

Review of
DRAFT
M/V *Selendang Ayu* Trustee Response to May 31, 2008 Comments on Behalf of the
Responsible Party on the

Draft M/V *Selendang Ayu*
2008 Study Plan for Assessment of Remaining Oil (Ver. 4-18-08)

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In our May 21, 2008 review of the trustees Draft M/V *Selendang Ayu* 2008 Study Plan for Assessment of Remaining Oil, we proposed a series of recommendations. The trustees have responded and we appreciate their comments. The following is the RP's response to the trustee comments. We reiterate our positions on the following issues.

PEMDs

1. Multiple Sources. The statement in the introduction: "*Composition of PAH accumulated by PEMDs can be used to identify hydrocarbon sources in situations not complicated by multiple sources*". is accurate, but raises questions as to the ability of the PEMDs to determine that whatever signal is seen (i.e., PAH levels) is from the *Selendang*: Multiple sources may confound the interpretation of results.

2. Field Blanks. NOAA realizes the potential for sampling artifacts and the need for field blanks. That's good. However, NOAA does not present "Data Quality Objectives (DQOs)" for this determination. In other words they need to state that, for example, "PAH data from field PEMDs must be 5 times the field blank, in order for any measurement to be considered real". Previous studies by NOAA/ABL have indicated that these blanks may be high (several hundred ng PAH per device). Careful analysis of blanks should be made so as to determine what the minimum real "signal" is (i.e., the DQO). We suggest that EPA's definitions of the data qualifier for blanks be used. EPA requires that data that are within 5 times the blank are to be qualified (i.e., are suspect). NOAA needs to consider this critical point and clearly state their DQOs for PEMDs, taking into account regulatory guidance on the treatment of blanks.

3. Intertidal deployment. We have raised concerns in the original plan on the intertidal deployment. The issue here is potential burial in sediment thus causing either fouling of the device or artifacts. Any buried PEMD that comes in contact with any buried oil is, by definition, contaminated as a severe artifact is produced, which has nothing whatsoever to do with bioavailability of buried subsurface oil. We do have concern that the SOP allows for such burial: "*PEMDs can be buried or placed on the surface, depending on objectives*". NOAA/ABL should exclude intentional or unintentional burial from the SOP and they should make it clear that PEMDs are not to be buried. If they become buried in the 30 days between deployment and

retrieval, the results from that PEMD should be discarded.

Analytical Chemistry

1. Biomarker SOPs. The trustees have agreed to include the Auke Bay Laboratory analytical Standard Operating Procedures (SOPs) for each chemical analysis. They specifically stated on page 3 of their response that “*SOP’s will be appended to the Study Plan*”. These SOPs have been received and reviewed. *If* the total petroleum hydrocarbon, alkane, and PAH analyses are carried out according to the trustee SOPs, the data will be of sufficient quality for the proposed study. However, there is no discussion or SOP for the proposed biomarker analysis (e.g., hopane analysis). These analyses are critical to objectives of the program because they provide a means to reliably determine the weathering state of the spilled oil. The trustees have agreed in their response to our comments that this technical approach would be used (Page 4). In addition, the biomarker analysis is critical for source identification and the application of the Nordtest source ratio approach used to identify mixtures of M/V *Selendang Ayu* oils in the marine environment (discussed below).

Recommendation: The trustees should prepare a detailed SOP for the quantitative analysis of biomarker compounds (triterpanes and steranes) in soil/sediment and tissue samples. Using the current SOP hopane will not be detectable because it comes out in the F1 (aliphatic) oil fraction which is only analyzed by GC/FID. Hopane will need to be analyzed by the GC/MS method, separate from the aromatic hydrocarbon analysis (F2). In addition, the gravimetric oil weight in the F1 (aliphatic) and F2 (aromatic) sample extracts should also be measured. We require a complete data package with all supporting sample processing and analysis information, and the raw Enviroquant electronic data files from the GC/MS and GC/FID analyses. If the trustees will not perform adequate analysis of hopane and biomarkers as requested, the RP requires that sample extract and associated quality control extracts be supplied to Alpha Woods Hole Laboratories to allow for analysis sufficient to support the Nordtest model.

2. Biomarkers use in source attribution. Regarding recommendation #2 (see above), the trustees responded as follows. “*In lieu of mixing model, we will focus on samples collected at or near the study segments soon after the spill to establish source oil. Additional details are included in the Study Plan. Discernment of what mixtures of oil from the specific S. Ayu tanks is not of interest and efforts to do so with 2008 data may well be futile because of intervening weathering processes.*”

Based on this approach the trustees will be *assuming* that all sediment oiling is from the M/V *Selendang Ayu*. This may or may not be true but verification is important to the RP and should be to the trustees. From data previously supplied to the trustees, multiple non-*Selendang Ayu* oils have been confirmed in the spill area. Importantly, without using the mixing model approach at each pit site, the initial hopane concentration in the oil cannot be determined and therefore accurate estimates of hydrocarbon weathering cannot be performed. This is because the hopane method used to estimate the degree of oil/PAH weathering in the environment depends on the time = 0 concentration of hopane in the spilled oil. This can only be determined with the mixing model approach. Finally, the statement that “*Discernment of what mixtures of*

oil from the specific *S. Ayu* tanks is not of interest and efforts to do so with 2008 data may well be futile because of intervening weathering processes.” is highly unlikely. With the mixing model approach we are able to identify the source(s) of even the most the highly degraded oil residues.

Recommendation: The RPs will adopt, and the trustees should adopt, the mixing model approach at each site, not only to verify oil source(s), but to accurately apply the quantitative hopane oil/PAH weathering calculations, a cornerstone of the study. The RP expects that sufficient sediment and tissue samples to repeat laboratory analyses will be achieved for future use if necessary.

3. Biomarkers use in weathering analysis. The trustees have agreed to perform direct measurements of oil weathering using C₃₀ 17 α (H),21 β (H)-hopane based percent oil depletion estimates (Page 4). This is clearly the most defensible method for measuring oil/PAH weathering at this site¹. The method compares the concentration of the degradation resistant biomarker compound hopane (on an oil weight basis) in the oil that was originally spilled on the beach to the hopane concentration (on an oil weight basis) present in the pit samples. The PAH and alkane % depletion estimates are calculated in a similar fashion relative to the hopane. The end results are quantitative estimates of individual PAH and alkane degradation results that will assist the trustees evaluate the degree of oil weathering.

A confounding factor at this site is that the oil that actually reached the shoreline is a variable mixture of two different fuels. Therefore, in order to know the time = 0 hopane concentration in the spilled oil, the mixing model must be used. Without this analysis, direct measurements of oil weathering using C₃₀ 17 α (H),21 β (H)-hopane based percent oil depletion estimates will not be accurate.

Recommendation: The trustees should provide an SOP for the quantitative analysis of biomarkers in the oiled sediments (e.g., C₃₀ 17 α (H),21 β (H)-hopane) and tissues, and adopt the mixing model approach as a component of their data analysis program. If the trustees will not perform adequate analysis of hopane and biomarkers as requested, the RP requires that sample extract and associated quality control extracts be supplied to Alpha Woods Hole Laboratories to allow for appropriate analysis to support the Nordtest model.

Data interpretation and end points

1. Risk Criteria. We remain concerned that the plan still does not provide adequate detail on data analysis and interpretation to allow all parties to agree on the criteria for determining whether there is or is not a significant ecological risk from any remaining oil. We agree that the essential component of this study is to demonstrate if there is continuing exposure of key ecosystem components to bioavailable, toxic components of the Selendang Ayu oil. However, the methods

¹ Prince, R.C., Elmendorf, D.L., Lute, J.R., Hsu, C.S., Haith, C.E., Senius, J.D., Dechert, G.J., Douglas, G.S. and Butler, E.L. 1994. 17 α (H) 21 β (H)-hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environ. Sci. Technol.* 28(1): pp. 142-145.

described for demonstrating bioavailability and exposure to environmentally significant (toxic) fractions of the spilled oil are highly problematic.

2. Use of Sediment Data. The plan includes the analysis of sediment samples for PAHs, but other than looking for the presence of potentially toxic compounds in these samples, the plan is silent on the use of the data and their interpretation in establishing the need, if any, for further investigation. We reiterate that PAH compositional data in sediments without associated quantitative PAH concentration data is of little use and is prone to speculative interpretations. We suggest that the trustees establish a scientifically accepted (i.e., published by multiple authors), risk-based process for how the sediment PAH data will be interpreted.

3. Reliance on PEMD data. The authors of the study plan state that PEMDs are widely accepted for use in monitoring bioavailable PAH in water; this is not true. There remains substantial disagreement about the interpretation of the environmental significance of PAH and other nonpolar organic compounds in PEMDs and other membrane devices following brief (less than one month) deployment in water or air/water (intertidal) environments. We reiterate our preference for the use of mussels in evaluating bioavailability of oil. Mussels are better because they are indigenous intertidal biota that are prey or prey surrogates of intertidal foragers such as harlequin ducks and sea otters. Mussels are the best or among the best bioaccumulators of PAH in the intertidal in Alaska. Therefore, PAH residues in native mussels provide a good indication of the maximum bioavailable fraction of PAH in water washing the intertidal zone.

4. Use of Toxicity Reference Values. It is difficult to interpret results of analysis of PAH in PEMDs and mussels in terms of critical (potentially toxic) concentrations in the food of intertidally foraging wildlife. The amount of PAH in a PEMD cannot be related to an average concentration of PAH in solution in the water, particularly after a short deployment. The mussel PAH data can be used to compare to a toxicity reference value (TRV) for total PAH for harlequin ducks or sea otters. EPA provides guidance for developing TRVs for different taxa and contaminants. This EPA-approved approach to defining toxic dose is not being proposed by the trustees but should be incorporated in the evaluation.