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

Final Report

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Executive Summary

The *Selendang Ayu* discharged an estimated 354,218 gallons of oil [96% intermediate fuel oil (IFO 380) and 4% marine diesel oil] on December 8, 2004 that contaminated 112 kilometers of the coastline of Unalaska Island from Unalaska Bay to Konets Head and beyond. At the conclusion of the cleanup in June 2006, seven shoreline segments failed to reach final cleanup criteria, and they were left for cleaning by natural attenuation. In 2005, 2006, and 2008, cytochrome P4501A (CYP1A) induction in wintering harlequin ducks was higher at oiled locations (Humpback and Skan Bays) than in Chernofski Harbor[2]. Consequently additional study was needed to determine the presence, distribution, and relative amount of oil remaining, oil weathering, and biological availability (bioavailability) at selected shoreline segments. The segments were selected subjectively because they: 1) had not reached cleanup endpoint status; 2) were subject to alternative treatment techniques during cleanup, such as berm relocation and tilling; 3) were near harlequin duck trap sites; and/or 4) were sites with evident oil exposure in subsistence samples.

Field methods included excavation of randomly located pits to describe the degree of sediment oiling, collection of representative sediment samples for oil fingerprinting and weathering analysis, deployment of passive hydrocarbon samplers for about one month, and collection of intertidal mussels to determine oil fingerprinting and bioavailability. The field work was conducted during two cruises in July and August 2008.

Residual oil was biologically available in summer 2008 in areas oiled by the *Selendang Ayu* and contained toxic constituents, demonstrated by accumulation of low concentrations of hydrocarbons from oil in mussels and passive samplers[3]. The source of these hydrocarbons was petrogenic and distinctly different from the pyrogenic background hydrocarbons in the reference area and Chernofski Harbor[3]. Oil from the *Selendang Ayu* is the most likely source of biologically available hydrocarbons in previously oiled shorelines. At least 96% of the sediment samples with evidence of oil were consistent with *Selendang Ayu* oil[3]. Furthermore, 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[4].

The internal consistency of the data supports the conclusion that hydrocarbons from the *Selendang Ayu* spill were bioavailable at low concentrations during the summer of 2008 at the shoreline areas of study. These consistencies include 1) parallel variation in total PAH concentration, least in the reference area, greatest in Chernofski Harbor, and intermediate in oiled areas, repeated four times (once in mussels, and three times in passive samples deployed intertidally, subtidally, and in surface water; Fig. 1); 2) parallel variation in PAH sources as estimated by source modeling, pyrogenic in the reference area and Chernofski Harbor and petrogenic in the oiled area, also repeated four times (Fig. 2); 3) consistent variation in PAH sources as estimated by multivariate analysis, which distinguished oiled, reference and Chernofski Harbor areas in mussels and passive samplers; 4) weathering patterns in mussels and passive samplers that were consistent with weathering patterns in intertidal oil; and 5) the presence of intertidal oil containing PAHs which could serve as a source of observed petrogenic

PAHs in mussels and passive samplers. Sediments in formerly non-oiled areas were not sampled for hydrocarbons, thus there is not complete parallelism for this matrix with the other two (mussels and passive samplers). We also note that the indications of oil exposure in mussels (this study) and harlequin ducks[2] are mutually corroborative.

The presence of lingering *Selendang Ayu* oil in intertidal sediments in 2008 was verified several ways. 1) Oil was present where predicted by former distributions[5]. 2) Source modeling of PAH composition in intertidal oil indicated that oil discovered in 2008 was consistent with *Selendang Ayu* oil. 3) Multivariate analysis of PAH composition corroborated the modeling and illustrated how weathering-induced change integrated the data from 2004 through 2008 (Fig. 3). 4) The relationship between *Selendang Ayu* oil and oil collected from Unalaska beaches in 2004 to 2008 was also supported by similar multivariate analyses of alkane and biomarker data. 5) Equivalent weathering processes were observed for all three compound classes. The well-documented weathering of PAHs[1, 6-9] was strongly related to several principal components, demonstrating the mathematical link between the two analytical approaches. Furthermore, the results directly supported a relationship between PAH and alkane weathering; preferential loss of smaller alkanes was obvious, consistent with known weathering patterns[10]. In addition, weathering of smaller biomarker molecules (isoprenoids and triterpanes) were also related to PAH weathering, and loss patterns were consistent with known biomarker weathering[10]. 6) Persistent biomarker composition (hopanes and steranes) in oil collected from beaches in 2005 was highly similar to that in 2008, strongly substantiating a common origin. 7) Biomarker analysis further restricted the source of contamination primarily to intermediate fuel oil from the *Selendang Ayu*. Biomarker composition in spilled marine diesel oil was clearly different than in intermediate fuel oil but when relative oil volumes, densities, and total biomarker content in each source were accounted for, the potential influence of marine diesel oil on composition in spilled oil was <1% and can for all practical purposes be ignored. Principal component analysis coupled with source modeling provided a consistent framework to understand and explore these data. The time- and circumstance-dependent variation in all three compound classes thus identifies *Selendang Ayu* oil as the hydrocarbon source.

Several observations from 2008 are key to understanding current conditions of the oiled shorelines and nearshore habitats. 1) *Selendang Ayu* oil is present in 2008 on or in previously oiled beaches, based both on visual observation (on the surface and through excavation of pits to observe subsurface oiling) and by chemical analysis. As previously noted, these observations are consistent with the extensive 2004 to 2005 documentation of the distribution of *Selendang Ayu* oil[5] 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 are typically low on intertidal sediments compared to total sediment volumes. The often very high hydrocarbon concentrations recorded for oil resulted from targeted sampling and provided solid information regarding composition. However, hydrocarbon concentration in sediment 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 ranges from rather fresh to quite weathered, even within single beach segments, thus potential differences in weathering rates among beaches is difficult to discern. 4) *Selendang Ayu* oil is biologically available at low concentrations. However, observed contemporary PAH concentrations are unlikely to be damaging to mussels. The amount of bioavailable oil has likely declined since the *Selendang Ayu* spill by roughly two orders of magnitude. 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 cause.

Nearly four years after the *Selendang Ayu* oil spill (summer of 2008), there was subsurface oil in 21 of the 24 subjectively selected beach zones but very little surface oil. Nearly all subsurface oil (96% of oiled pits) occurred in the supratidal zone, where it was initially deposited during an intense storm, and where it remains above the zone of normal tidal flushing and sediment reworking (Fig. 4). Most (82%) of the subsurface oil was described as 0.1-10% cover on individual clasts; however, 9% occurred as thicker accumulations. The heaviest oiling increased with depth and occurred mostly at 20-50 cm. The zones classified as sheltered boulder rubble accumulations and high storm berms had the highest estimated fraction of oiled sediment volume (25-35%). Boulder rubble sediments have little potential for sediment reworking, and storm berms tend to build up over time (until a storm large enough to move them landward occurs). Thus, subsurface *Selendang Ayu* oil remaining on the shorelines of Unalaska Island is not likely to be removed by physical processes for decades.

The long-term implication of residual *Selendang Ayu* oil is continued potential for bioavailability, albeit at concentrations too low to be consequential for mussels.

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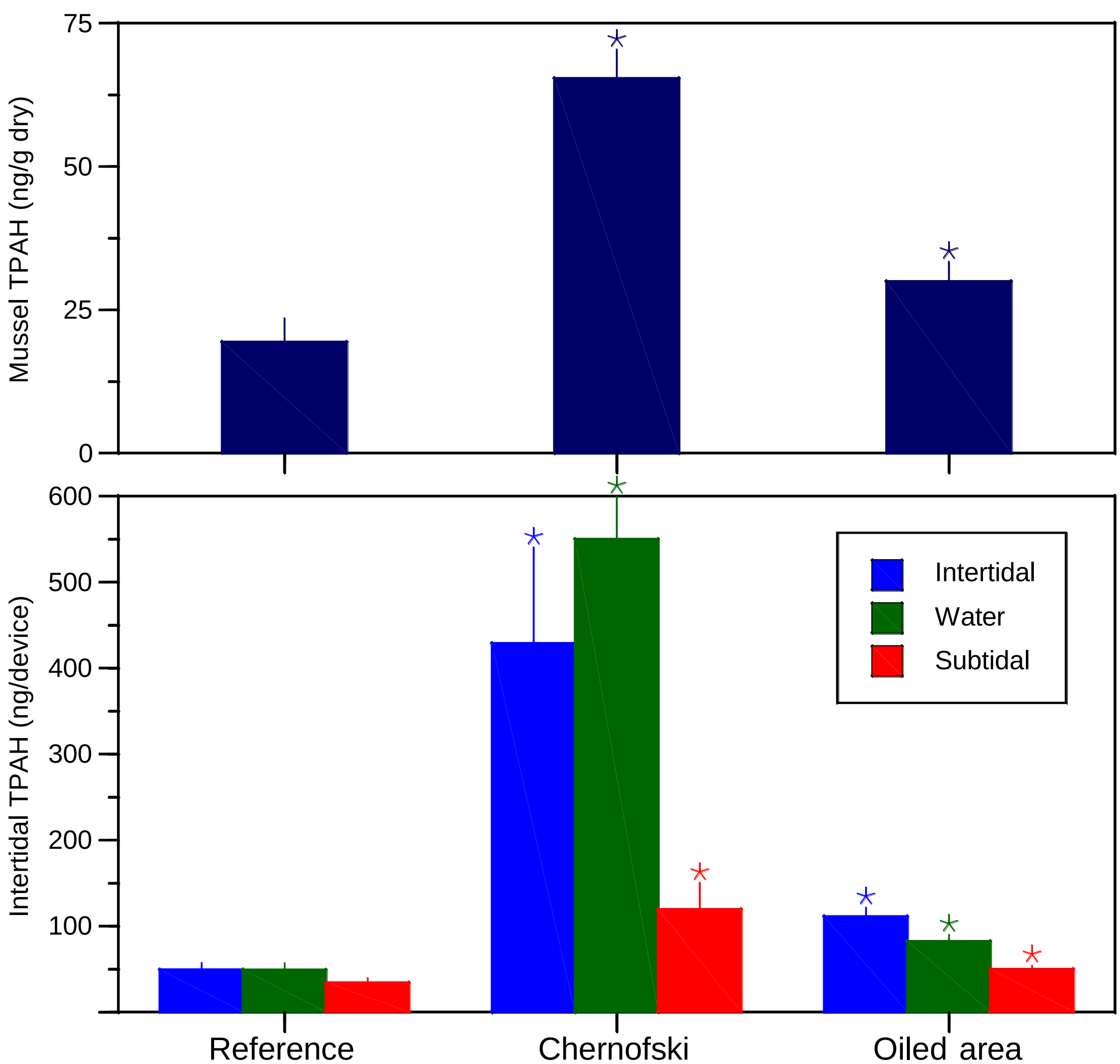

Figure 1. Geometric mean PAH dry weight concentrations in mussels (top panel) and passive samplers (bottom panel) by area [reference, historical impact (Chernofski Harbor), and oiled] and zone (subtidal, surface water, and intertidal). Mussels were collected intertidally. Error bars are ± SE. Asterisks indicate significant differences from corresponding reference measurements.

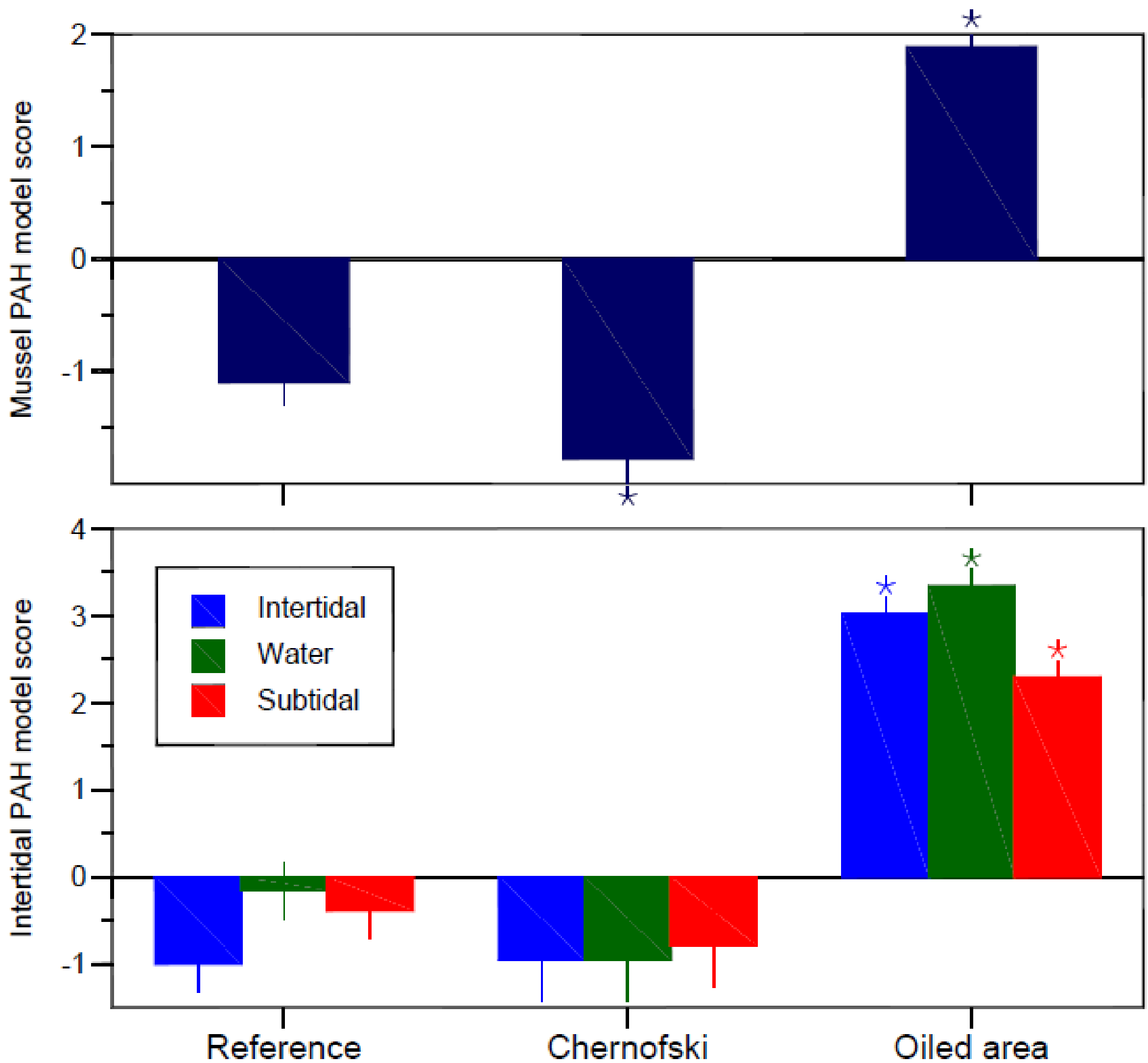

Figure 2. Mean PAH source model scores in mussels (top panel) and passive samplers (bottom panel) by area [reference, historical impact (Chernofski harbor), and oiled] and zone (subtidal, surface water, and intertidal). Potential model scores range from -6 (pyrogenic) to +6 (petrogenic); scores near 0 indicate ambiguous cources. Mussels were collected intertidally. Error bars are ±SE. Asterisks indicate significant differences from corresponding reference measures.

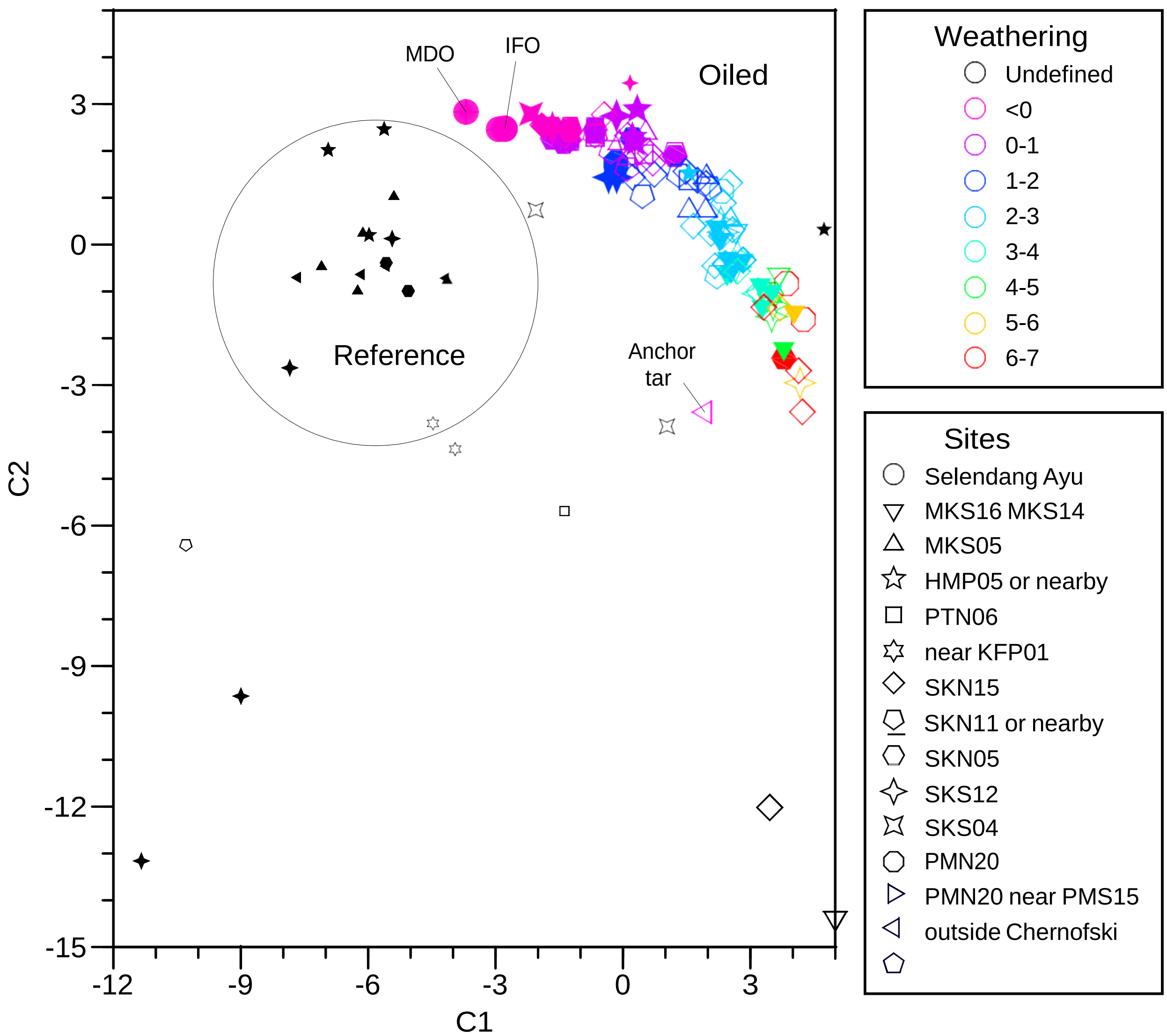

Figure 3. Summary of PAHs in sediment, oiled sediment, and oil. The abscissa and ordinate are the first and second principal components from the correlation matrix of normalized PAHs (2004 to 2008), color coded by weathering coefficient (w)[1]. Colored symbols indicate a petrogenic source consistent with *Selendang Ayu* oil except that anchor tar represents a non-*Selendang Ayu* source of hydrocarbons. Solid symbols indicate samples collected in 2004 or 2005; samples collected directly from the *Selendang Ayu* are identified as marine diesel oil (MDO) and intermediate fuel oil (IFO). The smallest symbols identify samples where total PAH concentration was < 100 ng/g; the largest symbols signify concentrations ≥1000 ng/g.

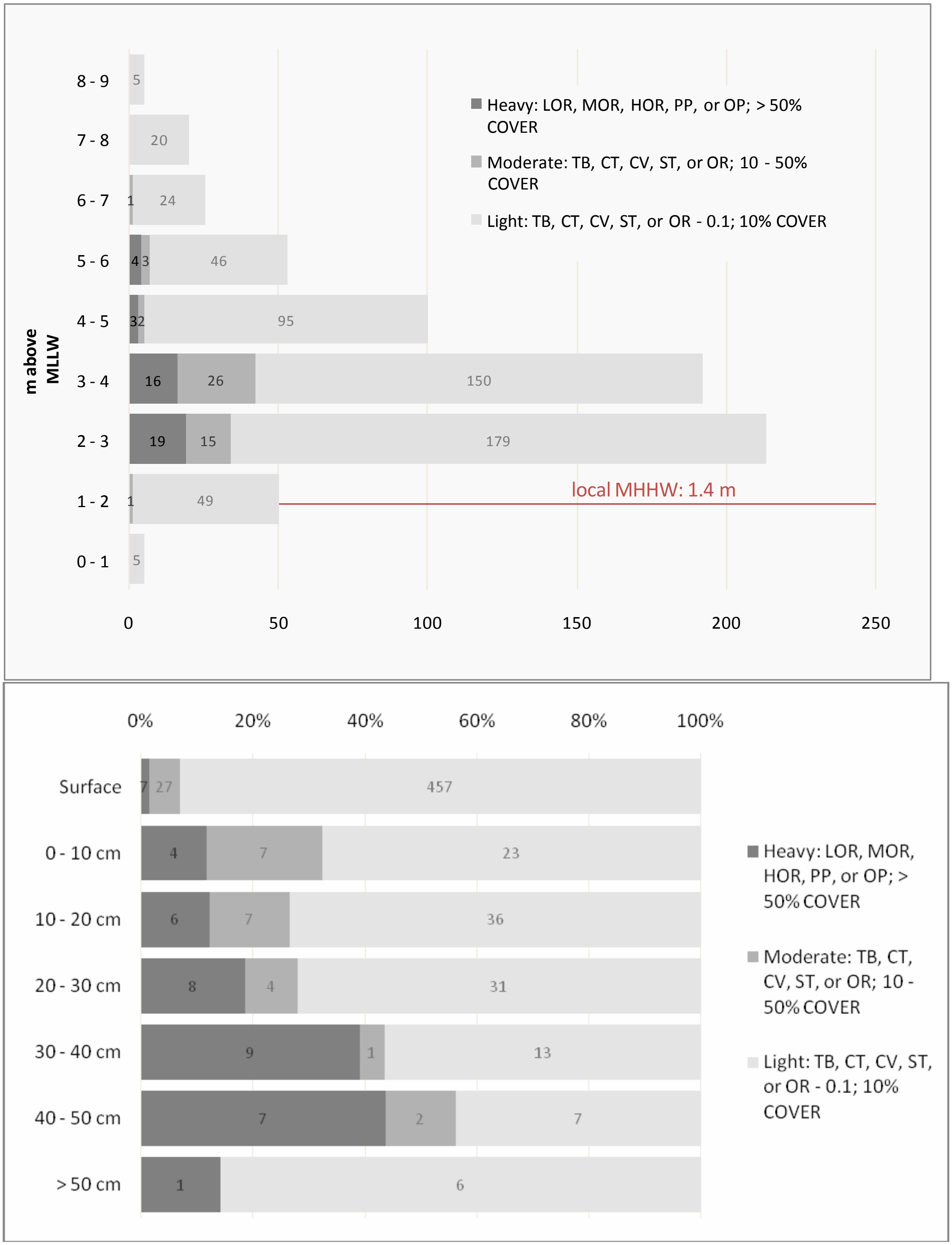

Figure 4. Counts of all oiled layers by oiling descriptor for various pit elevations in meters above MLLW (top panel). Percent composition of subsurface oiled layers by oiling descriptor for various burial depths (bottom panel).