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Toxicity of Gasoline, Diesel and Weathered Diesel Related Petroleum Hydrocarbons to Freshwater and Marine Organisms

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ABSTRACT

The purpose of this study was to determine environmental effects-based concentrations of total petroleum hydrocarbons for assessing the impacts of fresh gasoline and fresh or weathered diesel in the freshwater and marine environments. The study was conducted by the Washington State Department of Ecology (Ecology) and Nautilus Environmental to determine the NOEC and LOEC of gasoline, fresh diesel and weathered diesel, in addition to IC25 and IC50 endpoints, using aquatic toxicity bioassays.

In separate experiments, hydrocarbons within either the fresh diesel or gasoline range were spiked into toxicity test solutions, whereas weathered diesel in contaminated groundwater was obtained from a well-characterised site in Washington State. Freshwater organisms used were the fathead minnow, *Pimephales promelas* and a cladoceran, *Ceriodaphnia dubia*. Topsmelt, *Atherinops affinis* and the echinoderm, purple sea urchin, *Strongylocentrotus purpuratus* were the marine species tested. Tests were conducted according to US EPA test methods and Ecology's whole effluent toxicity (WET) guidance document. Toxicity tests were conducted at Nautilus Environmental in Burnaby, BC. Hydrocarbon concentrations in test solutions were determined at the Manchester Environmental Laboratory, Port Orchard, WA.

Gasoline caused similar toxicity between topsmelt, fathead minnow and *Ceriodaphnia*, which were more sensitive than the echinoderm. Diesel was generally more toxic than gasoline to all test organisms. With weathered diesel tests, this pattern changed and fish became the more sensitive organisms. All test organisms were less sensitive to the weathered diesel compared with fresh diesel. Volatile compounds present in the fresh diesel may be responsible for greater toxicity to the invertebrates in particular.

INTRODUCTION

Purpose:

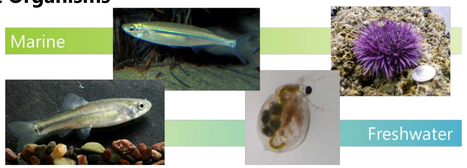
- Examine effects of gasoline, diesel #2, and weathered diesel on freshwater and marine organisms.
- Fill gaps in available data on common petroleum hydrocarbon mixtures.

Use:

- For assessing potential effects of fresh, recent, or old hydrocarbon spills
- Freshwater and marine environmental impact assessment
- Water quality criteria for total petroleum hydrocarbons (TPH), based on dose-response and effects-based concentrations.

METHODS

Test Organisms



Toxicity Test Information

- Table 1. shows tests used to examine hydrocarbon mixture toxicity.

Table 1. Toxicity Tests

Organism	Test Type	Duration	Endpoints
Cladoceran,	EPA-821-R-02-013, 1002.0	7 day	Survival, reprod.
Fathead minnow	EPA-821-R-02-013, 1000.0	7 day	Survival, growth
Echinoderm	EPA/600/R-95/136	40 min	Fertilization
Topsmelt	EPA/600/R-95/136, 1006.0	7 day	Survival, growth

- Toxicity tests were conducted using US EPA test methods & Ecology's Whole Effluent Toxicity (WET) guidance document, "Canary Book".
- Toxicity tests conducted at Nautilus Environmental, Burnaby
- Static renewal tests with limited or no headspace
- Daily renewal of test solutions and fresh hydrocarbon mixtures

Test Chemical Mixtures

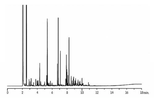
- Analytical standards obtained from Restek Corp.
- Unleaded gasoline (C7 – C12)
- Diesel #2 (C10 – C24) – Fresh Diesel
- Composed of blends from multiple refineries
- Weathered diesel in groundwater from contaminated site in Washington, US.

Test Solution Preparation

- Stock solutions - Water Accommodated Fractions (WAF)
- Stirred overnight in 5L aspirator bottles
- Allowed to settle 1 hr
- Drained from bottom to collect "dissolved fraction"
- Dilutions prepared from stock solution
- Weathered diesel in groundwater was diluted with appropriate test media

Test Solution Analysis

- Water samples analysed by Manchester Environmental Laboratory, Port Orchard, WA. GC-FID for gasoline and fresh and weathered diesel.
- Reporting Limits (µg/L)
  - Unleaded Gasoline: 70
  - Diesel: 50



RESULTS

Test Solution Concentrations

The measured concentrations of gasoline and fresh diesel in test solutions were lower than nominal concentrations due to the insolubility and volatility of the test items.

- Gasoline (C7-C12) measured concentrations:
  - Freshwater ≈ 60 to 80% of nominal
  - Marine water ≈ 80% of nominal
- Fresh Diesel (C10-C24) measured concentrations:
  - Freshwater:
    - In solutions concentrations <1.5mg/L ≈ 40 - 50% of nominal
    - In solutions concentrations >1.5 mg/L ≈ 8 - 15% of nominal
  - Marine water ≈ 7 - 20% of nominal
  - Lower concentrations due to lower solubility of the fresh diesel standard

Test Solution Concentration Stability

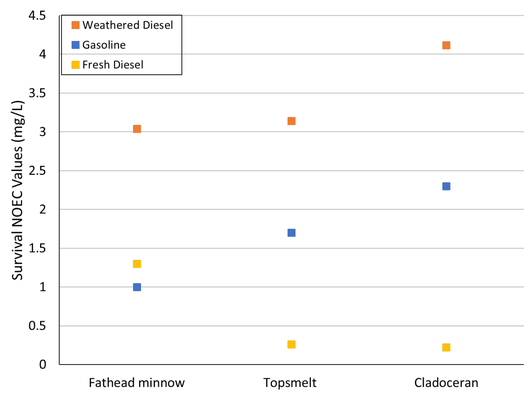
The loss of fresh diesel in test solutions was lower than that of gasoline in test solutions likely due to it's lower volatility and solubility. However, weathered diesel in groundwater was very stable in all test solutions.

- Gasoline – 70 – 80% loss overnight in fish chambers, but less in *C. dubia* tubes.
- Diesel – lower loss than gasoline in fish chambers. Unmeasurable loss in cladoceran test tubes due to concentrations near detection limit, variability in solution preparation, and analytical error.
- Weathered Diesel – Stable in test solutions, no loss over time.

Toxicity Test Endpoints - Survival

Test endpoints were calculated using measured concentrations of TPH. The survival NOEC values are presented in Figure 1.

Figure 1. Survival of Organisms in Gasoline, Fresh Diesel and Weathered Diesel

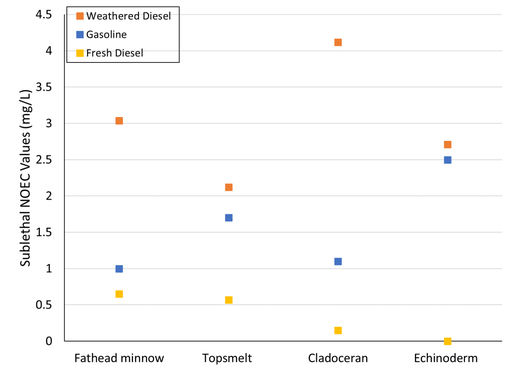


RESULTS

Sublethal Toxicity Test Endpoints

The sublethal toxicity NOEC values were calculated based on measured TPH test concentrations and are presented in Figure 2.

Figure 2. Sublethal Toxicity of Gasoline, Fresh and Weathered Diesel



Summary of Toxicity Test Endpoints

Point estimates were calculated based on the measured concentrations and toxicity test data. A summary of the toxicity point estimates and effects-concentrations for gasoline, fresh diesel and weathered diesel in freshwater and marine water is presented in Table 3.

Table 2. Overall summary of lowest toxicity point estimates and effects-concentrations for gasoline, fresh and weathered diesel.

	Freshwater			Marine water		
Values (mg/L)	Gasoline	Diesel	Weathered Diesel	Gasoline	Diesel	Weathered Diesel
LC50	2.5 (2.2 - 2.8)	0.23 (0.20 - 0.26)	>4.33	1.7 (1.5 - 2.1)	0.68 (0.55 - 0.83)	>3.14
IC25	1.5 (1.2 -1.7)	0.17 (0.16 - 0.19)	4.3 (3.8 - 4.6)	1.7 (0.4 - 2.2)	0.19 (0.12 - 0.19)	2.0 (1.4 - 2.6)
LOEC	2.1	0.22	4.33	>1.7	0.05	3.14
NOEC	1.0	0.15	3.04	1.7	<0.05	2.12

CONCLUSIONS

- Fresh diesel was generally more toxic than gasoline to all test organisms.
- Fresh diesel & gasoline results were comparable to literature values.
- Weathered diesel was less toxic than fresh diesel, probably due to loss of less polar compounds.
- NOEC values could be used to derive protective concentrations for fish and other aquatic life in surface waters.