

Chapter 5

Synthesis Discussion of Remaining Oil from the M/V *Selendang Ayu* Spill as of 2008

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The purpose of this chapter is to synthesize observational and chemical data collected approximately 4 years after the *Selendang Ayu* oil spill in Unalaska and integrate these data with previous observations. This study was initiated because of concerns of the persistence and bioavailability of residual oil remaining on some shorelines after cleanup was terminated, which were supported by a harlequin duck study that suggested long-term exposure to lingering oil¹. Two major types of data were combined in this study; 1) visual observation of surface and subsurface using methods consistent with Shoreline Cleanup Assessment Team (SCAT) procedures; and 2) chemical analysis of indigenous mussels, passive samplers, and oil collected from shorelines. Additional oil samples from 2004 and 2005 were also analyzed to provide a comprehensive assessment of change through time. Study objectives were to 1) determine the presence, distribution, and relative amount of oil remaining on shoreline segments of greatest concern to decide if *Selendang Ayu* oil remains on shorelines within the core spill area, 2) determine the weathering state of remaining oil to evaluate its potential toxicity, and 3) determine the bioavailability of the remaining oil to assist in evaluating exposure and potential biological effects. Each of these topics is discussed in detail below.

Several observations from 2008 are key to understanding current conditions of the oiled shorelines and nearshore habitats. 1) *Selendang Ayu* oil was present in 2008 on or in shorelines oiled by the spill, based both on visual observation (on the surface and through excavation of pits to observe subsurface oiling) and by chemical analysis. These observations are consistent with the extensive 2004 to 2005 documentation of the distribution of *Selendang Ayu* oil² and with chemical analysis of these earlier samples. Conversely, oil was not observed and not detected chemically in the reference area, also consistent with previous observations. 2) Quantities of *Selendang Ayu* oil were typically low on intertidal sediments compared to total sediment volumes. The often very high hydrocarbon concentrations measured on sediment samples resulted from targeted sampling and provided solid information regarding composition. However, hydrocarbon concentration in sediments cannot be inferred from this type of sampling; rather estimates of remaining quantities of oil were based on excavation of pits and visual assessment. 3) Oil condition ranged from rather fresh to quite weathered. 4) *Selendang Ayu* oil was biologically available at low concentrations; total PAH concentrations in mussels from the oiled area were elevated with respect to concentrations in reference mussels and significantly more petrogenic in character. However, observed concentrations are unlikely to be damaging to mussels. Total PAH concentrations in mussels have declined exponentially since 2005 and though elevated, were approaching background levels in 2008. 5) Elevated pyrogenic hydrocarbon concentrations were observed in Chernofski Harbor, which served as a reference area for previous harlequin duck studies. Former World War II activities are suspected as the source of this contamination.

Distribution of *Selendang Ayu* oil on Unalaska shorelines in 2008

The distribution of oil in summer 2008 was consistent with the previously documented distribution of *Selendang Ayu* oil; it was present in most previously oiled areas and absent in reference areas. Lingering oil was observed visually and confirmed chemically on seven of eight shorelines heavily oiled by the *Selendang Ayu* (Table 5.1). Oil was also detected in two lightly oiled segments (SKN11 and SKS12; Table 5.1). No attempt was made to locate or characterize oiled sediment in the reference areas or Chernofski Harbor as none was expected. However no oil was observed during other sampling activities in non-oiled areas, and no other matrices (mussels and passive samplers) detected oil in non-oiled areas. At least 96% of the oil collected from intertidal sediment was consistent with *Selendang Ayu* oil³. The extensive visual assessment that documented the original position and extent of *Selendang Ayu* oil and its rediscovery and visual appearance at expected locations in 2008 corroborates the chemical analysis and also provides strong evidence that nearly all of the remaining oil is from the *Selendang Ayu* spill.

Quantities of *Selendang Ayu* oil were typically low in shoreline sediments compared to total sediment volumes and to tidally cycled water volumes. Across all investigated zones, 2,336 m³ of a potentially excavated 13,751 m³ (16.9%) were estimated to be oiled. Of this estimated volume of all oiled sediment, 1,903 m³ (83%) were estimated to be composed of oiled sediments described as coat, cover, or stain with a percent cover of individual clasts of less than 10%. Nearly all of the remaining oil was high in the supratidal zone, where it had been initially deposited during an intense storm, and where it remains above the zone of normal tidal flushing and sediment reworking.

The condition of oil stranded in intertidal sediment ranged from relatively unweathered to relatively weathered in 2008 (based on PAH composition)³. This broad weathering distribution is consistent with similar variance after the *Exxon Valdez* oil spill in Prince William Sound^{4, 5} and indicates that weathering is dependent on circumstance as well as time. Evidence suggests that the visual oiling descriptors were related to weathering (based on PAH composition). Pooled oil, oil-filled pores, and partially filled pores (PO, OP, and PP) were the least weathered (mean $w = 0.2$, $n = 6$); tar balls were typically the most weathered (mean $w = 3.4$, $n = 8$; Table 5.2). Weathering was intermediate in heavy oil residues (HOR, mean $w = 0.8$, $n = 6$), moderate oil residues (MOR, mean $w = 1.5$, $n = 3$), and coat (CT) and cover (CV; mean $w = 2.9$, $n = 38$; Table 5.2). Differences between the least weathered group (PO, OP, and PP) and the two most weathered groups (CT and CV, TB) were significant ($P < 0.001$). Weathering was consistently most advanced in tar balls, where the minimum w was 2.3. Thus, weathering was most advanced where the oil was spread into thin layers, maximizing contact with the environment, or had progressed to tar ball formation. Conversely, weathering was least where oil loading was relatively large and appearance suggested fresh oil.

These data do not provide evidence for relationships between oil weathering indices and zone- or segment-level summary statistics or geomorphological classifications (Fig. 5.1). As has been previously observed, weathering was likely slowed by isolation of oil from exposure to the environment, such as when the oil strands above the zone of physical reworking by waves, an

asphalt layer forms around a deposit of fresher oil, or exchange is inhibited by the viscous nature of trapped oil⁵. However, current data do not allow specific prediction of when and where such processes might occur on Unalaska shorelines.

Potential differences in weathering rates among shoreline segments were difficult to discern because there was broad overlap in weathering rates within segments. Interpretation of variation in weathering based on chemical analysis must be treated with caution because sample collection was targeted, not random. However, assuming representative samples were collected (as intended), average weathering was least at HMP05, SKN15, and MKS14 (Table 5.1). Weighted ranking of visual oil descriptors also placed MKS14 and SKN15 in the least weathered category (Table 5.3). There was less agreement on which segments were on average most weathered: SKN11 and SKS04 were most weathered based on *w* (Table 5.1); SKN05 was most weathered based on visual assessment (where only tar balls were recorded; Table 5.3). Whether weathering processes were more effective in some locations than others, or how shorelines were oiled varied so that oil was more susceptible to weathering in some locations, or how cleanup procedures affected the results, or some combination thereof, is unknown.

Bioavailability of remaining oil

Residual oil was biologically available in areas oiled by the *Selendang Ayu* and contained toxic constituents, demonstrated by accumulation of low concentrations of oil in mussels in oiled areas³. These total PAH accumulations were small, yet marginally greater ($P = 0.056$) in the oiled area than in the reference area. Modeling indicated a petrogenic source, and distinct differences in PAH composition in mussels among areas were confirmed with principal component analysis (see Fig. 3.7 in Chapter 3). The bioavailability of oil was confirmed with passive samplers; PAH concentrations were significantly elevated intertidally, in surface water, and subtidally (in order of most to least elevation) and were correlated with those in nearby mussels. A petrogenic source was consistently and significantly likely in passive samplers deployed in the oiled area; composition tended toward pyrogenic sources in the reference area. Principal component analysis of PAHs in passive samples also distinguished oiled and reference areas, except in passive samplers deployed in surface water.

Accumulated PAH concentrations in mussels in summer 2008 were very small; the geometric mean total PAH concentration in mussels was 30 ng/g dry weight. This is small compared to the roughly 100 ng/g above-background estimate used in some Prince William Sound studies^{4,6}. However, other background estimates in Prince William Sound were < 10 ng/g dry weight⁷. Recovery of various sites in Prince William Sound from oiling suggests this lower estimate may be more accurate⁸⁻¹⁰; many total PAH concentrations in Prince William Sound mussel tissues are < 50 ng/g today¹⁰ and declining concentrations of < 10 ng/g were evident in some restored mussel beds⁸. Thus, the low concentrations observed in mussels on Unalaska shorelines within the spill zone likely have resulted from exposure to hydrocarbons from *Selendang Ayu* oil, and the detailed chemistry presented in Chapter 3 supports this argument.

Oil from the *Selendang Ayu* is the most likely source of biologically available hydrocarbons in previously oiled shorelines. *Selendang Ayu* was present on shorelines as described in the previous section (and Chapter 3). Concentrations of oil collected from sediment were sufficient

for unambiguous analysis; total PAH concentrations adjusted by method detection limits were >99% of unadjusted values in the 2008 samples. The petrogenic patterns and weathering in this oil was consistent with accumulations in mussels and passive samplers. Furthermore, the low level background composition was pyrogenic and was inconsistent with accumulations in mussels and passive samplers in oiled areas.

Amounts of bioavailable oil have declined since the *Selendang Ayu* spill, consistent with other spill experiences. Total PAH concentrations in mussels declined exponentially in SKN05, and SKN04 from 2005 to 2008 (Fig. 5.2). Source modeling consistently provided the strongest indications of oiling nearest the time of the spill; source identification became less clear with time (Fig. 5.2). Mean concentrations in mussels at oiled sites approached background levels in summer 2008, yet remained marginally elevated ($P = 0.056$, Chapter 3). Likewise, the mean total PAH concentration in passive samplers deployed in oiled bays in 2005 was about 10,000 ng/device¹¹, roughly 100 times greater than concentrations in 2008. (Oiled bays with passive samplers in 2005 were MKS05, SKN14, and SKN04; $n = 14$)¹¹. Declines in total PAH concentration in mussel tissue were also exponential after the *Exxon Valdez* oil spill^{9, 12}, consistent with these observations.

Total PAH concentrations in reference mussels were low and likely constant between 2006 and 2008 (Fig. 5.2). The slightly higher values in 2005 may have been influenced by the *Selendang Ayu* spill; total PAH in one replicate sample from Cannery Bay was substantially elevated (68 ng/g wet weight) and modeling strongly suggested the presence of oil. Some of the shoreline in the bays used for reference data in 2005 and 2006 were oiled, thus oil was in the general vicinity. Background levels in the only mussels collected during winter (February 2008) were unusually high (25 ng/g wet weight) compared to all other estimates. Increased lipid levels in pre-spawning mussels, hence an increased capacity to bioaccumulate hydrocarbons, might explain why total PAH background concentrations in the winter of 2008 were elevated (Fig. 5.2), although lipid content has not been measured. Late fall through early spring are critical months for adult mussel gametogenic activity¹³, hence reproductive lipid levels were likely higher in the winter than at any other time. Assuming that all total PAH concentrations in winter mussels (collected 1172 days after the spill) were elevated for reproductive reasons unrelated to the general availability of oil, these winter estimates fit quite well in the declining time series both in terms of total PAH concentration and with source modeling (see adjusted concentrations, Fig. 5.2). The slightly higher than expected adjusted concentrations in winter 2008 mussels may have been due to increased exposure to oil constituents because winter storm activity mobilized relatively more oil than in summer, though natural variance for other unknown reasons cannot be discounted. Further study, including lipid analyses, would be required to resolve this issue.

Potential toxicity of remaining oil

Toxic PAH constituents were present in oil in 2008. For example, oil in sediments contained fluorenes, dibenzothiophenes, phenanthrenes, and pyrenes, all toxic to fish embryos¹⁴. Weathering removes lower molecular weight compounds most rapidly, preferentially leaving the heavier and more toxic PAHs (compare Figs. 3.16 and 3.14), yet weathering was not so extensive that mobile, intermediate-sized, toxic PAHs were gone from the oil. Furthermore,

measured PAH concentrations in the oil were above previously established method detection limits in most samples (93%), thus verifying the presence of oil.

The mobility, hence bioavailability, of toxic constituents is supported both by logic and measurement. Logically, *Selendang Ayu* oil continues to weather, thus the toxic compounds in remaining stranded oil continue to leave the oil and enter water at the differential rates dictated by thermodynamics¹⁵. Indeed, toxic PAHs were evident in mussel tissue, though generally at low concentrations. Modeling did not unambiguously identify oil in 93% of mussels from oiled areas, rather only indicated a significant proclivity towards oil compared to reference mussels. However, aqueous transfer and subsequent uptake by living organisms tends to modify PAH composition, making interpretation more difficult^{16, 17}. Less hydrophobic compounds leave oil and enter water more rapidly than more hydrophobic compounds, explaining weathering and resulting in an aqueous PAH composition biased toward lower molecular weight PAHs with respect to oil^{15, 18}. Conversely, living organisms (and passive samplers) preferentially accumulate the more hydrophobic PAHs and animals, including mussels, are capable of metabolizing PAHs¹⁹. Visual examination of PAH composition in oiled mussels suggested the presence of oil constituents; in particular, phenanthrene distributions in tissue were frequently consistent with a petroleum source. Oil patterns were also apparent in the less frequently observed fluorenes, dibenzothiophenes, and pyrenes. The evidence that toxic oil constituents were biologically available is stronger in passive samplers. The frequency of positive model identification of oil in samples collected from oiled areas was considerably higher in passive samplers (47%) where exposure was more carefully controlled and there was no biological capacity to modify sequestered PAHs.

The risk posed by water-borne oil constituents in summer 2008 was likely small in areas oiled by the *Selendang Ayu*. The low PAH concentrations in mussel tissue (6 to 71 ng/g dry weight) and passive samplers in summer 2008 indicate that aqueous concentrations were low. Bioconcentration factors for petroleum hydrocarbon mixtures for the common mussel, *Mytilus edulis*, are approximately 2×10^5 for seawater concentrations of 1 to 400 $\mu\text{g/L}$ ^{19, 20}. This implies the mean aqueous TPAH concentration in oiled areas was roughly 0.15 ng/L (parts per trillion) if they were in equilibrium. Estimates based on passive samplers¹⁸ placed intertidally were similar, 0.14 ng/L [= (49 ng/device / 2.2 g/device) / 1.6×10^5 ml/g]. Estimates based on bioaccumulation factors estimated for suspension feeding yield similar results (1.8×10^5 for pristane in mussels²¹). Although the potential influence of nonequilibrium conditions on these estimates is unknown, such as how concentration might increase in occasional erratic pulses of unusually contaminated water, the implication is that mean aqueous TPAH concentrations in areas oiled by the *Selendang Ayu* spill were probably several orders of magnitude smaller than concentrations damaging to sensitive early life stages such as embryonic fish²²⁻²⁶.

The PAH concentrations in mussels due to *Selendang Ayu* oil in summer 2008 were unlikely to cause damage to mussels even though molluscs can be adversely affected by low quantities of oil. Invertebrate immune systems are very sensitive to environmental contaminants²⁷. For example, exposure via contaminated plankton may interfere with hemocyte maturation or differentiation in soft shell clams (*Mya arenaria*) at PAH concentrations of 0.05 $\mu\text{g/L}$ ²⁸. Exposure to produced water inhibited cell viability phagocytosis and cytotoxicity at 0.4 $\mu\text{g/L}$ total PAH in *M. edulis*; this water also contained heavy metals and other contaminants, so

relative contributions are unknown²⁹. Hemocyte counts and protein levels were elevated and cell membrane stability and phagocytosis were reduced in Arctic scallop (*Chlamys islandica*) at 0.3 to 2.2 µg/L TPAH, resulting in tissue burdens of 3365 and 5700 ng/g dry weight³⁰; significant effects were more frequent at the higher concentration. Lysosomal destabilization was observed at 2100 ng/g TPAH in oysters (*Crassostrea virginica*) fed oiled food³¹. Mussels (*M. trossulus*) collected from an oiled area in Prince William Sound with 655 ng/g dry weight TPAH burdens in tissue were significantly less tolerant to air exposure than reference mussels³²; 39 of the 44 PAHs measured in this study were measured in the former study. The mean TPAH burden observed in Unalaska mussels from the oiled area, 26 ng/g dry weight, is consistent with background levels in Prince William Sound, about 2.5 to 28 ng/g dry weight^{4,33}. Mean TPAH burdens in mussel tissue from oiled areas in summer 2008 were 25 times smaller than the smallest known detrimental burden³²; the maximum was 9 times smaller, suggesting that any PAH effects caused by residual oil in Unalaska mussels were likely negligible in 2008. In contrast, concentrations in one Chernofski Harbor mussel sample (2780 ng/g dry weight) were high enough to suspect impairment and several were <5 times the minimum known impairment level.

Prediction of long-term, persistent toxicity of *Selendang Ayu* oil from these chemical data is not possible. Toxicity is a function of the exposure composition and concentration and both are controlled by weathering rate. Persistence of potential toxicity of intertidal *Selendang Ayu* oil deposits into the future might be estimated from weathering, though there are insufficient observations across time for adequate prediction. Mean PAH weathering in oiled areas increased from $w = 0.4$ (in 2004 to 2005) to $w = 2.6$ (in 2008), with broad, overlapping ranges in both groups. If the progression were linear, about six more years would be required to reach a mean w of 7, and evidence from the most weathered *Selendang Ayu* samples indicates toxic PAHs would remain (e.g., Fig. 3.15, bottom panel). However, weathering may be a nonlinear process as suggested by principal component analysis (e.g., Fig. 3.18); if so, predicting future weathering without more data is not possible. Estimation of the time *Selendang Ayu* oil will persist on the shorelines is not possible from the available chemical data because contemporary concentrations are unknown, precluded by sampling decisions to target oil to characterize source and degree of weathering instead of collecting very large samples designed to characterize concentration distributions.

However, long-term oil retention can roughly be predicted from visual assessment of the tidal elevation and degree of subsurface oil. The subsurface oil remaining after four years occurs mostly in the supratidal zone (96% of oiled pits); 36% of the oil occurs at depths greater than 10 cm. Oil stranded at supratidal elevations has the potential to be physically removed only when storms equal to or greater than the event that stranded the oil occur. The occurrence of such storms in 2006 was proposed as a factor in release of subsurface oil³⁴. However, during storms gravel tends to be transported landward, building up the storm berm and burying subsurface oil deeper (see discussion in Chapter 2). A very large storm would be necessary to physically rework the storm berm sediments in the supratidal zone on exposed shoreline, such as KFP-01. On the more sheltered shorelines, wave exposure from such storms is very unlikely; thus, for the oil in segments with significant amounts of subsurface oil in boulder rubble, such as MKS-14, removal processes are likely limited to microbial degradation. In these cases, there will be a persistent residue of the most highly resistant petroleum hydrocarbons. For example, oil residues from spills during the 1964 earthquake in Prince William Sound are readily found in the

intertidal zone 40 years later^{6,7}. Heavily contaminated sediments from the 1970 T/V *Arrow* spill of a heavy fuel oil in Nova Scotia, Canada have persisted in low-energy sites for at least 30 years³⁶.

Summary

Some *Selendang Ayu* oil remains on shoreline segments within the core spill area. This oil has weathered to various degrees; rates of weathering were highly variable within and among shoreline segments. However, combined analysis of weathering across years (2004 to 2008) clearly demonstrates that weathering progresses through time and is consistent with a single oiling event. Toxic PAH constituents remain in intertidal oil deposits including fluorenes, dibenzothiophenes, phenanthrenes, and pyrenes. The oil continues to weather, thus toxic compounds remain biologically available. Although biologically available oil constituents were detected in mussels, observation with passive samplers provided the most definitive proof of bioavailability. The amount of mobile oil during the summer months was relatively small, yielding uptake concentrations that are likely inconsequential for mussels. However, all pathways of exposure were not assessed, particularly the potential for increased oil bioavailability during winter conditions.

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Tables

Table 5.1. Comparison of conditions in shoreline sediments immediately after the *Selendang Ayu* spill (2004-2005) with visual and chemical results in 2008. Position indicates oil position in sediment [surface and or subsurface³⁵]. Volume is the estimated volume of remaining oil³⁵. Frequency is the number of pits with any evidence of oil (n_{oil}) divided by the total number of pits (n_{total}) expressed as a percentage; for greater detail, see Chapter 2. Chemical results are based on PAH composition; oil was confirmed (or not) by modeling³; weathering (w , mean and range) indicates how fresh (small negative values) or weathered the oil was; n indicates number of samples with estimable w .

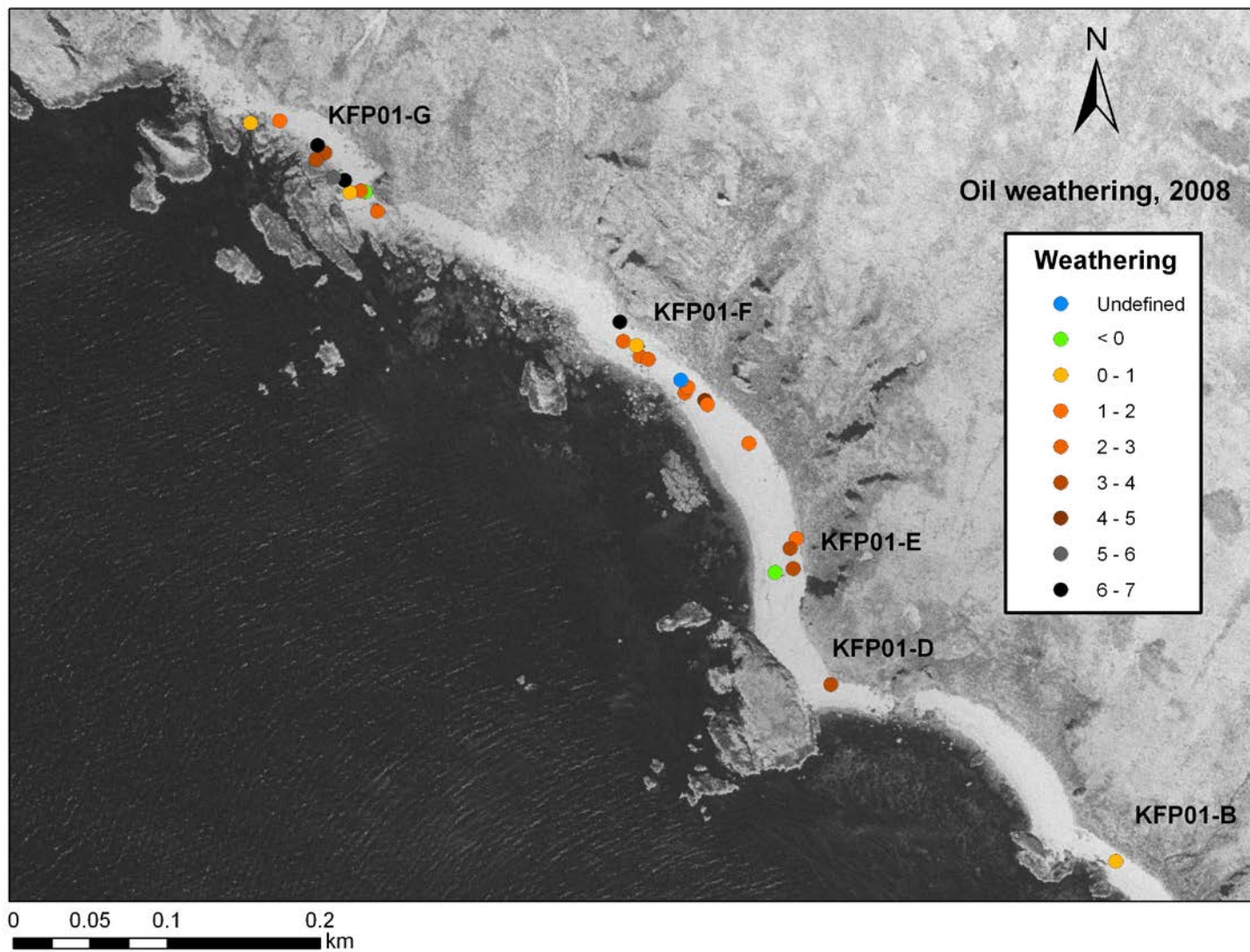
Site	2004-2005	2008 visual					2008 chemical				
		position	volume	frequency							
			(m ³)	n_{oil}	n_{total}	%	PAH model	n	mean w	w range	
PTN03	heavy	NOO	0	0	80	0	no oil detected	0		-	-
SKS12	light	surface	10	2	33	6.06	oil confirmed	2	3.7	2.7	4.7
SKN11	light	surface	0	1	10	10	oil confirmed	1	4.6	-	4.6
SKS04	NOO to heavy	surface & subsurface	4	6	40	15	oil confirmed	3	5.1	2.1	6.7
SKN05	heavy	surface & subsurface	132	22	80	27.5	oil confirmed	8	3.5	2.3	5.7
HMP05	heavy	surface & subsurface	236	27	60	45	oil confirmed	3	0.8	0.3	1.4
MKS16	heavy	surface & subsurface	197	26	55	47.27	oil confirmed	11	3.4	2.3	5.2
SKN15	heavy	surface & subsurface	268	70	100	70	oil confirmed	8	1	-0.1	2.9
KFP01	heavy	surface & subsurface	1125	160	210	76.19	oil confirmed	28	2.5	-0.1	6.9
MKS14	heavy	surface & subsurface	365	48	56	85.71	oil confirmed	8	1.7	0.3	4.5

Table 5.2. Comparison of verbal description of oiling and weathering (based on PAH composition, w_{PAH}). Pooled oil (PO), oil-filled pores (OP), and partially filled pores (PP) were combined as a single category; heavy oil residues (HOR), moderate oil residues (MOR) and tar balls (TB) were analyzed separately, and coat (CT) and cover (CV) were combined. Differences between the least weathered (PO, OP, & PP) and most weathered (CT & CV, TB) were significant (bold text).

Description	n	mean	sd	se	ci	min	max
PO, OP, & PP	6	0.2	0.4	0.2	0.4	-0.1	0.8
HOR	6	0.8	0.5	0.2	0.6	0.3	1.8
MOR	3	1.5	1.1	0.6	2.6	0.3	2.2
CT & CV	38	2.9	1.6	0.3	0.5	0.8	6.9
TB	8	3.4	1.1	0.4	0.9	2.3	5.7

Table 5.3. Frequency (%) and ranking of observed oil condition among shoreline segments. Weights were 1) pooled oil or oil-filled pores or partially filled pores (PO/OP/PP), 2) heavy oil residues (HOR), 3) moderate oil residues (MOR), 4) coat or cover (CT/CV), and 5) tar balls (TB). This sequence is arranged from generally least to most weathered (see text). Estimated ranks are the frequencies of each category multiplied by their weight.

segment	n	PO/OP/PP	HOR	MOR	CT/CV	TB	
<i>Percentages</i>							
MKS16	10	0	0	0	100	0	
MKS14	3	0	67	0	33	0	
HMP05	3	0	0	33	67	0	
PTN03	1	0	0	0	100	0	
KFP01	28	18	4	7	68	4	
SKN15	8	13	38	0	50	0	
SKN11	1	0	0	0	100	0	
SKS12	1	0	0	0	100	0	
SKS04	1	0	0	0	100	0	
SKN05	7	0	0	0	0	100	
<i>Weighted ranks</i>							Σ rank
MKS14		0.0	1.3	0.0	1.3	0.0	2.7
SKN15		0.1	0.8	0.0	2.0	0.0	2.9
KFP01		0.2	0.1	0.2	2.7	0.2	3.4
HMP05		0.0	0.0	1.0	2.7	0.0	3.7
SKS12		0.0	0.0	0.0	4.0	0.0	4.0
SKS04		0.0	0.0	0.0	4.0	0.0	4.0
MKS16		0.0	0.0	0.0	4.0	0.0	4.0
SKN11		0.0	0.0	0.0	4.0	0.0	4.0
PTN03		0.0	0.0	0.0	4.0	0.0	4.0
SKN05		0.0	0.0	0.0	0.0	5.0	5.0



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Figure 5.1. Example weathering distribution of oil within a single shoreline segment (KFP01).

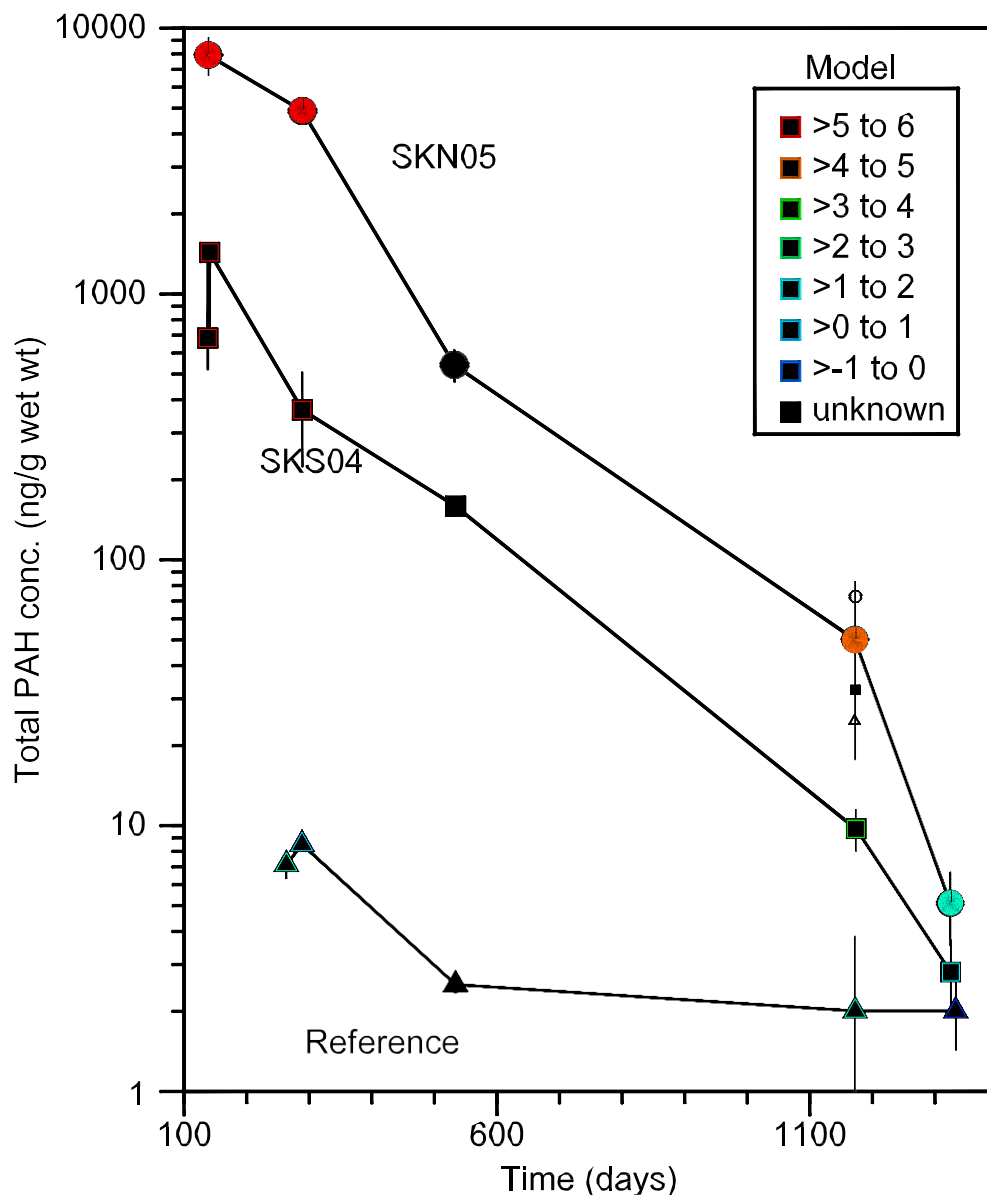


Figure 5.2. Total PAH concentrations in mussel tissue as functions of time after the *Selendang Ayu* oil spill. Shoreline segments SKS04 and SKN05 were located in heavily oiled Skan Bay. Data collected in 2005 to 2006 (through 534 d) are from Mauseth et al.³⁶. Winter 2008 data (1172 d) are from Flint et al.¹. The final data are from this study (~1330 d). Lightly oiled and reference sites were composited from Anderson and Cannery Bays in 2005³⁶, Wide and Volcano Bays in 2006³⁶, Cannery and Anderson Bays in winter 2008¹, and Outer Pumicestone and Pumicestone Bay in 2008³. One sample collected from reference Cannery Bay in 2005 where source modeling indicated contamination (model = 4, total PAH = 68 ng/g) was excluded from the reference group. The winter 2008 data are presented both as measured (small open symbols, 1172 d) and corrected to match summer 2008 background levels (solid symbols). Symbols are color coded to indicate mean source model estimates; petrogenic sources are increasingly more likely as values approach 6. Analytes quantified were identical in all data sets except for the inclusion of C4-fluorenes in our data set.