Response to EPA's Hazard Characterization of the Heavy Fuel Oils Category

The American Petroleum Institute Petroleum HPV Testing Group

June 17, 2013

The following comments are in response to EPA's Hazard Characterization (HC) for the Heavy Fuel Oils Category (U.S. EPA, 2012). This Category was sponsored by the American Petroleum Institute (API) Petroleum HPV Testing Group (Testing Group) as part of EPA's HPV Chemical Challenge Program (www.petroleumhpv.org).

Below is EPA's generic table of content for all the HPV Hazard Characterizations they have prepared, including Heavy Fuel Oils. The Testing Group's comments are found on the page numbers indicated below.

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Summary

1. The EPA hazard characterization for several Petroleum HPV Categories including Heavy Fuel Oils, refers to the category members as complex mixtures when in fact they are Class 2 UVCB substances. (HC pages, 5, 11, 28, 38 and Table 2)

Substances on the US TSCA Inventory are divided into two classes for ease of identification (EPA 1995). Class 1 substances are those single compounds composed of molecules with particular atoms arranged in a definite, known structure. However, many commercial substances that are subject to TSCA are not Class 1 substances, because they have unknown or variable compositions or are composed of a complex combination of different molecules. These are designated Class 2 substances. Class 2 includes substances that have no definite molecular formula representation and either partial structural diagrams or no structural diagrams. These are the "UVCB" substances (Unknown or Variable compositions, Complex reaction products and Biological materials). An example of this kind of substance is given below.

CAS Number: 64741-80-6
CAS Name: Residuals (petroleum), thermal cracked
CAS Definition: A complex combination of hydrocarbons produced as the residual fraction from distillation of the product from a thermal cracking process. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F). This stream is likely to contain 5 wt % or more of 4- to 6-membered condensed ring aromatic hydrocarbons.

Petroleum substances are subject to nomenclature rules developed jointly by the U.S. EPA and the American Petroleum Institute (EPA, 1995b). In that guidance document, EPA adopts the definitions of petroleum process stream terms provided in API's published reference document Petroleum Stream Terms Included in the Chemical Substance Inventory under TSCA (1983, reprinted in 1985). The Stream Terms definitions include the CAS definition and registry number, the source of the substance and process (i.e., last refining step), short name, indication of carbon number, and indication of distillation range (or other appropriate characteristic). Therefore all members of the Heavy Oil Fuels Category are UVCB substances, not mixtures, under EPA's nomenclature guidance.

3. Human Health Hazard

The key reason for the data "gaps" identified by EPA for this Category is the organization of the 32 substances into several subcategories. The Testing Group abandoned the use of subcategories for its final Category Assessment (CAD) submission in December 2012. However, EPA stuck with the approach in the HC and treated subcategories as barriers that don't allow read-across of mammalian data between them. The Testing Group believes the Heavy Fuel Oils Category is better described as a continuum of similar substances and the human health hazards of this category are associated with the presence of polycyclic aromatic compounds (PACs). This knowledge coupled with existing and new test data should satisfy all the HPV Challenge requirements for human health data in this Category.

The Testing Group described a modeling approach for assessing the repeat-dose, developmental, and gentox endpoints of substances in this Category. However, EPA did not acknowledge the utility of the statistical models to evaluate untested samples of Heavy Fuel

Oils. In the original Test Plan, a relationship between mammalian toxicity and the polycyclic aromatic compound (PAC) content of the substances in that category was asserted or implied. To study this relationship, toxicology studies and analytical reports on high-boiling petroleum substances (HBPS) like Heavy Fuel Oils were collected from the Testing Group's member companies and analyzed in order to address two key questions: 1) Are there quantitative relationships between PAC content of petroleum substances and their critical effects as identified in repeat-dose, developmental, bacterial genotoxicity, and reproductive toxicity studies, and 2) can the critical effects/levels of untested petroleum substances be predicted from their PAC content?

The assessment by the Testing Group showed (a) that the toxicological effects of high boiling petroleum-derived substances (i.e., final boiling points > 650 ^{o}F) were associated with PAC content, (b) that subchronic effects associated with PAC content included liver enlargement, thymic weight reductions, reduced hematological parameters, and developmental effects including reduced live-births and birth-weight, and (c) that the effects of these high boiling petroleum-derived substances could be predicted from PAC contents using predictive statistical models for several repeat-dose and developmental toxicity endpoints. The models used the weight percent of each of the aromatic ring classes (the "PAC profile") as the independent variable. The effects found to be associated with the PAC profile are consistent with those reported for a number of individual PAHs and PAC-containing materials. A predictive model for bacterial mutagenesis was also developed. The Testing Group had the results of its model building exercise reviewed through an expert peer consultation process (TERA, 2008). The Testing Group has followed up the peer consultation with additional testing and analysis and has prepared several detailed manuscripts for publication (Murray et al., 2013; Nicolich et al., 2013; Roth et al., 2013; McKee et al., 2013).

Repeated-Dose Toxicity

In the Testing Group's December 2012 CAD submission (Table 13 on page 46) repeat-dose toxicity data on 9 members of the Heavy Fuel Oils Category are presented. Without the subcategories imposed by EPA this data is adequate to fulfill the HPV Challenge requirements. The use of the predictive models developed by the Testing Group would also fulfill the requirements.

Developmental Toxicity

In the Testing Group's December 2012 CAD submission (Table 21 on page 76) developmental toxicity data on 8 members of the Heavy Fuel Oils Category are presented. Without the subcategories imposed by EPA this data is adequate to fulfill the HPV Challenge requirements. The use of the predictive models developed by the Testing Group would also fulfill the requirements.

Genetic Toxicity

In the Testing Group's December 2012 CAD submission (Tables 17 and 20 on page 63 and 65) genetic toxicity data on numerous members of the Heavy Fuel Oils Category are presented. Without the subcategories imposed by EPA this data is adequate to fulfill the HPV Challenge requirements.

Reproductive Toxicity

EPA identified mammalian reproductive toxicity as a data gap under the HPV Challenge Program for several Petroleum HPV Categories including Heavy Fuel Oils. However, the original guidance provided by EPA for fulfilling the reproductive toxicity data requirement was developed by the Organization for Economic Cooperation and Development (OECD) Guidance for Meeting the SIDS Requirements (http://www.epa.gov/HPV/pubs/general/sidsappb.htm). That guidance says that when a 90-day repeat dose study (such as OECD 408) is available and is sufficiently documented with respect to studying effects on the reproductive organs and a developmental study (such as OECD 414) is available, the requirements for the reproduction toxicity endpoint are satisfied. Other studies that satisfy the endpoint are screening-level tests defined by such guideline protocols as the OECD 421 or 422, or a one- or two-generation study defined by such guideline protocols as OECD 415 or 416. The Testing Group believes the data cited in the December 2012 Category Assessment Document for Heavy Fuel Oils is sufficient to satisfy the SIDS requirements for reproductive toxicity.

4. Hazard to the Environment

EPA provides the following statements of findings and effects (HC page 10 and Data Matrix Table 5, page 120): "No adequate data are available for the sponsored substances. Based on the supporting chemicals (C7-C10 iso-alkanes, CASRN 90622-56-3; 1-tetradecene, CASRN 1120-36-1; and 1-hexadecene, CASRN 629-73-2), the 96-h LC50 for fish is 0.11 mg/L, the 48-h EC50 for aquatic invertebrates is 0.9 mg/L, and the 72-h EC50 for aquatic plants is 0.4 mg/L for biomass. Based on the supporting chemical (naphtha (petroleum) hydrotreated light, CASRN 64742-49-0), the 21-d chronic NOEC and LOEC for aquatic invertebrates is 0.17 mg/L and 0.32 mg/L, respectively. Based on CASRNs 1120-36-1 and 629-73-2 there are no aquatic toxicity effects at saturation for chemicals in this category with a carbon chain of fourteen or greater. No data gaps for Aquatic toxicity were identified under the HPV Challenge Program."

The Testing Group believes that results for multi-constituent, poorly soluble hydrocarbons should be expressed as lethal loadings (LL) rather than lethal/effect concentrations (LC, EC). The Testing Group maintains that when toxicity endpoints are more accurately expressed as 'loading rates', substances in the Heavy Fuel Oils category are expected to exhibit aquatic toxicity at approximately 1 mg/L or higher for the three trophic levels. Loading is a more effective means of comparing two substances to each other because the hydrocarbon composition in the WAF varies with composition of these streams. Loading is a reflection of the composition and chemistry of the substance and implicitly accounts for multicomponent dissolution and volatilization.

Aquatic toxicity of petroleum streams is attributed to the neutral organic hydrocarbon constituents whose toxic mode of action is non-polar narcosis. Hydrocarbons are equitoxic in tissues where the toxic mechanism of short-term toxicity for these chemicals is disruption of biological membrane function (van Wezel and Opperhuizen, 1995). The differences between toxicities (i.e., LC/LL5O, EC/EL50) can be explained by the differences between the target tissue-partitioning behaviors of the individual chemicals (Verbruggen et al., 2000). The existing fish toxicity database for hydrophobic neutral chemicals supports a critical body residue (CBR, the internal concentration that causes mortality) of approximately 2-8 mmol/kg fish (wet weight) (McGrath and Di Toro, 2009). When normalized to lipid content the CBR is approximately 50 µmol/g of lipid for most organisms (Di Toro et al., 2000).

When compared on the basis of standard test methods and exposure solution preparation procedures, heavy fuel oils are expected to produce a similar range of toxicity for the three trophic level species. Results expressed as measured concentrations of the fraction of the substance in solution are of little value since it will be virtually impossible to extrapolate to spill situations where the only relevant measures of concentration will be the amount of product spilled and the volume of the receiving environment (i.e., the loading rates). Loading rates provide a unifying concept for expressing the results of a toxicity test with poorly-soluble substances (European Eco-Labeling Criteria; ASTM 2009; GESAMP; OECD 2006; ECHA). Preparation of independent WAFs based on test substance loading rates is the appropriate procedure for products in this category because these products are multi-constituent hydrocarbons whose constituent hydrocarbons vary in water solubility. The dissolution thermodynamics of a multi-constituent hydrocarbon in an aqueous medium limit the likelihood of consistent proportional concentrations of the constituent hydrocarbons at various test substance loading rates. For this reason,

- exposure solutions are not prepared from dilutions of a stock solution (the relative proportion of hydrocarbon constituents in the dilutions would not accurately reflect the relative concentration of those constituent chemicals in individually prepared, successively lower exposure solutions of the test material), and
- separate exposure solutions are prepared at each exposure loading for products that are multi-constituent hydrocarbons.

Additionally the Testing Group cannot evaluate the relevancy or reliability of the effects values cited by EPA due to the lack of citations/robust summaries for cited data. In EPA's matrix of SIDS screening data (Table 5, page 120 of the HC), the ecotoxicity values for fish, aquatic invertebrates, aquatic plants, and chronic aquatic invertebrates were derived from data cited in SIDS Initial Assessment Profile (SIAP) of the C7-C9 Aliphatic Hydrocarbons Solvents category. Although the web-site URL's cited in EPA's HC leads one to the SIAP, no details of the studies are provided. The SIDS Initial Assessment Report (SIAR), which may contain study details, has not been completed and not publicly available. EPA provides a one or two sentence summary of the findings, but these cannot allow a determination of the quality of the work, and full robust summaries of the original journal/study reports should be provided.

Further reason to contest values cited by EPA in Table 5, page 120, summary of SIDS data, is that the endpoint values for fish and aquatic invertebrates are all based on unspecified measures of concentration.

EPA's review of the Testing Group's Test Plan for the Heavy Fuel Oils category stated: "*The acute toxicity data are adequate for the purposes of the HPV Challenge Program, except that acute toxicity studies are needed in all three aquatic species on the atmospheric residue in order to address the concern for heteroorganic content. EPA also recommends a chronic toxicity study in aquatic invertebrates on the residual fuel oils because of the calculated Log Kow ranges."*

The Testing Group agrees with EPA's original conclusion of data adequacy stated in their review of the Heavy Fuel Oils category Test Plan (cited above). EPA does not explain the reason for the finding of 'no adequate data' stated in their HC for the same dataset.
The Testing Group agrees with statements made in EPA's HC concluding that heteroatom compounds are largely not bioavailable due to those substances existing in high molecular weight constituents of heavy fuel oils (Hazard Characterization, Category Identification/Justification, page 12).

With respect to chronic aquatic toxicity, the Testing Group believes sufficient data exists on lubricating oil basestocks and aromatic extracts that cover similar molecular weights of constituents in heavy fuel oils.

References cited in this response to EPA's HC for the Heavy Fuel Oils Category

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