ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION
DIVISION OF SPILL PREVENTION AND RESPONSE
CONTAMINATED SITES REMEDIATION PROGRAM

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Toxicity of the Polar Fraction in Petroleum

It became apparent to Alaska Department of Environment Conservation (ADEC) staff that there was a large discrepancy when split samples were analyzed using both the Alaska Series Methods, AK 102AA and AK 103AA, and the original Alaska Series Methods, AK 102 and AK 103. It appeared there was a fraction in the DRO and RRO ranges that remained attached to the silica gel following extraction using the AK 102AA and AK 103AA methods that could not be accounted for with biogenic interference. It was proposed that this group of compounds, termed the "polar fraction", was made up of polar constituents of weathered petroleum.

In attempts to account for the polar fraction, ADEC sought to evaluate its potential toxicity. To aid in this attempt, ADEC contracted Hart Crowser to provide a comprehensive literature search regarding the toxicity associated with the polar fraction. The literature obtained was reviewed to determine if there was known toxicity associated with the polar fraction and if that toxicity information could be used to develop regulatory standards consistent with current regulations.

Currently, ADEC uses a combined indicator and surrogate approach for evaluating the human health toxicity associated with petroleum contaminated sites. Indicators are compounds within petroleum that are evaluated individually, such as PAHs, and surrogates are compounds that are used to represent the potential toxic effect associated with a particular fraction of hydrocarbons within petroleum. Therefore, the polar fraction as a whole, as well as individual constituents assumed to be found in this fraction, were investigated. Thiophenes, amides, azaarenes, carbazoles, indoles, phenanthridines, pyridines and quinolines, in addition to the whole polar fraction, were investigated during the literature review. All of these compound classes are expected to be found in the polar fraction and assumed to be persistent in the environment, although this has not been supported with laboratory tests.

Review of the literature revealed there is little published information available on the toxicity of the polar fractions of weathered petroleum although, there are studies that show this fraction could be potentially toxic (Zemanek *et al.*, 1997; Neff *et al.*, 2000). Acute toxicity associated with petroleum has been related to polar fractions. Oxidative degradation products in sediment following the Exxon Valdez Oil Spill showed polar fractions were as toxic as the aromatic fraction (Wolfe, *et al.*, 1995). In contrast, studies show that nitrogen-, oxygen-, and sulfur-containing heterocycles found in crude oil are oxygenated during weathering to form polar compounds. These compounds are metabolized or chemically altered to less toxic products than the parent compounds (Catallo, 1996).

In addition to there being little toxicity data available, the polar fraction retained on the silica gel following extraction using AK 102AA or 103AA has not been characterized. There is little laboratory information available regarding what constituents are present in this fraction. In order to use a surrogate or indicator approach, the individual constituents must be identified and toxicity characterized. This step is essential prior to developing cleanup levels for the polar fraction.

Also, it is assumed that receptors will not be exposed to the polar fraction in great magnitudes. The polar fraction of interest is eluted in the carbon equivalency range of 10 to 35. These heavier weight polar compounds are thought be immobile in the environment (Rhodes, 2000; McMillan, 2000). As well the heavier weight polar compounds do not appear to be bioavailable to ecological receptors (McGraw, 2000). Based on this information, receptors are unlikely to be exposed to the compounds of interest.

Based on literature reviewed it was determined there was not sufficient data available to determine if the polar fraction was toxic or continue with establishing cleanup levels for the fraction. The lack of characterization of the polar fraction and lack of bioavailability and mobility of the polar fractions supports ADEC's decision not to

continue to determine toxicity or develop cleanup standards at this time. An external working group is currently being formed that will recommend revisions to AK 102AA and 103AA. Until such revisions are promulgated, it is recommended that use of these methods be discouraged. However, if these methods are used, ADEC should require appropriate checks such as duplicate sample runs of AK 102 or AK 103, as appropriate.

If you have questions or would like more information regarding the toxicity review of the polar fraction, please contact Stephanie Pingree at 907-465-5152.

References

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