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Aquatic hazard and biodegradability of light and middle atmospheric distillate petroleum streams

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HIGHLIGHTS

- Concentrations of dissolved hydrocarbons were stable in sealed test chambers.
- Acute toxicity (LL/EL$_{50}$) values ranged 0.3–5.5 mg L^{-1} loading rate.
- Chronic NOELR values ranged 0.05–0.64 mg L^{-1} loading rate.
- PETROTOX provided conservative estimates of acute and chronic toxicity.
- Biodegradation reflected extensive microbial oxidation of the test substances.

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ABSTRACT

Light and middle atmospheric distillate petroleum substances are blended to produce fuels used in transportation and heating. These substances represent the majority by volume of crude oil refined products in the United States. The goal of this research was to develop biodegradability and aquatic toxicity data for four substances; heavy, straight-run naphtha (HSRN), hydro-desulfurized kerosene (HDK), hydro-cracked gas oil (HCGO), and catalytic-cracked gas oil (CCGO). Ready biodegradability tests demonstrated rapid and extensive microbial oxidation of these test substances, indicating a lack of persistence in the aquatic environment. Differences in biodegradation patterns reflected compositional differences in the constituent hydrocarbons. Results of aquatic toxicity tests on alga, cladocera, and fish demonstrated that toxicity was greatest for catalytic-cracked gas oil, which contained a high proportion of aromatic hydrocarbons. Aromatic hydrocarbons are more soluble, and hence more bioavailable, resulting in higher toxicity. When expressed on the basis of loading rates, acute toxicity values (LL/EL$_{50}$) ranged between 0.3 and 5.5 mg L^{-1} for all three species, while chronic no-observed-effect loading rates (NOELR) ranged between 0.05 and 0.64 mg L^{-1}. PETROTOX estimates for acute and chronic toxicity ranged from 0.18 to 2.3 mg L^{-1} and 0.06 to 0.14 mg L^{-1}, respectively, which were generally more conservative than experimental data.

1. Introduction

This paper reports new data on biodegradability and aquatic toxicity for substances selected from the gasoline/naphtha, kerosene/jet fuel, and gas oils categories which are used to complete the fate and effects profiles for these distillates. Approximately 400 petroleum substances, sponsored by API's Petroleum HPV Testing Group (PHPVTG), were organized into 13 categories to share data and minimize animal testing. These petroleum substances are transported around the world and fall under one or more statutes for product classification and labeling (United Nations, 2005; OJEU, 2008). Environmental fate and effects data are used to assign hazard ranking under these regulations.

These petroleum substances, listed as Class II (TSCA) chemicals or "Chemical Substances of Unknown or Variable Composition, Complex Reaction Products and Biological Materials (UVCB)", do not exhibit specific and exact properties, but are characterized by a range for physical–chemical, toxicological, and environmental hazard values. Gasoline, kerosene, and gas oils can be grouped as light or middle atmospheric distillates. Light atmospheric naphtha distillates are low boiling point streams that are a major component in gasoline (US EIA, 2013). Kerosene and gas oils are middle

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atmospheric distillates used to produce jet and diesel fuels. These light and mid-atmospheric distillates have complex and variable compositions of *n*- and *iso*-paraffins, naphthenes, olefins, and aromatics hydrocarbons. Hydrocarbons comprising gasoline and their blending naphthas have approximately 4–12 carbon atoms, those comprising kerosene have 9–16 carbon atoms, and those consisting of gas oils have 9–30 carbon atoms (API, 2008, 2010, 2012). Each test substance was selected to provide new information on the environmental fate and hazards of the types of substances that they represent. Detailed compositional analyses of the kerosene and gas oil samples were used in the PETROTOX model to estimate aquatic toxicity. These results, together with existing data (API, 2008, 2010, 2012) provide a dataset that can be used to characterize the environmental fate and hazard of the broader categories.

2. Materials and methods

2.1. Test substances

HSRN was tested for biodegradability, HDK was tested for chronic aquatic toxicity, and HCGO and CCGO were tested for biodegradability, acute, and chronic aquatic toxicity. Samples of each test substance were characterized for boiling point range, density, and hydrocarbon type using ASTM methods. Carbon number range was determined either from comprehensive gas chromatography-mass spectrometry (GC–MS) analysis (petroleum naphtha) or from two-dimensional gas chromatography/flame ionization detection (2D-GC/FID). High resolution hydrocarbon analysis (2D-GC/FID) for the kerosene and two gas oil test substances was performed following published methods (Blomberg et al., 1997; Edam et al., 2005; Forbes et al., 2006). Data and sample identification are reported in Table 1.

2.2. Aquatic toxicity tests

Testing of green algae (*Pseudokirchnerella subcapitata*), cladocera (*Daphnia magna*), and fish (*Oncorhynchus mykiss*) followed US EPA and OECD standard guidelines (OPPTS 850.5400, 850.1010, 850.1075; OECD 201, 202, 203). Fish tests employed the upper threshold concentration (UTC) approach in order to reduce the number of test organisms (Jeram et al., 2005; ECVAM, 2006). The UTC approach is based on the observed trend where acute fish toxicity is often less severe than algae and *D. magna* when exposed to a variety of toxicants (Weyers et al., 2000). The UTC was defined as the lower of the two EL_{50} values from the *P. subcapitata* and *D. magna* tests. Fish were tested at the single UTC limit. When less than 50% mortality occurred at the UTC, no further testing was necessary since fish was not the most sensitive organism. *D. magna* 21-day reproduction tests followed OECD 211, and test endpoints were based on the numbers of neonates produced per surviving adult. Test details are summarized in Tables 2 and 3.

Water accommodated fractions (WAFs) were used as exposure solutions in all tests (Girling et al., 1992, 1994; ASTM, 2009). All WAFs were independently prepared on the basis of the loading rate (total mg test substance added L^{-1} dilution water). Test substances were added to dilution media in glass mixing bottles using stainless steel and glass syringes. Loading rates were determined from the volumes added and converted to mass per unit volume ($mg\ L^{-1}$) based on the density of test substance. The solutions were stirred at a rate to maintain a vortex of <10% of the static liquid depth for approximately 24 h, then permitted to settle one hour. The aqueous phase was collected from a bottom port in the mixing vessel, with the initial 75–100 mL solution being discarded. Prior to testing, a WAF equilibration trial was conducted to assess dissolution times and stability of dissolved hydrocarbons.

2.3. Estimation of aquatic toxicity by PETROTOX

PETROTOX (Redman et al., 2012) was used to estimate toxicity of the two gas oils and hydro-desulfurized kerosene. PETROTOX computes toxicity of complex petroleum substances based on the summation of the aqueous-phase concentrations of hydrocarbon blocks that represent each test substance and uses the Target Lipid Model (TLM) to calculate toxicity (Di Toro et al., 2000; CONCAWE, 2007; Redman et al., 2012). Input data for the model were provided by the 2D-GC/FID analyses. PETROTOX modeling was not done for the heavy straight-run naphtha because the aquatic hazard of this substance was previously characterized (API, 2008).

Table 1
Test substances and physiochemical characterizations.

CAS No.	Name	TSCA definition	Carbon number range	ASTM D2887 or D86 boiling point range (°F)			ASTM D4052 density ($g\ mL^{-1}$)	ASTM D1319 hydrocarbon type (Vol%)		
				Initial	50%	Final		Aromatics	Olefins	Saturates
64741-41-9	Naphtha (petroleum), heavy straight run	A complex combination of hydrocarbons obtained by the fractional distillation of petroleum. This fraction boils in a range of approximately 20–135 °C (58–275°F)	6–12	210	252	352	0.7535	10	1	89
64742-81-0	Kerosene (petroleum), hydro-desulfurized	A complex combination of hydrocarbons obtained from a petroleum stock by treating with hydrogen to convert organic sulfur to hydrogen sulfide which is then removed. It consists of hydrocarbons having carbon numbers predominantly in the range of C9–C16 and boiling in the range of approximately 150–290 °C (302–554 °F)	6–22	226	408	646	0.8204	17	3	80
64741-77-1	Distillates, (petroleum), light hydro-cracked	A complex combination of hydrocarbons produced by the distillation of products from a hydrocracking process. It consists predominantly of saturated hydrocarbons having carbon numbers predominantly in the range of C10–C18, and boiling in the range of approximately 160–320 °C (320–608 °F)	8–30	274	412	555	0.8238	17	1	82
64741-59-9	Distillates (petroleum), light catalytic-cracked	A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers predominantly in the range of C9–C25 and boiling in the range of approximately 150–400 °C (302–752 °F). It contains a relatively large proportion of bicyclic aromatic hydrocarbons	6–30	288	522	676	0.9618	75	7	18