We welcome the opportunity to respond to the Comment of Bence et al. (2000) regarding the suitability of the new geochemical parameter we have introduced. Part of their comment, however, addresses issues either not directly related to our paper, or issues published elsewhere. The lengthy comment seems a disproportionate reaction to what was a paper of limited scope, simply introducing one new geochemical parameter, the refractory index (RI). The RI is a ratio of triaromatic steranes (T) to methyl chrysenes (C) (T/C); these compounds are ubiquitous in petroleum and are two of the most refractory components of the suite of polycyclic aromatic hydrocarbons (PAH) found in petroleum. The RI, therefore, was proposed as a source parameter potentially useful, in concert with other relevant geochemical parameters, in the correlation of oils over a wide range of environmental weathering conditions.

The following paragraphs address some of the issues raised by Bence et al. (2000).

1. Sampling

With respect to what Bence et al. (2000) refer to as “Inadequate Sampling”, we acknowledge that we had a limited sample set. The key question, however, is whether it is adequate to address the issues raised in our paper. Our work focused on three known oils from the Prince William Sound (PWS) area: North Slope crude oil from the Exxon Valdez oil spill, California/Monterey oil spilled during the 1964 Great Alaskan Earthquake (Kvenvolden et al., 1995), and Katalla seep oil, an onshore oil from the Gulf of Alaska (GOA). The main point of our paper was to apply the refractory index to these oils and determine whether it could reliably discriminate among them at different weathering stages, which it did. We also analyzed a few coal samples from the region, including coal distributed in strands all along the intertidal beach at Katalla, to see if they contained the same compounds used in the RI. In general, the coals gave very low or zero RI values, due to the absence, or extremely low amounts, of triaromatic steranes. In addition, we examined benthic sediments from the study area to see if the RI could help evaluate whether any of the above oils contribute to the hydrocarbon background therein. These benthic sediments also gave very low to zero RI values, at least an order of magnitude lower than any of the above oils, but comparable to the RI range of the coal samples.

Bence et al. (2000) fault our work for not examining other GOA oils in addition to Katalla, such as seep oil from Yakataga, located further east along the shore of the GOA, and Tertiary shales. Our choice of Katalla seep oil was a direct response to the large body of work in which Katalla oil is emphasized (Bence et al., 1996; Douglas et al., 1996; Boehm et al., 1997, 1998; Page et al., 1996), and hydrocarbon distributions for the Katalla seep oil are characterized as “…representative of other Gulf of Alaska seep sources” (Page et al., 1996). It is only recently, after our above work was completed, that Page et al. (1998) abandoned Katalla seep oil and abruptly shifted emphasis to Yakataga seep oil. The focus on the Tertiary shales mentioned by Bence et al. (2000) is even more recent. Work from as late as 1998 and 1999 (Boehm et al., 1998; Page et al., 1999) still referred to a PWS/GOA “seep-derived background of PAH”, with no mention of the Tertiary shales. When our work was
done (completed for oral presentation at the National American Chemical Society meeting, March, 1998), it was following the lead of the above-cited studies.

In fact, however, we had examined a sample of Yakataga seep oil, Johnston Creek oil, and had two primary reasons to exclude it from the above work. First, Yakataga is significantly further east of PWS in the GOA than Katalla. Even the published aerial photographs in Page et al. (1995) of the turbidity and suspended sediment plumes carried by the Alaskan Current from the Yakataga area toward PWS show that Kayak Island, Okalee Spit, and Cape Suckling disrupt the flow towards PWS, leaving a partial disconnect which appears to hinder sediment transport.

Second, we examined the aliphatic biomarker and the PAH profiles of the Johnston creek oil. We did find that its RI is low, similar to those of the coals and the benthic sediments, as stated in the Comment by Bence et al. However, even with a low RI, triaromatic steranes were present. These, and the regular steranes, had a somewhat uncommon distribution. The sterane profile (SIM of m/z 217, Fig. 1B) shows a strong dominance of C29 steranes, which may indicate that terrestrial higher plants were the dominant precursors of the organic matter in the oil (Lu and Kaplan, 1992; Clayton, 1993). Because C29 steranes give rise to C28-triaromatic steranes, this distribution carries over to the triaromatic sterane profile (extracted ion profile m/z 231, Fig. 1B). This profile shows a less common distribution pattern of dominance by the C28-triaromatic sterane epimers, as compared to the very common and more typical distribution found in most oils (see discussion of triaromatic steroids (steranes) in Volkman et al., 1997). A typical pattern, such as that seen in Exxon Valdez oil (EVO), is shown in Fig. 1A. The distributions of regular and triaromatic steranes in the Johnston creek oil, coupled with low biomarker levels in general, probably indicate that this oil was originally sourced from coal. The important point, however, is that this distinctive pattern of regular steranes and triaromatic steranes is not evident in the biomarker or PAH profiles of any of the offshore GOA or PWS sediments that we have examined (Fig. 1E and F). This is the primary reason why we did not include Johnston creek oil in our discussion of RI.

Additionally, since the completion of our earlier work, we have examined several other Yakataga seep oils. We have found that oil from Mundy creek, Smokey creek, another sample from Johnston creek, and even Samovar Hills oil, all share this particular sterane and triaromatic sterane distribution (Fig. 1C and D), making them all questionable sources for the hydrocarbon background in the benthic sediments.

We would, however, very much like to examine the newly suggested Tertiary shales in future work. The shales, in particular, seem plausible in that their PAH are probably sufficiently adsorbed within the shale matrix so as to make them non-bioavailable and resistant to weathering. These two factors were the primary reasons for the Short et al. (1999) challenge to the claim that "seep-derived PAH" were the source of the PAH background in PWS, since seep-derived PAH would be both bioavailable and subject to weathering, and no substantive evidence of oil-sediment associations obviating these processes has yet been provided.

2. Katalla coal

The next issue raised by Bence et al. (2000) regards our identification of the "coaly" material which was collected from the surface of Katalla beach in 1997 (latitude 60° 11.2' N and longitude 144° 31.2' W). Examination of the grain morphology of the sample collected from the surface of Katalla beach in 1997 (latitude 60° 11.2' N and longitude 144° 31.2' W) has provided new material which is similar in appearance and yields comparable Total Organic Carbon (TOC) values: 82 and 74% by weight (J. Kolak, personal communication). These analyses contrast markedly with Bence et al.'s highest value for Katalla beach sediment of 11.62% TOC. While beaches are highly dynamic environments, the fact that our two distinct samples yield nearly identical results may indicate that Bence et al. (2000) were not successful in obtaining a representative sample of the material constituting the strand lines on Katalla beach. We found abundant material on the beach, and were easily able to collect black material from thick (> 5 mm) accumulations. Whereas our sampling collected only the coal material, theirs may have included extraneous inorganic beach material.

Conventional aliphatic biomarker ratios for the 1997 Katalla coal sample given in Carlson et al. (1997) show this sample to have parameters indicating immaturity. However, new vitrinite reflectance data on the 1997 and 1999 Katalla beach samples indicate high maturity, that is, 2.47 and 2.53% Rm, with indication of possible inclusion of small amounts of lower rank coal or solid bitumen (vitrinite data by DGSI, Inc.). This beach coal is, therefore, probably a mixture of particles from within the Bering River drainage, dominated by recycled high rank coal. One of the premises put forth by Short et al. (1999) is that coals from multiple sources with widely varying maturities become progressively more mixed during transport to GOA and PWS sediments, with
Fig. 1. C_{27–29} sterane (SIM, m/z 217) and C_{26–28} triaromatic sterane (extracted ion profile, m/z 231) distributions in: (A) a typical oil, Exxon Valdez oil; (B,C,D) representative Yakataga seep oils — Johnston creek, Mundy creek, Samovar hills; (E) GOA benthic sediment near Yakataga; (F) PWS benthic sediment, Snug Harbor. Key: Steranes — 27,28,29 = carbon number; a,b = βα-diasteranes (S,R); c,d = ααα-steranes (S,R); e,f = ββ-steranes (R,S). Triaromatic steranes: 26,27,28 = carbon number; S,R = epimers.
broad convergence of hydrocarbon parameters to values characteristic of these sediments.

3. Mass balance

Another problem noted by Bence et al. (2000) was the issue of “Mass Balance Constraints”. Consideration of TOC and total PAH (TPAH) was outside the scope of our paper, and the comment really is directed at work published in Short et al. (1999). However, in response to the concern of Bence et al. (2000), we will mention some of our current work that resolves the inconsistency with TOC, TPAH, and carbon mass-balance in GOA sediments. New analysis of TPAH in coal particles isolated directly from GOA sediments (near Kayak Island) via density separation (J. Kolak, personal communication) gives a concentration of TPAH exceeding 400 μg/g coal (Short et al., 2000). Work in progress in conjunction with these separations shows that there is a large particle-size/surface-area effect on the efficiency of PAH extraction from coal. TPAH analyses on source coal particles of a grain size similar to the coal particles isolated from GOA sediment yield comparable TPAH concentrations (~300 μg/g coal). Both these measurements, therefore, give significantly greater concentrations of TPAH in coal than we had previously reported and, together, are of a magnitude that obviates Bence et al.’s mass balance concerns.

4. Thermal maturity

Bence et al. (2000) attempt to limit the applicability of the RI by raising thermal maturity considerations having to do with the thermal stability of long chain vs. short chain triaromatic steranes. However, thermal maturity is not the relevant issue in this context. The three oils and the coals under consideration for the RI parameter are petrogenic substances which are separated from their respective source reservoirs. This means that they carry their molecular signatures into the environment; thermal maturity is already incorporated into that signature. In the environment the relevant issue is susceptibility to weathering. The two terms in the RI, the triaromatic steranes and the methyl chrysenes, have been shown in other studies (e.g. Killops and Howell, 1988; Munoz et al., 1997) and acknowledged within Bence et al. (1996) and the Current comment, to be highly resistant to weathering.

Furthermore, we note an apparent double standard in the Bence et al. Comment, in that the index used throughout the entire body of their work as the primary discriminant to differentiate PWS oils, the DPI or C2-Dibenzoathiophene/C2-Phenanthrene Index, has been rigorously evaluated for its source and weathering characteristics (Douglas et al., 1996), but not for thermal maturity. The reason is that, as with the RI, thermal maturity is not the relevant issue in this context.

5. Other molecular indicators

We strongly agree that a single parameter, like the RI, is insufficient to make a case for source correlation. We state in the publication that the parameter “supports” other data. It was never intended to stand alone. Sometimes, even with an apparently compelling correlation, conclusions can be in error or may not consider all the alternatives. For example, although the body of work supporting the Bence et al. Comment used the DPI extensively to evaluate oils and the natural petrogenic background in PWS/GOA benthic sediments, the possibility of a coal contribution was dismissed (Page et al., 1996). Yet Short et al. (1999) showed that the DPI for Katalla seep-oil and Katalla beach coal, for example, are essentially identical, and that the DPI value is also in the same range as those of the benthic sediments. Also, the biomarker oleanane was put forth as “a specific indicator for seep-derived petrogenic background” (Page et al., 1997) and coals were discounted, without analysis, as unlikely sources of substantial amounts of oleanane (Bence et al., 1996). But Short et al. (1999) demonstrated that the oleanane index has a comparable value in GOA coals as well as in Katalla oil. There is not adequate justification for dismissal of coal as a potential source of PAH — we now have preliminary data on benthic sediment from near Kayak Island in the GOA which show coal to contribute at least 20% of the total PAH. Bence et al. in their Comment finally acknowledge the presence of coal in the benthic sediments, although they claim the coal is in low abundance and too mature to contribute significant amounts of PAH to the background. The coal in the Kayak Island benthic sediment provides some evidence to the contrary, and additional work in progress will further address this claim.

6. Conclusion

The refractory index was intended only as a single piece of evidence which can be used in the correlation of oils at various stages of weathering, in conjunction with other relevant data and within an appropriate geological framework. The RI works as one of several reliable discriminants of the three oils in the PWS/GOA area. It also provides additional evidence that a dominant source of PWS background PAH is not Katalla seep oil, a point with which Bence et al. (2000) now seem to agree, despite their earlier focus on Katalla. As Bence et al. (2000) point out, other regional seep-oils, coals, shales, and benthic sediments have very low triaromatic steroid contributions and thus low RI values. Therefore,
the parameter provides information but is not useful as a discriminant among them. In all cases, additional correlating factors must be used.

There are other issues raised in the comment by Bence et al., but again, they are beyond the scope of our original paper and are best addressed in a separate publication. This is an evolving study of a very complex system and there is still more to be learned.

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References


