* Total PAH concentrations were at least 1 to 2 orders of magnitude greater in stream SKN14 than in others; visibly, this stream was the most extensively and heavily oiled of all streams sampled (Fig. 2) and the passive samplers confirmed the visual observations with chemical evidence of bioavailability. Total PAH concentrations in the lower three elevations (within the oiled zone) initially ranged from 42,044 to 463,080 ng/g with the highest concentrations at the lowest elevation (Fig. 2). Oil was present in all these PEMD samples (Table 1). Concentrations dropped exponentially in the following months, except trends reversed in the last sample period (August – September 2005; Fig. 2). The decline in concentrations over time suggests that even higher concentrations were possible in the earlier months of the spill. Oil was not present in passive samplers placed above the oiled zone (the stream-specific background), where the TPAH concentration ranged from 23 to 93 ng/g, or in the site blanks where the TPAH concentration ranged from 30 to 140 ng/g (Table 1). In the contaminated tributary of SKN14, TPAH concentrations within the oiled zone peaked at 426 ng/g, substantially less than in the main stream. Total PAH concentrations above oil in the tributary ranged from 31 to 67 ng/g with no evidence of oil (Fig. 2). PAH composition in SKN14, including the lower portion of the tributary, was consistent with oil from the *Selendang Ayu* (Fig. 2, Table 1).

**SKN4:** oil was observed only near the mouth and in the intertidal berm, consistent with SCAT observations (Fig. 1). Oil was probable in a PEMD placed below an oil band on the bank near site 1 and the mouth (4547 ng/g TPAH) but not in adjacent stream water (111 ng/g, retrieved April 2005; Table 1). Total PAH concentration dropped from 111 to 25 ng/g in the upstream direction. The site blank was 56 ng/g.

**MKS5.** Oil was present in stream MKS5 (Glacier Valley Creek) in Makushin Bay at concentrations about 1 to 2 orders of magnitude lower than in SKN14 (Fig. 2). Visible oil extended well above tidal influence but oiling levels were light compared to those at SKN14 and these qualitative differences were consistent with the differences in TPAH concentration between streams. Oil was detected in PEMDs at site 2 and peaked at 976 ng/g (in June) before dropping to 98 ng/g (in August; Fig 2). Low concentrations of oil were also possible in water at site 1 (near the stream mouth). Oil was not detected at site 3. Total PAH at the stream reference site ranged from 10 to 35 ng/g and was 23 to 178 ng/g in the site blanks; oil was not present in either (Table 1).

*Oiled bays.* Total PAH concentrations in marine water of Skan Bay near SKN14 were greater than in other bay samples (4,150 to 18,278 ng/g) with clear compositional evidence of oil in the PEMDs (Fig. 2, Table 1). Oil was also present near SKN4; TPAH concentrations ranged from 4,844 to 6,295 ng/g (Table 1).

*Comparison of oiled bays and oiled streams.* The composition of PAH in Skan Bay marine PEMD samples was more weathered than in adjacent streams. This relationship is clear in SKN14 where initial and final TPAH concentrations in stream water were high and the oil was fresh (Fig. 3 and Appendix 4). Naphthalenes (which are dominant in unweathered oil) accounted for 61 to 76% of the TPAH near the mouth of SKN14 (site 1) in March through May and August—September 2005. As concentrations in the stream declined during the summer (and after oil removal from banks in April and May), composition became more weathered; percent naphthalenes dropped to 40 to 43%. Total PAH concentrations increased in the final sample (August—September) and the oil was less weathered. In contrast, PAH in the bay was consistently more weathered than water near the stream mouth, ranging from 19 to 22% naphthalenes in March—April to 15 to 18% naphthalenes in August—September. The same contrast was evident between the single definitively oiled sample in stream SKN4 (74% naphthalenes) and adjacent bay water (18 to 23% naphthalenes; March—April).

*Reference streams and bays.* Except at the mouth of PMN20, no oil was visible or detected in either reference stream, both sampled from March to April 2005. Total PAH concentrations in PEMDs in PMS16 ranged from 14 to 16 ng/g ( $n = 4$ ); the site blank was 28 ng/g (Fig. 2; Table 1). There was no evidence of oil in these samples (Table 1). Concentrations in PMN20 were similar at most elevations (6 to 37 ng/g,  $n = 3$ ) with no evidence of oil; the site blank was 21 ng/g (Fig. 2; Table 1). Analyte concentrations were below calibration standards or there was no signal at these sites. However, the TPAH concentration at the lowest PMN20 elevation was 589 ng/g and the composition was consistent with *Selendang Ayu* oil (Table 1). Some beaches along the coastline both north and south of PMN20 were characterized as oiled by the SCAT team (Fig. 1).

Total PAH was slightly elevated (115 to 135 ng/g,  $n = 3$ ) in PEMDs in adjacent reference bays (Fig. 4) compared to the reference streams and composition was consistent with a petrogenic source (Table 1). These concentrations were greater than in the site blanks (21 to 28 ng/g) but 1 to 2 orders of magnitude less than in bays with visibly oiled beaches (Fig. 4).

*Quality assurance: PEMD blanks.* There was no evidence of oil in laboratory blanks; mean TPAH concentrations were lowest in this group and ranged from 0 to 18 ng/g. Analyte concentrations in laboratory blanks were below calibration standards or there was no signal (Table 1).

Total PAH concentrations in site blanks (exposed briefly to air) ranged from 0 to 178 ng/g and there was no evidence of oil in them (Table 1). Analyte concentrations generally were below calibration standards or there was no signal.

### **Oil in sediment.**

*Selendang Ayu* oil was detected in visibly oiled stream banks (Table 2). The TPAH concentration was 94000 ng/g in an oily band at the mouth of SKN4 and composition was consistent with *Selendang Ayu* oil; oil was not detectable in sediment slightly below this band where the TPAH concentration was 13 ng/g. *Selendang Ayu* oil was detected in SKN14 stream banks at all sites including the oiled portion of the tributary (1100-89700 ng/g) except the

reference sites (3 to 19 ng/g). *Selendang Ayu* oil was detected in stream banks at all MKS5 sites ( $\leq 727000$  ng/g TPAH) except the reference site (0 ng/g).

With one exception, *Selendang Ayu* oil was not detected in stream channels (Table 3). Sediment from the mouth of SKN14 was exceptional (2300 ng/g TPAH) with a composition consistent with *Selendang Ayu* oil. Elsewhere the mean TPAH concentration in stream channels was 2.6 (95% CI, -1.1 to 6.3). No detection of PAHs was typical.

### **Oil in pink salmon alevins.**

There was little evidence of oil in pink salmon alevins (Table 4). Pink salmon spawning habitat and oiled stream reaches rarely overlapped, thus few alevins samples were collected. Of these, TPAH concentrations were slightly elevated in two samples collected in the oiled portion of the SKN14 tributary (54-81 ng/g). *Selendang Ayu* oil could not be verified in either and naphthalenes were the only detectable PAH in one of them. Elsewhere, TPAH concentrations in alevins ranged from 0 to 16 ng/g (mean 2.8 ng/g,  $n = 10$ ), significantly lower than in the oiled portion of the tributary ( $P = 0.017$ ). The tissues of resident coho and Dolly Varden juveniles have not been analyzed.

### **Relationship between oil in PEMDs and oil in sediment.**

Dissolved *Selendang Ayu* oil constituents were consistently detected in PEMDs in streams where banks were oiled despite the nearly ubiquitous absence of *Selendang Ayu* oil in stream sediment. Consistent with a dissolved source, the relative quantities of the smallest PAHs (naphthalenes) were significantly enhanced in PEMDs [ $P = 0.002$ , mean 48%, 95% confidence interval (CI) 33 to 63%,  $n = 6$ ] with respect to those in oiled sediment (mean 21%, 95% CI 11 to 31%,  $n = 9$ ). Also consistent with a dissolved source, few high molecular weight PAHs were observed in PEMDs (mean 0.1%, 95% CI -0.1 to 0.2%,  $n = 6$ ). Significantly more high molecular weight PAHs were observed in oiled sediment ( $P < 0.001$ ; mean 2.8%, 95% CI 1.4 to 3.4%).

## **Discussion**

### **Pink salmon embryo exposure and risk**

Polynuclear aromatic hydrocarbons (PAH) from the *Selendang Ayu* oil spill were biologically available at detrimental concentrations in 1 of 14 streams examined (SKN14), likely placing resident juvenile fish and possibly embryos at risk. (Assessment began several months after the spill; aqueous TPAH concentrations were likely higher before sampling commenced.) In most cases (12 of 14 streams examined), spawning and rearing habitat did not intersect oiled habitat. Two of the 12 streams may not host salmon runs (SKS14 and SKN8). The other 12 spawning streams examined represent 63% of all known salmon streams in the spill area ( $n = 19$ , from Kashega Bay to Volcano Bay; Appendix 5). No oil was reported by SCAT surveys in any of the 7 spawning streams not examined and oiling on adjacent beaches was light with no evidence of buried oil. Oiling near salmon streams was generally confined to beach areas; suitable spawning and rearing habitat was consistently located further upstream. No intertidal spawning habitat was observed and gradients were generally low in lower stream reaches thus usually not suitable for spawning due to the lack of appropriate gravel substrate. The intertidal and lower reaches of the streams in Unalaska were fundamentally different than the short streams in PWS where oil and spawning habitat intersected on all oiled stream mouths.

Pink salmon spawning habitat utilization in Unalaska differs sharply with that in PWS, where oil from the *Exxon Valdez* had a significant impact on pink salmon embryos in the intertidal portions of streams (Rice et al. 2001). In Unalaska, pink salmon generally do not utilize intertidal habitat for spawning (A. Shaul, ADF&G, personal communication) and we found no evidence of intertidal spawning activity. In contrast, up to 75% of spawned pink salmon eggs are deposited intertidally in PWS (Helle et al. 1964; Heard 1991). At least three prominent physical differences probably explain the differences: 1) There is a much smaller tidal range in Unalaska (range -0.5 to 1.5 m above MLLW) versus that in PWS (range -1.0 to 4.7 m above MLLW), thus the potential size of suitable intertidal habitat in Unalaska is far more limited. 2) The average wave energy in Unalaska is apparently greater than in PWS, reducing the likelihood of embryo retention in intertidal gravel and increasing substrate coarseness. Inland incursions of oil along Unalaska streams but not along PWS streams is an indication of the energy differences between these locations as is a dearth of mussels on gravel beaches in Unalaska. 3) Many of the Unalaska streams had low gradients near stream mouths, precluding the occurrence of suitable gravels for spawning.

Salmonids were at risk in stream SKN14, where stream banks were heavily oiled and dissolved oil was detected chemically about 400 m from the mouth and above some of the spawning habitat. Oil was deposited along the river banks and generally followed their course, suggesting deposition by a storm surge flood event. River substrate was oil-free, except for contamination in the high-energy environment at the mouth. Observed bioavailability of PAH was greatest at the first sampling in March, when alevins were still present. The decline in TPAH concentrations measured from March to August indicates that exposure concentrations were likely higher prior to sampling. Even though this stream was heavily contaminated for at least 900 m, including some spawning habitat, the risk to pink salmon in this stream was still not great, as most of the spawning habitat was above the oiled zone (oil and spawning habitat overlapped in less than 1% of the study area in SKN14 and the estimate for the entire stream system would be much smaller). Thus, the principal risk in this stream system was to resident coho and Dolly Varden juveniles.

Given the physical nature of the bunker oil spilled, persistence of the oil is virtually guaranteed in the freshwater environment for several months if not physically removed<sup>2</sup>. Prior to the March sampling, higher TPAH concentrations in earlier months (December 2004 – February 2005) were likely in oiled streams (SKN14 and MKS5) and unlikely in streams without visible oil. If the streams were oiled, the oil would have persisted through the March sampling, and been both visible and detected with the passive samplers.

The observed movement of dissolved PAHs from stream banks into stream water is consistent with the mechanism previously observed in Prince William Sound after the *Exxon Valdez* oil spill (Heintz et al. 1999; Carls et al. 2003, 2004). Dissolved PAHs leached from *Selendang Ayu* oil in stream banks into stream water; PAHs were absent in stream channel sediment (with one exception) and composition in PEMDs was consistent with accumulation from PAHs dissolved in water. Even where stream sediment was oiled (at the high-energy

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<sup>2</sup> Similarly long exposure times damaged pink salmon embryos at part-per-billion levels (Marty et al. 1997; Heintz et al. 1999, 2000; Carls et al. 2005). However, experimental exposures began shortly after fertilization, whereas any pink salmon embryo exposure to *Selendang* oil began about 3 to 4 months later. The toxicological implications of this offset are not known with certainty. Larval salmonids may be as sensitive to PAH as embryos if the relationship observed in short-term acute bioassays with monoaromatic hydrocarbons applies (Moles et al. 1979); more study is needed for definitive understanding.

mouth of SKN14), accumulation in the PEMD was characteristic of a dissolved source. Flowing stream water generally protected stream sediment from contact with whole *Selendang Ayu* oil just as was observed in Prince William Sound after the *Exxon Valdez* oil spill (Brannon et al. 1995). Thus, although protected from direct oiling, biota that inhabit streams surrounded by oil deposits are placed at risk by movement of oil-contaminated water. The principal source of contaminated water in Prince William Sound streams was groundwater driven by tidal exchange; in Unalaska the principal source was groundwater movement driven by precipitation.

Despite the obvious physical differences between bunker and crude oils, the PAH toxins that leached into the water from *Selendang Ayu* oil are the same as those leached from *Exxon Valdez* crude oil, thus previous research focused on the effects of crude oil is applicable to the Selendang spill. Composition of the biologically available PAH from *Selendang Ayu* oil (IFO 380, a refinement residue plus diesel fuel) was so similar to biologically available PAH from *Exxon Valdez* crude oil that the highly discriminatory first-order loss-rate model of Short and Heintz (1997) generally failed to distinguish the two<sup>3</sup>. Not only was PAH composition about the same, it also followed the weathering patterns observed for crude oil (more rapid loss of smaller molecular weight PAH). Similar effects in the Selendang spill could be expected if exposure concentrations and conditions (similar exposure periods, comparable life stages and species) were similar to the *Exxon Valdez* crude oil spill.

Estimating aqueous exposure concentrations from the passive samplers is challenging, and requires interpretation. It is not an exact science. Relative exposure differences from the integrating passive samplers can be compared from site to site, but the exact concentration history in the water during sampling periods remains unknown. There is no way, for example, to determine if accumulations represent a constant aqueous TPAH concentration or transient higher concentration spikes (Carls et al. 2004). Direct aqueous observation was not attempted because it was not feasible to conduct these measurements in the field and because such samples only represent brief periods of time.

A rough, order-of-magnitude estimate of aqueous TPAH in Unalaska streams is possible by comparison of PAH concentrations in PEMDs to data from a controlled laboratory experiment. The consistent overall pattern was an exponential TPAH decline in the heavily oiled SKN14 stream. A similar decline was evident in PEMDs serially deployed in a laboratory experiment where measured aqueous concentrations were falling exponentially (Appendix 6; Carls et al. 2004b; 2005a). The PAH composition, temperature, and deployment times were similar in both. Naphthalene concentrations initially dominated in the laboratory (70%) and ranged up to 76% in SKN14, attributes of fresh oil. Relative phenanthrene concentrations increased with weathering, reaching 32% in the laboratory and 41% in SKN14. Temperatures in the laboratory and SKN14 ranged from 2 to 10° C and 3 to 13° C, respectively. Deployment times in the laboratory<sup>4</sup> were 26 and 52 d, those in SKN14 were 24 to 41 d. With this approach, we estimate that 1,000,000 ng/g TPAH in PEMDs corresponds to roughly 20 µg/L in water and 100,000 ng/g corresponds to roughly 2 µg/L.

Based on these approximations, fish in portions of stream SKN14 were at risk for a portion of the sampling period; this risk probably extended back to the oiling event and was probably even greater in the months prior to sampling. PAH are highly toxic to fish embryos (0.4 to 23 µg/L TPAH; Marty et al. 1997; Carls et al. 1999; Heintz et al. 1999, 2000; Barron et

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<sup>3</sup> This model is included in the combined composition model used for source identification in this study.

<sup>4</sup> In the laboratory experiment, TPAH concentrations in PEMDs deployed 52 d were similar to those in PEMDs deployed 26 d (94% retention).

al. 2003; Colvaecchia et al. 2004; Rhodes et al. 2005) and concentrations in this range and above represent a risk. Aqueous concentrations in SKN14 may have ranged up to about 10 µg/L at the lowest sample elevation and up to 1 µg/L at other oiled sites (March-April), placing developing embryos and other young salmon at risk, particularly in the lowest reaches of the stream<sup>5</sup>. Although apparently very few pink salmon developed successfully in the main channel of SKN14 between 2004 and 2005 due to lack of suitable habitat, sculpin eggs and juvenile salmonids that utilized this habitat for rearing were potentially at risk: a few pink salmon fry were also observed in the main channel. However, TPAH concentrations fell exponentially, progressively reducing the risk except for a reversal in the fall<sup>6</sup>. Estimated aqueous TPAH concentrations near the mouth of SKN14 were greater than 2 µg/L in April, May, and June and 0.5 µg/L in September, placing fish in this area at risk for most of the observation period. After April, estimated aqueous concentrations upstream of the mouth were less than 0.2 µg/L, suggesting the risk was low for the majority of the stream for the majority of the study.

Risk in the lightly oiled stream MKS5 was negligible. Embryos and alevins were probably exposed to less than 0.02 µg/L, well below concentrations of concern.

### **Risk to juvenile salmonids in freshwater and marine environments**

Oil was detected, visually on the beaches and chemically in the passive samplers, in both the marine environment (5 bays) and the lower reaches of 4 streams, particularly in the Skan Bay area (Table 1, Appendix 2). Concentrations were likely highest in the first month of the spill and greater than when first sampled in March. While oil exposure was evident in these areas, risk assessment is difficult. In freshwater, overwinter rearing habitat was contaminated for juvenile coho and Dolly Varden in two streams and possibly HMP11. We do not know the length of exposure nor the fidelity to the contaminated sites for these fish. Out migrating pink salmon would have transited the area from spawning habitat upstream, but again, the length of exposure would have been relatively short. Likewise, in the marine environment, we do not know the length of time outmigrating fry or smolts would have spent transiting and foraging in the shallow nearshore environment. Exposure to elevated PAH concentrations was likely in Skan Bay but these life stages are less susceptible to transient sublethal concentrations than embryos.

Risk to species that utilized the oiled reach of SKN14 for rearing before emigration (coho and Dolly Varden) was greater than for the nearly absent pink salmon embryos. Juvenile salmonid growth can be reduced by aqueous exposure to crude oil and by ingestion of oil particles or oiled food and high concentrations are lethal (Carls et al. 1996a,b). After the 1989 *Exxon Valdez* oil spill, wild juvenile pink salmon in PWS were exposed to roughly 1 to 3 µg/L TPAH in saltwater<sup>7</sup> and growth was reduced (Wertheimer et al. 1996; Willette et al. 1996; Short

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<sup>5</sup> At 10 µg/L, the risk of embryonic abnormalities caused by fresh oil (as was the case in initial SKN14 samples) is roughly 10% and roughly 10% of the embryos may die (Carls et al. 1999; Heintz et al. 1999). However, growth of pink salmon, measured 6 months after exposure, was significantly reduced when exposed to 1 µg/L fresh Alaska North Slope crude oil (Carls et al. 2005). Because pink salmon rely on rapid growth to escape mortality from size-selective predation (Hargreaves and LeBrasseur 1985), such effects can lead to depressed marine survival (significant at 5 µg/L; Heintz et al. 2000).

<sup>6</sup> The estimated aqueous TPAH concentration at site 1 in September was 0.5 µg/L, slightly above the lowest concentration (0.4 µg/L) known to adversely affect fish embryos (Carls et al. 1999); this toxicity estimate was based on moderately weathered oil ( $w \sim 3.3$ ).

<sup>7</sup> Exact estimates are not available. Total PAHs in mussel tissue were analyzed as site-specific surrogates of exposure; mean concentrations at oiled sites ranged from 3772 to 8282 ng/g (Carls et al. 1996b). Assuming peak concentrations in water and peak concentrations in mussels observed in two specific areas where mussel and aqueous TPAH data were collected concurrently (Short & Harris 1996a,b; Carls et al. 2002) provide a reasonable

& Harris 1996a,b; Carls et al. 2002). Reduced growth translates into increased predation and reduced adult returns (Gieger et al. 1996; Heintz et al. 2000). Comparing the previous rough estimates of aqueous TPAH concentration in SKN14 to those in PWS suggests juvenile salmonids in this stream were at risk. Analysis of hydrocarbon body burdens and CYP1A induction would determine if the fish sampled had been exposed to oil but cannot demonstrate population effects.

Juvenile salmon in bays affected by the *Selendang Ayu* were potentially placed at risk. A large volume of water over a very wide area was apparently affected by the spill, with evidence of oil in marine water extending to the southern-most reference area (Pumicestone Bay) to oil-contaminated Makushin Bay. The most affected bay by far was Skan Bay; TPAH concentrations in Makushin Bay were roughly an order of magnitude smaller and concentrations in the reference bays were yet another order of magnitude smaller with little risk in the latter at the time of sampling. However, concentrations between the time of the spill and sampling were likely greater than those observed.

### **Oil persistence.**

The oil in Skan Bay was persistent; the highest observed TPAH concentration was in a cove south of SKN14 in September, perhaps a result of disturbances caused by ongoing shoreline cleanup activities. Evidence from other spills suggests that not all intertidal oil will be removed by cleanup activity and that remaining oil will be a persistent source of biologically available hydrocarbons for many years. Persistent cryptic patches *Exxon Valdez* oil were present 12 years after the spill in PWS beaches and remain today (Short et al. 2004). Oil retention in sediment is consistent with data from other spills, e.g., the *Amoco Cadiz*, the BIOS experiment, and the West Falmouth spill (Mille et al. 1998; Prince et al. 2002; Reddy et al. 2002; White et al. 2005). The sticky nature of the bunker oil spilled by the *Selendang Ayu* may increase persistence, now present more than a year in some beaches. Some similarly viscous Monterey oil spilled in 1964 remains adherent to PWS beaches (Kvenvolden et al. 1995; Short et al. 2004).

Not only does oil persist in the environment, but it often remains biologically available and toxic for many years. Pink salmon embryos bioaccumulated *Exxon Valdez* oil for at least 3 years in oiled streams in PWS and mortality was elevated for 4 years (Wiedmer et al. 1996; Bue et al. 1998). Contaminated prey and disturbance of oiled substrate during feeding activities explains the failure of sea otter and harlequin duck populations to recover in oiled areas of PWS for more than a decade (Esler et al. 2000; Bodkin et al. 2002). For both species, chronic exposure to oil (elevated cytochrome P4501A) and struggling populations in the most heavily oiled areas of Prince William Sound were observed in the decade after the spill (Esler et al. 2000; Bodkin et al. 2002). Salt marsh fiddler crabs (*Uca pugnax*) populations, feeding rates, and burrowing have been affected by buried oil for greater than 30 years in a West Falmouth marsh (Culbertson et al. 2005). In a review of seven well-studied oil spills, Teal and Howarth (1984) conclude that oil effects can persist for at least 6 to 12 years in sediment.

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measure of bioaccumulation by PWS mussels (mean 2652 times), then aqueous exposure concentrations ranged from about 1.4 to 3.1  $\mu\text{g/L}$ . This estimate is within the directly observed range of aqueous TPAH concentrations (range of means 0.9 to 6.2  $\mu\text{g/L}$ ) observed elsewhere in the slick area in 1989 (Short and Harris 1996a). The derived bioaccumulation factor is far lower than theoretically possible in mussels ( $2 \times 10^5$ ; Livingstone 1991); bioaccumulations this high would imply aqueous TPAH concentrations less than 0.1  $\mu\text{g/L}$ , i.e., background concentration. This concentration is too low to explain the observed significant CYP1A induction in the juvenile pink salmon fry in PWS and too low to explain the significant TPAH differences in mussel tissue between reference and oiled areas of PWS (Carls et al. 1996b, Carls et al. 2005a).

Intuitively, removal of oil from surrounding banks during cleanup should have reduced aqueous PAH concentrations in stream water, although temporary increases in bioavailability were anticipated during removal. However, exponential depletion of biologically available PAH was evident before oil was removed in SKN14 and there was no abrupt concentration drop after cleanup. Because PEMDs integrate concentration over time, failure to observe an abrupt change may be due in part to concentration averaging and cleanup activity. That may not be the entire story, however. Some oil may have penetrated into the ground surrounding the rivers and thus remained after cleanup. Limited visual observation of slicks weeping from banks after cleanup supports this hypothesis. Stronger support for the hypothesis and for aqueous transport comes from an unexpected reversal in TPAH concentration and weathering in SKN14. Oil in bay water was considerably more weathered than in stream water between August and September, eliminating marine input as the source of increased oil in the river. Stream bed disturbance by salmon digging redds might explain the greater oil mobility and freshness, but only if there were substantive quantities of oil on stream sediment that had avoided weathering; this is unlikely. Measurement of PAH in stream sediment will likely eliminate this possibility. That leaves oil in surrounding banks as the most likely source of dissolved PAH and increased fall precipitation as a possible reason for renewed transportation of fresh oil into the stream: precipitation declined during deployments in May through August and increased between August and September (Appendix 3).

### **Timing of sampling**

With the first sampling in March, peak concentrations in the marine environment and in oiled streams were missed because concentrations in the first month of the spill were probably highest in both habitats. Repeated sampling during the summer months provided a loss rate curve, indicating stream recovery due to cleaning activity and natural processes.

The March sampling preceded the emergence of pink salmon fry from the spawning gravels. The alevins sampled were relatively immature and had considerable yolk, indicating that peak emergence was probably in late April at the earliest.

### **Summary**

In summary, PAH from the *Selendang Ayu* posed a risk to developing pink salmon embryos and resident fish in 1 of 14 streams sampled and probably 1 of all 19 recognized salmon streams in the affected area. This conclusion is predicated on correspondence between visual observation of oil and measured TPAH concentrations, the minimal overlap of spawning habitat based on observation of spawning habitat and hydraulically sampled alevins, and limited evidence of oil exposure in these embryos. Estimated aqueous TPAH concentrations in that stream (SKN14) were theoretically high enough to have negative impacts on survival and growth of pink salmon embryos in the oiled zone, although the majority of the spawning habitat was above the oiled zone. The lower reaches of stream were generally not suitable for spawning habitat, thus posing little risk to pink salmon despite the oil contamination. However, this habitat may have been overwintering habitat for juvenile coho and Dolly Varden; juveniles were present but assessing risk is difficult without knowing exposure levels and residence time. Direct analysis of potentially affected fish tissues may allow confirmation of exposure but will still not permit an estimate of risk for the population. Estimated risk to resident fish and embryos in a second, lightly oiled stream was negligible because estimated aqueous concentrations were below the level of concern (less than 0.02 ug/L). Risk was very low in 13 other streams because

spawning and rearing habitat did not overlap with oiled areas and oil was not detected in PEMDs placed where oil was not visible<sup>8</sup>.

Although bioavailable PAH in bays was widely distributed, only the water of Skan Bay posed a potential risk to emigrant juvenile pink salmon. Total PAH concentrations were significant in the passive samplers during the observation period but concentrations were probably higher in the first months of the spill. Risk to outmigrant smolts and pink salmon fry from Skan Bay streams is difficult to assess: exposure was probable, but residence time in the nearshore area is unknown. Contamination levels in prey are unknown. Overall, we conclude that the *Selendang Ayu* oil spill placed a relatively small number of salmon at risk. Because PAH concentrations remained elevated in bays and the most heavily oiled stream (SKN14) during the final sampling interval, some risk remained at the end of sampling. However, trends in freshwater salmon habitat and experience with other spills suggest that the oil concentrations will decline to background levels; persistence will be dependent primarily on how much oil is retained by surrounding sediment.

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<sup>8</sup> Except at the mouth of reference stream PMN20, apparently oiled by incursion of marine water.

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**Table 1.** Summary TPAH concentrations and composition model scores. Total PAH concentrations greater than the maximum observed in reference samples (108 ng/g) are printed in bold type. Model scores and means greater than 3 are printed in bold type to signify that the PAH source is consistent with *Selendang Ayu* oil.

stream	zone	TPAH concentration (ng/g)				PAH composition model results			
		mean	se	min	max	mean	min	max	n
laboratory blanks	blank	8	3	0	18	0.2	0	1	6
site blanks (all)	blank	71	14	21	178	0.9	0	2	14
references (all)	reference	39	6	6	108	0.7	0	2	23
PMS16	blank	28				0.0			1
	reference	15	0.5	14	16	0.3	0	1	4
	intertidal	38				1.0			1
	bay	<b>134</b>	1	132	135	<b>4.0</b>	<b>4</b>	<b>4</b>	2
PMN20	blank	21				1.0			1
	reference	21	9	6	37	0.3	0	1	3
	oiled	<b>589</b>				<b>4.0</b>			1
	bay	<b>115</b>				<b>4.0</b>			1
SKN14	blank	78	24	28	140	0.8	0	2	5
	reference	55	15	23	93	0.6	0	1	5
	oiled	<b>58872</b>	31711	260	463080	<b>5.2</b>	<b>4</b>	<b>6</b>	15
	bay	<b>8169</b>	2149	4150	18278	<b>6.0</b>	<b>6</b>	<b>6</b>	6
SKN14-tributary	reference	55	6	31	67	1.0	1	1	5
	oiled	<b>194</b>	67	42	426	2.8	1	<b>4</b>	5
SKN4	blank	56				2.0			1
	reference	53	27	25	108	1.3	1	2	3
	oiled	<b>111</b>				2.0			1
	intertidal	<b>4547</b>				<b>4.0</b>			1
	bay	<b>5569</b>	726	4844	6295	<b>6.0</b>	<b>6</b>	<b>6</b>	2
MKS5	blank	84	24	23	178	0.8	0	2	6
	reference	23	7	10	35	1.0	1	1	3
	oiled	<b>218</b>	88	16	976	2.6	1	<b>4</b>	11
	bay	<b>531</b>	44	382	695	<b>4.7</b>	<b>4</b>	<b>6</b>	6

1 Table 2. Oil in stream bank sediment. Units are ng/g for all concentrations, including alkanes, the unresolved complex mixture  
 2 (UCM), total polynuclear aromatic hydrocarbons (TPAH), and sum naphthalenes (sNaph), sum fluorenes (sFluor), sum  
 3 dibenzothiophenes (sDibenz), sum phenanthrenes (sPhena), sum chrysenes (sChry), and sum higher molecular weight PAH (sHMW).  
 4 Site 1 is at the mouth of the stream; site 4 is the stream reference site (highest elevation); the others are intermediate; SKN14t is the  
 5 tributary. Model scores greater than 3 are printed in bold type to signify that the PAH source is consistent with *Selendang Ayu* oil.

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Date	Stream	Site	Alkanes	UCM	TPAH	Model	sNaph	sFluor	sDibenz	sPhena	sChry	sHMW	comments
3/20/2005	PTN6	-	27207389	71073584	12186865	<b>6</b>	5414293	780213	1475464	3559689	180150	8485	tar ball
5/16/2005	SKN14	1	116788	2602462	1141	<b>6</b>	20.3	53.9	258.6	490.0	96.9	8.0	
3/19/2005	SKN14	3	155864	560431	89672	<b>6</b>	27704.2	8977.6	16058.3	24099.9	3903.3	267.9	
4/12/2005	SKN14	4	2328	4991	19	0	2.6	0.0	0.0	0.0	0.0	15.9	
4/13/2005	SKN14t	4	1245	4381	3	0	3.4	0.0	0.0	0.0	0.0	0.0	
4/14/2005	SKN14t	1	46775	329582	46516	<b>6</b>	5379.6	4027.7	9404.1	21642.4	1192.0	162.7	
3/20/2005	MKS5	1	63	502	13	1	0.0	0.0	5.5	7.4	0.0	0.0	
3/20/2005	MKS5	1	387032	1159965	132197	<b>6</b>	27809.4	14704.0	23742.8	51133.3	3717.9	177.7	tar balls
4/15/2005	MKS5	2	496072	1516041	179769	<b>6</b>	37122.6	17027.6	33870.7	68963.5	5571.9	350.9	
3/20/2005	MKS5	3	420	5181	126	2	11.0	7.2	31.4	62.6	0.0	0.0	no oil visible
3/20/2005	MKS5	3	2352302	6831061	727293	<b>6</b>	162515.2	61818.5	145927.8	276336.9	22312.2	1240.2	visibly oiled
3/20/2005	MKS5	4	0	1981	0	0	0.0	0.0	0.0	0.0	0.0	0.0	
3/20/2005	MKS5	4	133	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0	
3/16/2005	SKN4	1	64	869	13	1	2.6	1.1	2.9	6.1	0.0	0.0	no oil visible
3/16/2005	SKN4	1	346440	1127383	94253	<b>6</b>	25185.1	11645.0	17807.0	28845.2	3264.5	150.3	visibly oiled
4/12/2005	SKN4	2	7907	3791	8	0	2.3	0.0	0.0	0.0	0.0	5.8	
4/13/2005	SKN4	3	7504	4389	1	0	0.0	0.0	0.0	0.0	0.0	0.8	
4/14/2005	SKN4	4	7354	4690	2	0	1.6	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMN20	1	414	3762	7	0	7.1	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMN20	2	403	3452	2	0	2.2	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMN20	3	229	3287	3	0	3.2	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMN20	4	458	3121	0	0	0.0	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMS16	1	1373	0	2	0	1.5	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMS16	2	380	3	0	0	0.0	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMS16	3	500	0	2	0	1.9	0.0	0.0	0.0	0.0	0.0	
4/11/2005	PMS16	4	2318	3431	7	0	3.9	0.0	0.0	0.0	0.0	2.8	

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9 Table 3. Oil in stream channel sediment. Units are ng/g for all concentrations, including alkanes, the unresolved complex mixture  
 10 (UCM), total polynuclear aromatic hydrocarbons (TPAH), and sum naphthalenes (sNaph), sum fluorenes (sFluor), sum  
 11 dibenzothiophenes (sDibenz), sum phenanthrenes (sPhena), sum chrysenes (sChry), and sum higher molecular weight PAH (sHMW).  
 12 Site 1 is at the mouth of the stream; site 4 is the stream reference site (highest elevation); the others are intermediate; SKN14t is the  
 13 tributary. Model scores greater than 3 are printed in bold type to signify that the PAH source is consistent with *Selendang Ayu* oil.  
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Date	Stream	Site	Alkanes	UCM	TPAH	Model	sNaph	sFluor	sDibenz	sPhena	sChry	sHMW
3/19/2005	SKN14	1	3187.4	31639.1	2328.567	<b>6</b>	186.249	249.892	466.906	1053.1	140.315	7.71469
3/19/2005	SKN14	2	36.0	1034.9	0	0	0	0	0	0	0	0
3/19/2005	SKN14	3	0.0	171.2	27.49341	1	2.86737	1.73165	5.83503	15.6522	0	0
3/19/2005	SKN14	4	0.0	0.0	26.51628	0	0	0	0	0	0	26.5163
3/21/2005	SKN14t	1	0.0	22.7	0	0	0	0	0	0	0	0
3/19/2005	SKN14t	4	0.0	0.0	0	0	0	0	0	0	0	0
3/20/2005	MKS5	1	0.0	0.0	0	0	0	0	0	0	0	0
3/20/2005	MKS5	2	230.9	777.4	0.971498	0	0.9715	0	0	0	0	0
3/20/2005	MKS5	3	0.0	519.4	0	0	0	0	0	0	0	0
3/20/2005	MKS5	4	0.0	0.0	0	0	0	0	0	0	0	0
3/16/2005	SKN4	1	0.0	0.0	0	0	0	0	0	0	0	0
3/16/2005	SKN4	2	0.0	0.0	0	0	0	0	0	0	0	0
3/16/2005	SKN4	3	836.9	0.0	0	0	0	0	0	0	0	0
3/16/2005	SKN4	4	12.7	0.0	0	0	0	0	0	0	0	0
3/17/2005	PMN20	1	0.0	1575.0	0	0	0	0	0	0	0	0
3/17/2005	PMN20	2	0.0	103.8	0	0	0	0	0	0	0	0
3/17/2005	PMN20	3	0.0	1328.0	0	0	0	0	0	0	0	0
3/17/2005	PMN20	4	59.4	783.7	0	0	0	0	0	0	0	0
3/18/2005	PMS16	1	0.2	281.0	0	0	0	0	0	0	0	0
3/18/2005	PMS16	2	0.0	317.0	0	0	0	0	0	0	0	0
3/18/2005	PMS16	3	0.0	0.0	0	0	0	0	0	0	0	0
3/18/2005	PMS16	4	0.0	0.0	0	0	0	0	0	0	0	0

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18 Table 4. Oil in pink salmon alevins. Units are ng/g for all concentrations, including alkanes, the unresolved complex mixture (UCM),  
 19 total polynuclear aromatic hydrocarbons (TPAH), and sum naphthalenes (sNaph), sum fluorenes (sFluor), sum dibenzothiophenes  
 20 (sDibenz), sum phenanthrenes (sPhena), sum chrysenes (sChry), and sum higher molecular weight PAH (sHMW). Site 1 is at the  
 21 mouth of the stream; site 4 is the stream reference site (highest elevation); the others are intermediate; SKN14t is the tributary. Model  
 22 scores greater than 3 are printed in bold type to signify that the PAH source is consistent with *Selendang Ayu* oil.  
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Date	Stream	Site	Alkanes	UCM	TPAH	Model	sNaph	sFluor	sDibenz	sPhena	sChry	sHMW
3/21/2005	SKN14t	1	16427.0	855.2	53.70504	0	53.705	0	0	0	0	0
3/19/2005	SKN14t	1	14564.7	3584.8	81.33157	1	49.6754	0	7.76996	23.8862	0	0
3/19/2005	SKN14t	4	10570.1	1521.8	0	0	0	0	0	0	0	0
3/20/2005	MKS5	2	21704.9	3568.0	0	0	0	0	0	0	0	0
3/20/2005	MKS5	3	11090.7	5805.2	0	0	0	0	0	0	0	0
3/20/2005	MKS5	4	10555.4	19235.9	10.62139	0	10.6214	0	0	0	0	0
3/20/2005	SKN4	4	12096.8	4921.9	2.069591	0	2.06959	0	0	0	0	0
3/17/2005	PMS16	1	6262.3	13779.6	0	0	0	0	0	0	0	0
3/18/2005	PMS16	1	11214.6	2651.2	0	0	0	0	0	0	0	0
3/17/2005	PMS16	2	10006.4	0.0	0	0	0	0	0	0	0	0
3/17/2005	PMS16	4	12845.6	2831.8	0	0	0	0	0	0	0	0

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