Response to EPA's Hazard Characterization of the Residual Hydrocarbon Wastes from Petroleum Refining Category

The American Petroleum Institute Petroleum HPV Testing Group

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The following comments are in response to EPA's Hazard Characterization (HC) for the Residual Hydrocarbon Wastes from Petroleum Refining Category (U.S. EPA, 2011). 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 Residual Hydrocarbon Wastes. The Testing Group's comments are found on the page numbers indicated below.

EPA HC Content	Testing Group Comments
Summary	
Introduction	
Category Justification ……..	page 2
Justification for Supporting Chemicals ……..	Page 2
1. Chemical Identity	
2. General Information on Exposure	
Conclusion	
3. Human Health Hazard ……	page 4
Acute Oral Toxicity	
Acute Dermal Toxicity	
Acute Inhalation	
Repeated-Dose Toxicity	
Reproductive Toxicity ……	page 5
Developmental Toxicity	
Genetic Toxicity – Gene Mutation	
Genetic Toxicity – Chromosomal Aberrations	
Skin Irritation	
Eye Irritation	
Skin Sensitization	
Carcinogenicity	
Neurotoxicity	
Conclusion	
4. Hazard to the Environment	
Acute Toxicity to Fish	
Acute Toxicity to Aquatic Invertebrates	
Toxicity to Aquatic Plants	
Chronic Toxicity to Aquatic Invertebrates	
Conclusion	
5. References	
Appendix	

Category Justification

1. The EPA hazard characterization for several Petroleum HPV Categories including Residual Hydrocarbon Wastes from Petroleum Refining Category, refers to the category members as mixtures when in fact they are Class 2 UVCB substances. (HC pages 5, 6, 8, 9, Tables 3 & 4)

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: 68476-53-9
CAS Name: Hydrocarbons, C ≥20, petroleum wastes
CAS Definition: A complex combination of hydrocarbons produced as waste material from slop oil, sediments, and water. It consists of hydrocarbons having a carbon number predominantly greater than C20 and boiling above approximately 350 °C (662 °F).

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 Residual Hydrocarbon Wastes from Petroleum Refining Category are UVCB substances, not mixtures, under EPA's nomenclature guidance.

Justification for Surrogate Chemicals

For the ecotoxicity endpoints, the sponsor provided robust summaries for the aquatic toxicity of the proposed supporting chemicals fuel oil, residual (CASRN 68476-33-5) and fuel oil No. 6 (no CASRN); however, results were reported based on nominal loading rates, not measured concentrations. EPA determined that the measured data from 1-tetradecene (CASRN 1120-36-1) and 1-hexadecene (CASRN 629-73-2) were more appropriate to support this category based on their similar physico-chemical properties, environmental fate and mode of toxic action (narcosis). In addition, 1-tetradecene (C14) and 1-hexadecene (C16) cover the low and high carbon numbers in the category (C14 - ≥ C20) with respect to toxicity. EPA said, "Therefore, data from these supporting chemicals can adequately characterize the aquatic toxicity hazard for this category and were used for the preparation of this hazard characterization" (HC page 6).

The supporting chemical 1-tetradecene (CASRN 1120-36-1: SIAM 11) has been assessed in the OECD HPV program as a member of the alpha olefins category. (http://www.chem.unep.ch/irptc/sids/OECDSIDS/AOalfaolefins.pdf).

The supporting chemical 1-hexadecene (CASRN 629-73-2: SIAM 19) has been assessed in the OECD HPV program as a member of the higher olefins category. (http://www.chem.unep.ch/irptc/sids/OECDSIDS/HigherOlefins.pdf).

1. EPA cites 1-tetradecene (CASRN 1120-36-1) and 1-hexadecene (CASRN 629-73-2) as model hydrocarbons that can be used to represent the aquatic toxicity of petroleum UVCB ('Class 2') substances having similar solubility and partitioning (Log Kow) characteristics. Yet the studies supporting the aquatic toxicity of both supporting chemicals employed the same testing methods that EPA criticized in their review of the studies submitted by the Testing Group for the Residual Hydrocarbon Wastes category. The robust summary for the test of 1-tetradecene to fish is shown as an example in the Appendix (page 5). This summary shows that exposure solutions were prepared as WAFs, at concentration well above the solubility limit of 1-tetradecene (calculated solubility of 0.004 mg/L by WSKOW V1.41, EPI-Suite™ V4.0) without analytical data to accompany the values for loading rates. Studies of the other aquatic species and those for 1-hexadecene were similarly performed.

EPA's use of these surrogate data, although redundant, supports API's use of lethal loading based on WAF preparations. Therefore, the Testing Group interprets EPA's use of the surrogate data as accepting studies run employing WAF preparations.

2. The Testing Group agrees with EPA's conclusion that these substances show no aquatic toxicity at their water saturation limit. However, the Testing Group believes that results for petroleum UVCBs like Residual Hydrocarbon Wastes from Petroleum Refining Category members (multi-constituent, poorly soluble hydrocarbons) should be expressed as lethal loadings (LL) rather than lethal/effect concentrations (LC, EC). 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 dissolution and volatilization of individual hydrocarbon constituents.

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, kerosene/jet fuel category members 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 the petroleum UVCB substances in this category because these substances 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 substances that are multi-constituent hydrocarbons.

3. EPA has been critical of aquatic hazard data based on tests conducted using WAFs and without the support of analytical measurements of exposure concentrations (see the HC for Lubrication Oil Basestocks Category). When properly prepared, WAFs represent the equilibrium condition of maximally dissolved test substance for its respective loading rate. Any excess test substance is separated from the solutions used in testing, allowing the use of only dissolved constituents or those that create stable dispersions.

3. Human Health Hazard

The Testing Group said of the Residual Hydrocarbon Wastes Category that, "The available test data with residual fuel oil blending streams and two types of waste hydrocarbons indicate that the substances are systemic and developmental toxicants following repeated dermal exposure. These finding are not surprising considering their potential PAC content [*polycyclic aromatic compounds*] and the recognized health hazards from this class of chemicals." (CAD, August, 2010)

The Testing Group has shown (a) that the toxicological effects of high boiling petroleum-derived substances (i.e., final boiling points > 650 ^{o}F) are associated with their 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 Testing Group had the results of the 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). Animal testing for several human health endpoints may be unnecessary if the material is covered in the domain of these statistical models.

Reproductive Toxicity

EPA identified mammalian reproductive toxicity as a data gap under the HPV Challenge Program for several Petroleum HPV Categories including Residual Hydrocarbon Wastes from Petroleum Refining. 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 Category Assessment Document for Residual Hydrocarbon Wastes from Petroleum Refining is sufficient to satisfy the SIDS requirements for reproductive toxicity. Additional toxicology testing to address the reproductive hazard is unnecessary. The relevant data for reproduction is summarized in the Testing Group's Category Assessment Document (CAD page 33 – 37) and the critical studies include;

API Separator Sludge

- Mobil (1990a). Thirteen-week Dermal Administration of API Separator Bottom Sludge to Rats. Study Number 63036. Mobil Oil Corporation. Princeton. NJ.
- Mobil (1990b). Developmental Toxicity Study in Rats Exposed Dermally to API Separator Bottom Sludge. Study Number 63239. Mobil Oil Corporation. Princeton, NJ.

DAF Float

- Mobil (1995). Thirteen-week Dermal Administration of DAF Float Blend to Rats. Study Number 63266. Mobil Oil Corporation. Princeton, NJ.
- Mobil (1990c). Developmental Toxicity Study in Rats Exposed Dermally to DAF Float Blend. Study Number 63264. Mobil Oil Corporation. Princeton, NJ.

References cited in this response to EPA's HC for the Residual Hydrocarbon Wastes Category

ASTM. 2009. ASTM D6081 – 98 (2009) Standard Practice for Aquatic Toxicity Testing of Lubricants: Sample Preparation and Results Interpretation.

Di Toro DM, McGrath JA, Hansen DJ. (2000). Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. Environ Toxicol Chem. 19:1951-1970.

ECHA Guidance on information requirements and chemical safety assessment. Chapter R.7b: Endpoint http://echa.europa.eu/documents/10162/13632/information_requirements_r7b_en.pdf

European eco-lubricant labeling criteria:
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:118:0026:0034:EN:PDF

GESAMP: The Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships
http://www.gesamp.org/publications/publicationdisplaypages/rs64

McGrath JA, Di Toro DM. (2009). Validation of the target limpid model for toxicity assessment of residual petroleum constituents: moncyclic and polycyclic aromatic hydrocarbons. Environ Toxicol Chem 28:1130-1148.

McKee, R.H., Schreiner, C., Nicolich, M.J., and Gray, T. (2013) Genetic toxicity of HPV petroleum streams containing polycyclic aromatic compounds. Regulatory Toxicology and Pharmacology. Accepted for publication.

Mobil (1990a). Thirteen-week Dermal Administration of API Separator Bottom Sludge to Rats. Study Number 63036. Mobil Oil Corporation. Princeton. NJ.

Mobil (1990b). Developmental Toxicity Study in Rats Exposed Dermally to API Separator Bottom Sludge. Study Number 63239. Mobil Oil Corporation. Princeton, NJ.

Mobil (1995). Thirteen-week Dermal Administration of DAF Float Blend to Rats. Study Number 63266. Mobil Oil Corporation. Princeton, NJ.

Mobil (1990c). Developmental Toxicity Study in Rats Exposed Dermally to DAF Float Blend. Study Number 63264. Mobil Oil Corporation. Princeton, NJ.

Murray J, Roth R, Nicolich M, Gray T, Simpson B. (2013). The relationship between developmental toxicity and aromatic ring class content of high boiling petroleum substances. Regulatory Toxicology and Pharmacology. Accepted for publication.

Nicolich M, Simpson B, Murray J, Roth R, Gray T. (2013). The development of statistical models to determine the relationship between the aromatic ring class content and repeat-dose and developmental toxicities of high boiling petroleum substances. Regulatory Toxicology and Pharmacology. Accepted for publication.

OECD: Guidance for Testing of difficult substances and mixtures: http://search.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono(2000)6&doclanguage=en

Roth R, Simpson B, Nicolich M, Murray R, Gray T. (2013). The relationship between repeat dose toxicity and the aromatic ring class content of high boiling petroleum substances. Regulatory Toxicology and Pharmacology. Accepted for publication.

Toxic Substances Control Act Inventory Representation for Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials: UVCB Substances (March 29, 1995a); available from http://www.epa.gov/oppt/newchems/pubs/uvcb.txt

Toxic Substances Control Act Inventory Representation for Certain Chemical Substances containing Varying Carbon Chain Lengths (Alkyl Ranges Using the Cx-y Notation) (March 29, 1995b); available from: http://www.epa.gov/oppt/newchems/pubs/alkyl-rg.txt

U.S. EPA (2011). Screening Level Hazard Characterization of High Production Volume Chemicals; Reclaimed Petroleum Hydrocarbons: Residual Hydrocarbon Wastes from Petroleum Refining Category. http://www.epa.gov/chemrtk/hpvis/hazchar/Category_Residual%20Hydrocarbon%20Wastes_March%202011.pdf

van Wezel AP, Opperhuizen A. (1995). Narcosis due to environmental pollutants in aquatic organisms: residue-based toxicity, mechanisms, and membrane burdens. Critical Rev Toxicol. 25(3):255-279.

Verbruggen EMJ, Vaes WHJ, Parkerton TH, and Hermens JLM. (2000). Polyacrylate-coated SPME fibers as a tool to simulate body residues and target concentrations of complex organic mixtures for estimation of baseline toxicity. Environ Sci Technol. 34:324-331.