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Short Communication

Preliminary ecotoxicity assessment of new generation alternative fuels in seawater

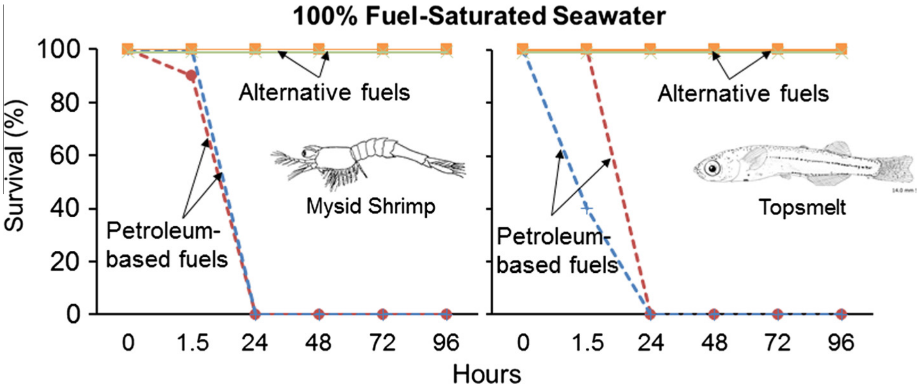
Gunther Rosen [a,*], Renee E. Dolecal [b], Marienne A. Colvin [a], Robert D. George [a]

[a] *Space and Naval Warfare (SPAWAR) Systems Center Pacific, 53475 Strothe Rd., San Diego, CA 92152, United States*
[b] *San Diego State University Research Foundation, 5250 Campanile Drive, San Diego, CA 92182, United States*

HIGHLIGHTS

- Initial findings on aquatic toxicity of new generation alternative fuels.
- US Navy alternative fuels less environmentally toxic than fossil fuels.
- Comparison of ecotoxicity of petroleum-based and new generation biofuels.
- Alternative fuel PAH and VOCs in seawater lower than conventional fuels.
- Sea urchin embryos more sensitive than other endpoints to alternative fuels.

GRAPHICAL ABSTRACT



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ABSTRACT

The United States Navy (USN) is currently demonstrating the viability of environmentally sustainable alternative fuels to power its fleet comprised of aircraft and ships. As with any fuel used in a maritime setting, there is potential for introduction into the environment through transport, storage, and spills. However, while alternative fuels are often presumed to be eco-friendly relative to conventional petroleum-based fuels, their environmental fate and effects on marine environments are essentially unknown. Here, standard laboratory-based toxicity experiments were conducted for two alternative fuels, jet fuel derived from *Camelina sativa* (wild flax) seeds (HRJ5) and diesel fuel derived from algae (HRD76), and two conventional counterparts, jet fuel (JP5) and ship diesel (F76). Initial toxicity tests performed on water-accommodated fractions (WAF) from neat fuels partitioned into seawater, using four standard marine species in acute and chronic/sublethal tests, indicate that the alternative fuels are significantly less toxic to marine organisms.

1. Introduction

Alternative fuels refined from renewable resources, as opposed to conventional petroleum from fossil fuels, are of growing interest due to their potential benefits, such as reduced dependence on foreign oil supplies (i.e. energy security) and lower net greenhouse gas emissions (i.e. increased environmental sustainability; Shonnard et al., 2010; Ahmad et al., 2011; ITRC, 2011). The USN (and other Department of Defense services) has traditionally used petroleum-based jet fuel (JP5) and diesel fuel marine for ships (F76) to power its fleet, but is actively acquiring, testing, and certifying alternative fuels for use as fossil fuel replacements. In 2012, the Navy demonstrated the use of biofuel, blended with petroleum-based fuels, in a carrier strike group comprised of nuclear-powered ships and petroleum fueled aircraft (Blakeley, 2012). By 2020, the Navy plans to meet 50% of its total energy consumption from alternative sources (Blakeley, 2012).

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* Corresponding author.
E-mail address: gunther.rosen@navy.mil (G. Rosen).

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Conventional jet fuels are considered highly toxic and among the top spilled petroleum products in the US (Irwin et al., 1997; Bluhm et al., 2012). These fuels contain multiple contaminants of concern including polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and straight-chained alkanes (Irwin et al., 1997). New generation alternative fuels, however, do not naturally contain many of these compounds, or are processed using methods that reduce or eliminate them, subsequently reducing potential fuel toxicity. Modern production methods such as hydroprocessing (hydrotreating) or hydrocracking, for example, eliminate compounds such as sulfur, oxygen, and aromatics, or reduce the size of larger molecules (Al-Sabawi and Chen, 2012). Not only does this increase the solubility and biodegradability of such fuels, but it also reduces noxious emissions when combusted or burned (Shonnard et al., 2010; Bezergianni and Dimitriadis, 2013). An improved understanding of the interactions of alternative fuels and the environment, used both independently and blended with petroleum-based fuels, is important in predicting their ecological risk.

Alternative fuels may originate from a variety of sources (e.g. starch, vegetable oils, animals fats, and cellulose), however, two 'new generation' biofuels currently being evaluated by the Navy to power its fleet include hydrotreated renewable microalgae-derived fuel (HRD76) and hydrotreated renewable *Camelina*-derived jet fuel (HRJ5). These are to be blended with petroleum marine diesel F76 and jet fuel JP5, respectively. Unlike earlier generation food crop-based biofuels (e.g. bioethanol, biodiesel), these plant- and algae-derived fuels can meet engine performance specifications and do not require modified infrastructure. Additionally, non-food feedstocks are more sustainable because they reduce pressure on standard agricultural crops. Microalgae, for example, can be grown in high densities in non-arable, nutrient-poor land, under harsh conditions (Ahmad et al., 2011), and *Camelina* is a weed that grows well on arid, marginal lands (Shonnard et al., 2010). For both feedstocks described in this study, lipids (triglycerides) are extracted and converted into hydrocarbons via hydroprocessing technology (Pearson et al., 2013).

In addition to enhanced sustainability, alternative bio-based fuels have potential for lower air emissions, and may be easier to bioremediate due to higher biodegradability (Bluhm et al., 2012; Yassine et al., 2012). Some recent studies have shown generally lower toxicity for *Daphnia* and rainbow trout (e.g. Hollebone et al., 2008, Khan et al., 2007), while others have shown enhanced toxicity in some cases to both freshwater (Bluhm et al., 2012) and saltwater species (Ginn et al., 2010) relative to conventional diesel fuels, indicating that there may be a lack of predictability for how these fuels will behave in the environment. Those studies, however, used earlier generation biofuels including biodiesel derived from vegetable or animal oils. To our knowledge, no data have been previously reported for the aquatic toxicity of HRJ5 or HRD76.

Because transport, storage, and handling of fuels often occur in marine environments adjacent to bays, harbors, and estuaries, it is important to determine the effects of new generation biofuels on marine-specific organisms. Here we report results from a preliminary empirical study to assess toxicity of chemical components in seawater that are present from partitioning of neat fuels (with and without relevant additives for jet fuel) and fuel blends during mixing. The seawater phase exposed to fuel is termed the water accommodated fraction (WAF). These preliminary findings are primarily the result of range-finding experiments, a critical first step in developing an understanding of the environmental behavior of alternative fuels relative to conventional fossil fuels. The efforts described here have focused on characterizing the chemical content in WAFs on the basis of broad chemical classes of compounds considered environmentally relevant. These are specifically long-chain hydrocarbons (alkanes), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs). These preliminary distinctions between classes of compounds, made on the basis of total concentrations (total alkanes, total VOCs, total PAHs), form the basis for and will be used to assist in the design of detailed chemical characterizations in future studies. Definitive, multi-concentration testing for development of precise median lethal concentrations (LC50) and median effective concentrations (EC50) is currently underway, including detailed characterization of chemical constituents in the WAF, as well as the effects of weathering processes on the environmental fate of these materials once introduced into seawater.

2. Materials and methods

2.1. Fuel acquisition

Relevant conventional and alternative fuels were procured from the Navy's Fuels Program at Naval Air Systems Command (NAVAIR), Patuxent River, MD, USA. Fuels included JP5, F76, HRJ5, and HRD76, stored in tightly-capped 5 gal metal cans, under cool, dry conditions until use. NAVAIR acquired both alternative fuels from Honeywell UOP. HRJ5 and HRD76 were refined from oils derived from *Camelina* and microalgae, which were provided by Sustainable Oils (Seattle, WA, USA) and Solazyme, Inc. (San Francisco, CA, USA), respectively. Three jet fuel additives, typically already added to JP5 by the manufacturer, were also acquired. These additives included icing inhibitor, diethyleneglycol monomethylether (DiEGME); antioxidant, di-tert-butylphenol (DTBP), 1000 ppm in kerosene; and lubricity improver/corrosion inhibitor, (DCI-4A), proprietary formulation, per the military specifications for JP5 (MIL-DTL-5624V).

2.2. Chemical characterization

Seawater samples were chemically characterized using USEPA approved methodologies and protocols. Solvent-based extraction methods or purge-and-trap techniques were used prior to Gas Chromatography (GC), which was combined with flame ionization detection (FID) optimized for detection of alkanes, Mass Spectrometry (MS) detection for VOCs, and MS in selection ion monitoring mode (SIM) for PAHs. Alkane analyses used USEPA Methods 3510C and 8015 M for evaluating fuel range organics with carbon chain lengths from C6–C44; VOCs were characterized using USEPA Methods 5030B and 8260C for common small aromatics (e.g. benzenes, xylenes, etc.), including substituted benzenes, and some short-chain hydrocarbons (e.g. hexane, octane, etc.); and PAHs were characterized using USEPA Methods 3520C and 8270D for napthalenes and higher order PAHs, including alkylated homologues. For data reported here, totals for each chemical class of compounds, alkanes, VOCs, and PAHs were quantified as the sums of all identifiable peaks (ΣAlkanes, ΣVOCs, ΣPAHs). These were quantified against appropriate internal calibration standards for each class of compound, prepared at concentrations suitable for determining concentrations at relevant sample-specific quantitation levels. In addition, standard surrogate compounds were added to seawater samples for each chemical class and percent recovery assessed to ensure extraction efficiency targets were met. Care was taken to ensure that National Environmental Laboratory Accreditation Program (NELAP)–approved quality assurance (QA) standards were followed, evaluated and achieved throughout.

2.3. Toxicity experiments

Two preliminary experiments were conducted, each involving different means of obtaining the WAF for each fuel type: (Phase