Co-Optimization of Fuels & Engines

Toxicology and Biodegradability of Tier Three Gasoline Blendstocks

Literature Review of Available Data

September 2019

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About the Co-Optimization of Fuels and Engines Initiative

This is one of a series of reports produced as a result of the Co-Optimization of Fuels & Engines (Co-Optima) initiative, a U.S. Department of Energy (DOE)–sponsored effort initiated to simultaneously investigate advanced engine designs and the enabling fuel properties. This first-of-its-kind effort is designed to provide American industry with the scientific underpinnings needed to maximize vehicle performance and efficiency, leverage domestic fuel resources, boost U.S. jobs, and enhance energy security.

Co-Optima brings together DOE's Office of Energy Efficiency & Renewable Energy (EERE), 9 national laboratories, 13 universities, and numerous industry and government stakeholders in a collaboration exploring solutions with potential for near-term improvements to the types of fuels and engines found in most vehicles currently on the road, as well as to the development of revolutionary engine technologies for a longer-term, higher-impact series of solutions.

In addition to the EERE Vehicle Technologies and Bioenergy Technologies Offices, the Co-Optima team includes representatives from the National Renewable Energy Laboratory and Argonne, Idaho, Lawrence Berkeley, Lawrence Livermore, Los Alamos, Oak Ridge, Pacific Northwest, and Sandia National Laboratories. More details on the project—as well as the full series of reports—can be found at www.energy.gov/fuel-engine-co-optimization.

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Table of Contents

List of Figures vii

List of Tables vii

Abbreviations and Acronyms viii

Executive Summary 1

1. Background 2

2. Introduction 3

3. Methods and Results 6
- 3.1. Overall Approach 6
- 3.2. Compartmental Partitioning Model 6
- 3.3. Fate and Transport Indicators 9
- 3.4. EPI Suite™ Screening 11
- 3.5. Human Exposure and Toxicology 12
- 3.6. Ecological Exposure 15

4. Discussion 17

5. Conclusions 18

6. References 19

Appendix A: Environmental Partitioning Illustrations 24

List of Figures

Figure 1. Illustration of compartmental partitioning model 6
Figure 2. Illustration of compartmental partitioning model results for ethanol 7
Figure A-1. Environmental partitioning illustration of n-propanol 24
Figure A-2. Environmental partitioning illustration of isopropanol 25
Figure A-3. Environmental partitioning illustration of isobutanol 25
Figure A-4. Environmental partitioning illustration of cyclopentanone 26
Figure A-5. Environmental partitioning illustration of DIB 26
Figure A-6. Environmental partitioning illustration of 2-methylfuran 27
Figure A-7. Environmental partitioning illustration of 2,5-dimethylfuran 27
Figure A-8. Environmental partitioning illustration of benzene 28
Figure A-9. Environmental partitioning illustration of MTBE 28
Figure A-10. Environmental partitioning illustration of isooctane 29
Figure A-11. Environmental partitioning illustration of toluene 29
Figure A-12. Environmental partitioning illustration of 1-hexene 30

List of Tables

Table 1. Co-Optima Gasoline Blendstocks for Evaluation 5
Table 2. Percentage of Compounds Partitioning to Various Environmental Compartments 8
Table 3. Common Fate and Transport Indicators 10
Table 4. EPI Suite Output for Aerobic and Anaerobic Biodegradability 12
Table 5. Human Exposure and Toxicology Results 13
Table 6. Ecological Exposure Results 16

Abbreviations and Acronyms

µPa	micropascal
ACGIH	American Conference of Governmental Industrial Hygienists
BCF	bioconcentration factor
CAS	Chemical Abstracts Service
CFR	Code of Federal Regulations
Co-Optima	Co-Optimization of Fuels and Engines (initiative)
DIB	diisobutylene
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
EPI Suite™	Estimation Programs Interface Suite
g	gram
kg	kilogram
L	liter
LC_{50}	lethal concentration to 50% *Daphnia magna*
m	meter
MD	mobility descriptor
mg/L	milligrams per liter
mmHg	millimeters of mercury
MTBE	methyl tert-butyl ether
ng	nanogram
NOAEL	No Observed Adverse Effect Level
NRB	not readily biodegradable
P-65	California Proposition 65
ppb	parts per billion
psi	pounds per square inch
QSAR	quantitative structural activity relationships
RB	readily biodegradable
T.E.S.T.	Toxicity Estimation Software Tool
TSCA	Toxic Substances Control Act
vol%	percent by volume

Executive Summary

As the Co-Optima initiative continues to find success, and more potential bioblendstocks are identified that can be used in the domestic fuel supply, more detailed analyses are needed to support early data sets, allowing for fully informed decisions going forward. This project examined the biodegradability and toxicology of the tier three gasoline blendstocks, compared to several surrogate gasoline compounds. The potential bioblendstocks of interest were: ethanol; n-propanol; isopropanol; isobutanol; cyclopentanone; diisobutylene (DIB); and a mixture of 2-methyl furan and 2,5-dimethyl furan. For comparison, surrogate gasoline molecules were used including benzene; isooctane; toluene; and 1-hexene. As a worst-case scenario, the analysis also compared the bioblendstocks against methyl-t-butyl ether (MTBE).

The purpose of this study was to provide a framework suitable for decision makers going forward. The intended and use of this information is not as an absolute metric, but as guidance to consider in evaluating the potential for new bioblendstocks in the domestic fuel supply. There are several caveats worth noting that are critical for understanding the conclusions. Much of the available literature is based on chronic doses, when in fact, the potential for long-term subchronic exposure may be more likely. Additionally, the available literature on biodegradation and toxicity is sparse, as these chemicals have not been used in large quantities in this application, and a paucity of data exists. Mixture effects may also impact the conclusions, as this study looked at individual compounds in isolation, not as part of a more complex mixture where synergistic and antagonistic effects may be significant.

This study evaluated the impact of these compounds based on environmental transport and fate, environmental and human health toxicity, and environmental regulatory framework. The outcome of this work shows little compelling evidence to exclude any of the chemicals from continued research going forward. Some differences exist between the potential blendstocks, subject to the caveats discussed above.

A majority of the Co-Optima blendstocks will become either airborne or reside in the water in the event of a spill, with little potential to migrate between compartments (i.e. soil to water; water to air). Cyclopentanone, DIB, 2-methylfuran, and 2,5-dimethylfuran will predominantly go into the air compartment, while the alcohols will go into the water compartment.

Based on chronic doses and estimated toxicology, none of the potential blendstocks present significant toxicity to humans, though some developmental toxicity may exist. In particular, isobutanol, n-propanol, isopropanol, DIB, 2,5-dimethylfuran, 2-methylfuran, and benzene (gasoline surrogate) may have some developmental toxicity to humans. None of the blendstocks showed mutagenicity on the Ames test.

The high mobility of the bioblendstocks, coupled with aerobic and anaerobic biodegradability indicate that long-term environmental persistence is unlikely. An exception is DIB, which is slightly mobile and not readily biodegradable, indicating environmental persistence is more likely than the other bioblendstocks studied.

Given the limited data available on the use of these blendstocks as fuels, any future information will need to come from in-use determinations as these blendstocks rise to prominence in the fuel supply.

1. Background

In 2016, the U.S. Department of Energy (DOE) began a long-term collaborative effort across several national laboratories, universities, and industry partners to conduct research to co-optimize fuels and engines to achieve increased performance and carbon efficiency (U.S. DOE undated). The Co-Optimization of Fuels and Engines project, which aims to develop the fundamental scientific and technical foundation, is known as Co-Optima. Co-Optima has the broad goals to examine potential gains in both light- and heavy-duty vehicles, including spark-ignited, compression-ignited, and multi-mode combustion regimes.

The scope and breadth of this research effort require a well-thought out, step-by-step approach. Under Co-Optima, research platforms in the first two years focused mainly on potential improved efficiencies in light-duty engines. Advanced spark-ignited engines can be improved through technologies like higher compression ratio, turbocharging, engine downsizing, and operation at lower engine speeds (Stein et al. 2013; Anderson et al. 2014; Chow et al. 2014; Leone et al. 2014; Speth et al. 2014; Leone et al. 2015). For these engine modifications to be pursued more aggressively, fuels need to evolve to have a higher knock resistance than current market fuels.

A large potential pool of molecules might provide the necessary properties to enable these engine modifications. To identify the most promising, researchers conducted a three-tier screening. The first tier screening was applied to a database of over 400 potential molecules and utilized criteria to ensure minimum fitness for use. Molecules that were screened out did not meet minimum criteria for melting point, boiling point, hydrocarbon solubility, octane number, biodegradability and toxicity. Forty-one molecules met these properties. Tier 2 screening applied additional physical property measurements made on blends with conventional gasoline, along with state-of-technology and economic assessments. Seven molecules and a mixture of aromatic compounds (bioreformate) satisfied these criteria. Evaluation of the molecules in the third tier is nearing completion and included a detailed technoeconomic analysis, market assessment, and engine and emission system testing. Additional details of the screening have been published elsewhere (McCormick et al. 2017; Farrell et al. 2018)

During Tier 1, a gross assessment of toxicity and biodegradability was conducted, eliminating molecules that were Occupational Safety and Health Administration Category 1 or 2 for Acute Toxicity, Carcinogenicity, and/or Reproductive Toxicity (U.S. Department of Labor 2018). Biodegradability had to be as good as or better than methyl tert-butyl ether (MTBE) and have water solubility less than 10,000 milligrams per liter (mg/L). This study further examines the potential environmental impact of the eight molecules included in the third screening tier.

2. Introduction

The U.S. Environmental Protection Agency (EPA) has broad authority to conduct research, monitor environmental quality, and set standards and regulations to protect the environment (EPA 2018a). This authority covers myriad topics, including chemical toxicity, vehicle emissions, and drinking water.

EPA regulates chemicals produced and imported into the United States under the Toxic Substances Control Act (TSCA) of 1976. At the passage of TSCA, all chemicals imported or produced in the United States were grandfathered into the Act as "safe." This resulted in the listing of nearly 62,000 chemicals, with over 20,000 chemicals being added since that time. Under Section 4 of the Act, EPA has entered into either Enforceable Consent Agreements or promulgated regulations requiring additional toxicity data be gathered on 266 different chemicals (EPA 2017). In additional, EPA, along with Environmental Defense, the American Petroleum Institute, and the American Chemistry Council, have voluntarily launched the High Production Volume chemical program, which assesses the environmental effects of chemicals produced or imported at over 1 million pounds annually.

Gasoline accounted for 18% of the total U.S. energy consumption in 2018 (U.S. Energy Information Administration 2018a). Because gasoline is a complex chemical mixture, it is not directly listed in TSCA. However, the components used to produce gasoline are listed in TSCA (Swick et al. 2014). The pervasiveness of gasoline in the general population also equates to a higher potential risk from spills. The Pipeline and Hazardous Materials Safety Administration estimates nearly 2,500 refined petroleum product spills between 1998—2017 (this includes gasoline, diesel fuel, jet fuel and heating oil), costing over $1 billion (Pipeline and Hazardous Materials Safety Administration 2018). EPA confirmed releases from over 5,500 underground storage tanks in fiscal year 2018 (EPA 2018c). The potential impact of a spill of a novel blendstock in gasoline needs to be considered as gasoline formulations continue to evolve and expand.

Gasoline has changed significantly in recent decades and continues to have various formulations throughout the country. Additives have always been part of gasoline. In the 1920s, tetra-ethyl lead was used to enhance octane in gasoline. As the effects of lead on human health became more and more well known, lead in gasoline needed to be replaced with a different octane enhancer. Various chemicals, such as aromatics, can increase octane in gasoline, but MTBE was selected because it provided cost-effective octane as well as increasing oxygen content to reduce emissions.

However, the use of MTBE in gasoline also led to significant concerns about human health and contamination of groundwater. With five members of the MTBE Health Effects Testing Task Force[1] under the Oxygenated Fuels Association Inc., EPA entered into an Enforceable Consent

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[1] The five member companies were Amoco Corporation, ARCO Chemical Company, Exxon Chemical Company, Sun Refining and Marketing Company, and Texaco Chemical Company.

Agreement, which was published in the Federal Register March 31, 1988 (Federal Register 40 Code of Federal Regulations [CFR] 799 1988). The Enforceable Consent Agreement required additional toxicology testing of MTBE. Upon completion of the testing, EPA did not ban the use of MTBE in gasoline, although many states did (EPA undated). Results of the Enforceable Consent Agreement testing have been published (Bevan et al. 1997a; Bevan et al. 1997b; Bird et al. 1997; Daughtrey et al. 1997; Lington et al. 1997; McKee et al. 1990; Miller et al. 1997).

Due to the concerns about health effects, the statewide bans, and other confounding factors (the Renewable Fuel Standard, among others), MTBE has not been used in any significant quantity in the United States since 2005 (EPA Web Archive 2016). MTBE in gasoline was quickly replaced by ethanol. Currently, ethanol is found in nearly all gasoline in the United States as a low-level blend of 10 volume percent (vol%), commonly referred to as E10 (U.S. Energy Information Administration 2016).

One of the goals of Co-Optima is to blend novel blendstocks into E10 to enable advanced spark-ignited engines. The initiative's goal is to have up to 30% bioblendstock content in gasoline so these compounds may be blended at up to 20 vol% on top of the 10 vol% ethanol already in gasoline. Currently, the ethanol nameplate production capacity is 16 billion gallons in 2018 (U.S. Energy Information Administration 2018b). Assuming widespread adoption of these blendstocks, they could represent a significant volume in the gasoline market.

This study provides a further environmental impact assessment of Tier 3 gasoline blendstocks to supplement the simplified screening conducted in the first-tier assessment and presents a basic overview of the toxicology and biodegradability of the blendstocks in gasoline, considering the environmental impact from an accidental release to the environment. It is beyond the scope of this study to consider emissions impacts and health and welfare effects of new blendstocks in gasoline pursuant to 40 CFR Section 79.52(d).[2]

To provide additional context for the Co-Optima blendstock results, a comparison was made to other chemicals found or previously found in gasoline and several gasoline surrogate chemicals. These chemicals include MTBE, which may be considered as the worst-case scenario for future blendstocks in gasoline. Benzene, a well-known cancer-causing chemical, is also highly regulated and may be found in gasoline at no more than 0.62 vol% (EPA 2016b). Because gasoline is a highly complex mixture, many of the environmental databases and information sources do not contain sufficient information to make a reasonable comparison. Thus, toluene, 1-hexene, and isooctane are used as surrogates for gasoline. The Co-Optima blendstocks as well as the chemicals selected for comparison are listed in Table 1. Further details on the chemical properties of all the molecules considered are available in a publicly accessible database (National Renewable Energy Laboratory 2018).

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[2] New fuel additives (or blendstocks) require an in-depth literature review from 1982 to present, not only for the additives, but for any additional subject chemicals (emissions) not found during the baseline gasoline emission testing.

Table 1. Co-Optima Gasoline Blendstocks for Evaluation

Chemical	CAS #	Notes
Ethanol	64-17-5	Co-Optima blendstock
n-Propanol	71-23-8	Co-Optima blendstock
Isopropanol	67-63-0	Co-Optima blendstock
Isobutanol	71-36-3	Co-Optima blendstock
Cyclopentanone	120-92-3	Co-Optima blendstock
Diisobutylene (DIB)	25167-70-8 107-39-1	Co-Optima blendstock
Mixture of 2-methylfuran and 2,5-dimethylfuran	534-22-5 625-86-5	Co-Optima blendstock
Benzene	71-43-2	Baseline compound
MTBE	1634-04-4	Baseline compound
Isooctane	540-84-1	Gasoline surrogate
Toluene	108-88-3	Gasoline surrogate
1-Hexene	592-41-6	Gasoline surrogate

CAS: Chemical Abstracts System

For the purposes of this report, diisobutylene (DIB) is used colloquially to mean both isomers, 2,4,4-trimethyl-1-pentene (CAS 107-39-1) and 2,4,4-trimethyl-2-pentene (CAS 25167-70-8). The isomers are in a 3:1 ratio for other testing under Co-Optima (McCormick et al. 2017). For the purposes of this analysis, it is assumed that all references to DIB refer to this mixture.

3. Methods and Results

3.1. Overall Approach

The overall approach was to make relative comparisons among the Co-Optima blendstocks and gasoline surrogate and baseline compounds on common environmental impact metrics. The relative comparison is intended to help decision makers evaluate, on a relative basis, whether one blendstock had more or less environmental impact potential. This assessment included three broad categories. The approach to assessing these issues is discussed below.

- Environmental transport and fate: Is one blendstock more mobile or likely to pose a greater hazard than another?
- Environmental and human health toxicity: Is one blendstock more likely to pose a greater hazard than another?
- Environmental regulatory framework: Is one blendstock more likely to pose a greater regulatory burden than another?

3.2. Compartmental Partitioning Model

Developing an understanding of how a chemical will partition in an environmental system and where that chemical is likely to ultimately end up are important in assessing the impacts of its use. A common screening-level technique used in evaluating environmental mobility is compartmental partitioning modelling as illustrated in Figure 1.

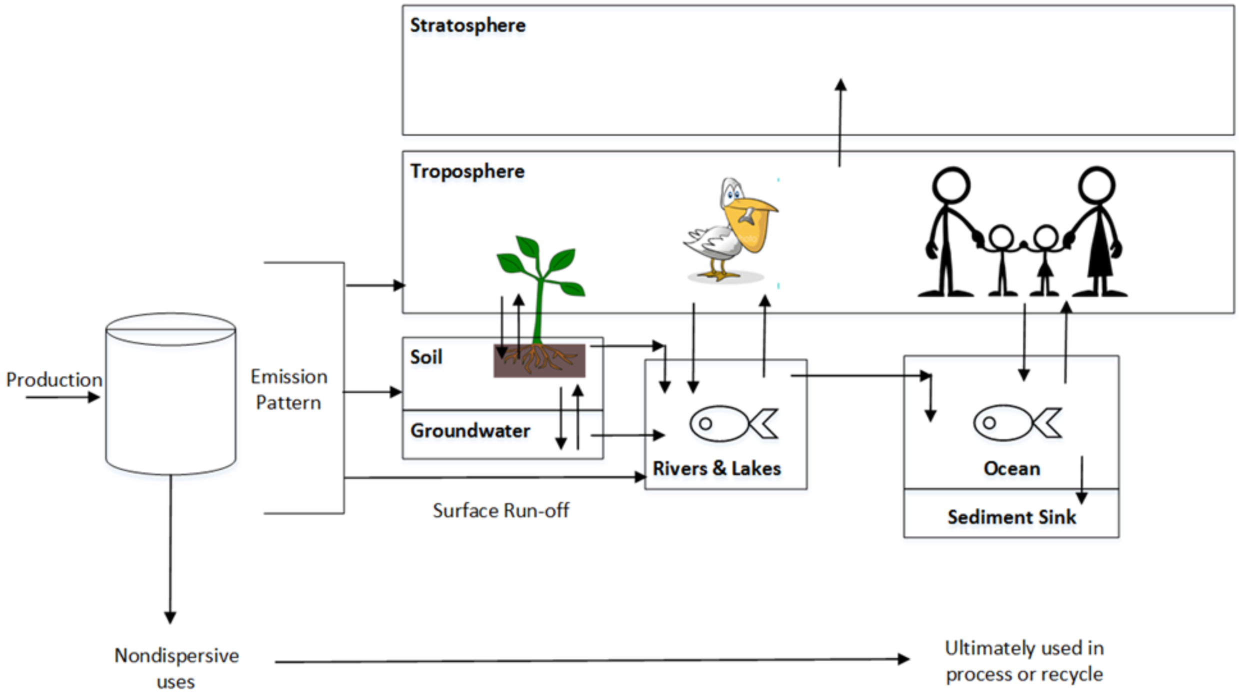

Figure 1. Illustration of compartmental partitioning model

Figure 1 illustrates how the environment can be segmented into compartments: stratosphere, troposphere, soil, groundwater, rivers/lakes, and the ocean, and how chemicals can move between the different compartments based on their inherent physical properties (e.g., vapor pressure, water solubility), and the intercompartmental fluid dynamics. This technique is highly useful in understanding how a chemical may migrate in the event of an accidental release to the environment. It should be noted that these estimates should be used only to gain an overall understanding of the transport phenomenon.

The compartment model used in this assessment is based on the work of Mackay (2001). Key features of the model include:

- The driving force is fugacity. Fugacity is a thermodynamic simplification describing the potential that a chemical will move between compartments and allows modeling the behavior of fluids within a mathematical framework using closed system, steady-state equations. This condition is termed a “Level I” model (Mackay 2001).
- Each compartment is homogeneous, i.e., there is no variability within a compartment (e.g., the atmosphere).
- Steady state is assumed, meaning all compartments are at equilibrium. The net movement of a chemical between compartments is zero.

These features are expressed in a software program, *Level I, Fugacity-Based Environmental Equilibrium Partitioning Model* (Trent University 2004). An example Level I equilibrium partitioning model result for ethanol is shown in Figure 2.

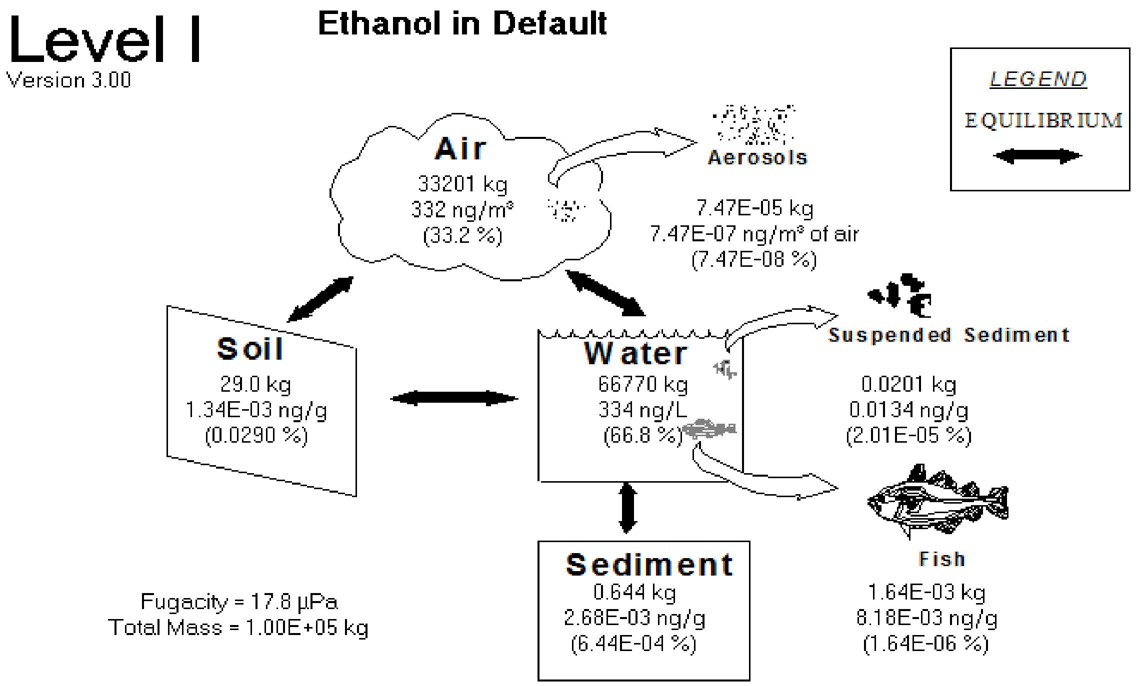

Figure 2. Illustration of compartmental partitioning model results for ethanol

Using the default compartment assumptions and fundamental ethanol chemical properties (e.g., vapor pressure, water solubility), Figure 2 illustrates that:

- 66.8% of a hypothetical ethanol release will partition to the water compartment (e.g., lakes, rivers, ocean)
- 33.2% of the ethanol will partition to the air compartment (mainly the troposphere, which extends approximately 11 miles above ground surface in the mid-latitudes, where most of the earth's weather takes place).

This indicates that, at steady-state conditions, virtually all ethanol would tend to partition to the water column and/or air compartment. Significantly smaller fractions would tend to partition to the soil, sediment, and fish phases. A similar assessment has been completed for all these chemicals. Illustrations of partitioning for the Co-Optima gasoline blendstocks similar to Figure 2 are presented in Appendix A.

Table 2 summarizes the relative percentage of each compound that would partition into the various compartments. Totals may not add up to 100% due to rounding within the program. Data for aerosols and fish are not included in Table 2, as none of the compounds would partition beyond trace levels. A hypothetical release of the alcohols would find much of the compounds going into water, while all the other compounds would have more significant partitioning into the atmosphere.

Table 2. Percentage of Compounds Partitioning to Various Environmental Compartments

Compound	Air, %	Soil, %	Water, %	Sediment, %	Suspended Sediment, %
Ethanol	33.2	0.0290	66.8	Trace	Trace
n-Propanol	2.36	0.154	97.5	Trace	Trace
Isopropanol	6.83	0.0925	93.1	0.00206	Trace
Isobutanol	19.5	0.408	80.1	0.00907	Trace
Cyclopentanone	73.7	0.0404	26.2	Trace	Trace
DIB	99.7	0.263	0.00838	0.00585	Trace
2-Methylfuran	97.6	0.141	2.25	0.00313	Trace
2,5-Dimethylfuran	66.5	4.46	29.0	0.0991	0.00310
Benzene	99.0	0.105	0.881	0.00234	Trace
MTBE	95.6	0.0439	4.32	Trace	Trace
Isooctane	100.0	0.0340	0.00613	Trace	Trace
Toluene	98.6	0.452	0.951	0.0101	Trace
1-Hexene	100.0	0.0261	0.0120	Trace	Trace

3.3. Fate and Transport Indicators

As indicated above, individual chemical fate and transport are dictated, in part, by the physical and chemical properties, an important first metric to understanding the potential environmental impact of chemicals, especially those identified under Co-Optima that either already have or are expected to have a significant share in gasoline composition going forward. The metrics described in Table 3 include the vapor pressure, which tells how volatile a chemical is and how likely it may be to volatilize into the atmosphere. The soil/sediment-to-water partition coefficient is an indicator of how likely a compound is to adhere to the organic matter in soil, meaning the chemical will persist in soil and may have impacts on terrestrial organisms. A higher number indicates a greater likelihood the chemical will remain in the soil. A lower partition coefficient coupled with a higher water solubility indicates a chemical will migrate from soil into water sources. This analysis is a next step after the compartmental partitioning model, which assumes no migration between compartments.

The relative mobility descriptor (MD) (Ford and Gurba 1984) is a good summary indicator of the propensity for a chemical to migrate in the environment and achieve the partitioning profiles shown in Table 2. The MD is estimated as:

$$MD = log\,\frac{Water\ Solubility * Vapor\ Pressure}{Soil\ Sediment\ Partition}$$

Ford and Gurba (1984) provide a categorical “relative” MD ranging from extremely mobile to very immobile. As indicated in Table 3, all of the Co-Optima blendstock chemicals, with the exception of DIB, are expected to be readily mobile in the environment. The Co-Optima blendstocks have similar mobility to both the baseline compounds and the gasoline surrogates, with the exception of iso-octane, which has limited mobility in the environment, meaning that traditional procedures to handle an accidental environmental release are likely valid as these Co-Optima blendstocks begin to penetrate the market.

Table 3. Common Fate and Transport Indicators

Chemical	Ambient Vapor Pressure, mmHg (psi)	Water Solubility, g/L	Soil/Sediment to Water Partition Coefficient	Relative MD	Predicted Biodegradability[a] (U.S. National Library of Medicine)
Ethanol	44 (0.851)	1,000,000	2.19	Extremely mobile	Rapid
n-Propanol	15 (0.290)	1,000,000	2.19	Extremely mobile	Readily
Isopropanol	45.4 (0.878)	1,000,000	2.19	Extremely mobile	Readily
Isobutanol	10.4 (0.201)	85,000	8.49	Very mobile	Readily; no data on anaerobic biodegradation
Cyclopentanone	11.4 (0.220)	9,175[b]	289	Very mobile	Rapidly with accumulation; no data on anaerobic biodegradation
DIB	44.7 (0.864)	11.3	1,150	Slightly mobile	Slowly; no data on anaerobic biodegradation
2,5-Dimethylfuran	53 (1.025)	<1	10.3	Very mobile	No data
2-Methylfuran	59 (1.171)	3,000	53.4	Very mobile	No data
Benzene	94.8 (1.833)	1,790	70.9	Very mobile	Aerobically biodegradable; recalcitrant to anaerobic degradation
MTBE	250 (4.834)	50,000	16.0	Extremely mobile	Very slow to no biodegradation under aerobic and anaerobic conditions, though system conditions may play a significant role
Isooctane	44.6 (0.862)	2.23	2,810	Slightly mobile	Slowly, though little data
Toluene	22 (0.425)	526	117	Very mobile	Readily
1-Hexene	184 (3.558)	50	176	Very mobile	Readily

[a] U.S. National Library of Medicine
[b] Source of data: Lyman (1982).

One of the metrics applied in the first screening tier for removal of a blendstock was anaerobic biodegradation rate worse than MTBE *and* water solubility greater than 10,000 mg/L (McCormick et al. 2017). MTBE is included in Table 3 as a comparison to the worst-case scenario, and has significant water solubility, even higher than the metric applied in the first tier of screening. The anaerobic degradation of MTBE has been shown to be very slow to nearly non-existent (Suflita and Mormile 1993; Mormile et al. 1993); hence, any compound with some biodegradability would show an improvement compared to MTBE.

Of the Co-Optima compounds, the alcohols have significant water solubility but are also readily biodegradable, potentially minimizing their enduring environmental impact. The compounds 2,5-dimethylfuran and 2-methylfuran have significantly less water solubility, but no biodegradability data are available.

Of the compounds in this list, DIB stands out compared to the other Co-Optima spark-ignited molecules due to very slow biodegradation, although water solubility is also quite low, and it is not very mobile in the environment (results are similar for isooctane, a gasoline surrogate). The vapor pressure of DIB likely means little environmental persistence in water or soil as volatilization to the atmosphere will be more significant. DIB also has the highest partition coefficient, meaning once the compound is in the soil, it will likely remain in the soil and not migrate into ground water.

A single environmental transport metric is not sufficient to fully describe the impact of these compounds on the environment. The combination of these metrics helps build a more complete picture of the impact of these compounds. The fate of these chemicals, once released into the environment, is highly complex. Testimony by Kinner (2001) on the fate of MTBE discussed how complex these analyses can be. It should be noted that Kinner's testimony considered unburned MTBE in vehicle exhaust, although there is no reason the same chemical transport and fate would not occur when MTBE was accidentally released into the environment. For example, Table 2 shows less than 3% of MTBE will be partitioned into the atmosphere. This information, coupled with the high water solubility illustrated in Table 3, leads to some insightful conclusions. Thus, even though little MTBE will volatilize into the air, once it is there, MTBE will quickly migrate into any precipitation, quickly bringing the chemical back into the water column. Similar concerns with the other chemicals in this study are not as significant. The alcohols are highly water soluble and have low migration into the air column. The chemicals that will end up in the atmosphere are not highly water soluble. The atmospheric fate of these chemicals, such as through hydrolysis, will need to be examined in further studies.

3.4. EPI Suite™ Screening

A first pass assessment on potential blendstocks was completed using The Estimation Programs Interface Suite™ (EPI Suite) developed by EPA and Syracuse Research Corporation. The program is publicly available (EPA 2016a). EPI Suite includes several estimators of physical and chemical properties and environmental fate. Of particular use to this project is the estimation of aerobic and anaerobic biodegradability using BIOWIN™. BIOWIN includes six different models estimating aerobic biodegradability and one model estimating anaerobic biodegradability. For this project, the aerobic biodegradability was simply "readily biodegradable (RB)" or "not readily biodegradable (NRB)" from the Bayesian battery approach output of EPI Suite.

Anaerobic biodegradability was estimated using BIOWIN7, which outputs a numerical probability of biodegradability, with values greater than 0.5 being biodegradable and values less than 0.5 being not readily biodegradable (due to the linear fragment contribution model, results may produce negative values). Additional details of the BIOWIN7 model and linear fragment contribution model are available from Meylan et al. (2007).

Table 4 summarizes the predicted results for the Co-Optima blendstock compounds and the gasoline surrogate and baseline molecules. The initial screening metric for Co-Optima blendstocks was less water soluble than 10,000 mg/L *and* at least as anaerobically biodegradable as MTBE. For a compound to be excluded, both these criteria had to be met. The water solubility was not measured in all cases and may have been predicted from EPI Suite.

Of the Co-Optima compounds in Table 4, DIB, 2-methylfuran, and 2,5-dimethylfuran are not readily anaerobically biodegradable, but also have a water solubility below the 10,000 mg/L threshold. Similar results were found for benzene, isooctane, toluene, and 1-hexene, all of which are found, at some levels in conventional gasoline. Limited water solubility means that in the event of an accidental release to the environment, these compounds will not migrate from soil into water sources. Based on this analysis, cyclopentanone is not readily anaerobically biodegradable and has water solubility above the 10,000 mg/L threshold, more similar to MTBE than any other baseline compound or gasoline surrogate on this list. Thus, cyclopentanone may present more environmental concern, and the wealth of historical data on MTBE supports this hypothesis.

Table 4. EPI Suite Output for Aerobic and Anaerobic Biodegradability

Compound	Bayesian Battery Approach Result for Aerobic Biodegradability	BIOWIN7 Result for Anaerobic Biodegradability	Water Solubility, mg/L[a]
Ethanol	RB	0.9153	1,000,000 (M)
n-Propanol	RB	0.9413	1,000,000 (M)
Isopropanol	RB	0.6439	1,000,000 (M)
Isobutanol	RB	0.6698	85,000 (M)
Cyclopentanone	RB	-0.0359	60,810 (P)
DIB	NRB	0.0625	4 (P)
2-Methylfuran	RB	0.1780	3,410 (P)
2,5-Dimethylfuran	RB	-0.0983	1,466 (P)
Benzene	NRB	0.000	1,790 (M)
MTBE	RB	-0.0737	51,000 (M)
Isooctane	NRB	-0.0539	2 (M)
Toluene	RB	0.2053	526 (M)
1-Hexene	RB	0.2962	50 (M)

[a] National Renewable Energy Laboratory (2018)
(M) indicates the value was experimentally measured, and (P) indicates the value is an estimate.

An advantage of the estimated results provided by EPI Suite is the ability to provide model-based information to decision makers. Both of the furan compounds lacked data on their biodegradability. Using the output from EPI Suite, the model-based data can supplement the measured data.

A quick comparison between the water solubility in Tables 3 and 4 also reveals some interesting differences. For example, the EPI Suite prediction (Table 4) for cyclopentanone is over 6 times greater than the predicted result in Table 3. This illustrates the variability and relative comparisons between metrics for this study. Knowledgeable interpretation of the data presented is critical to ensure a sound basis is developed for decision makers.

3.5. Human Exposure and Toxicology

Another key metric is the potential for adverse human health impacts. Table 5 lists common human health indicators: acute human toxicity, developmental toxicity, Ames mutagenicity, and occupational health risk index. These metrics, gathered from common public domain sources, provide information that, along with fate and transport, help form a lines-of-evidence perspective. Table 5 summarizes the assessment of adverse health impacts to humans.

Table 5. Human Exposure and Toxicology Results

Chemical	Human Acute Toxicity Category[a]	Human Chronic Toxicity Category[b]	Developmental[c]	Ames Mutagenicity Assay[c]	Occupational Risk Index, 1 (high) to 5 (low)[d]
Ethanol	Practically non-toxic	Practically non-toxic	Non-toxicant	Negative	5
n-Propanol	Slightly toxic	Practically non-toxic	Toxicant	Negative	5
Isopropanol	Practically non-toxic	Practically non-toxic	Toxicant	Negative	4
Isobutanol	Slightly toxic	Practically non-toxic	Toxicant	Negative	4
Cyclopentanone	Slightly toxic	Slightly toxic	Toxicant	Negative	No data
DIB	Practically non-toxic	Slightly toxic	Toxicant	Negative	No data
2,5-Dimethylfuran	Moderately toxic	Slightly toxic	Toxicant	Negative	No data
2-Methylfuran	Moderately toxic	Slightly toxic	Toxicant	Negative	No data
Benzene	Slightly toxic	Slight toxic – recognized carcinogen[e]	Toxicant	Negative	2
MTBE	Slightly toxic	Practically non-toxic	Non-toxicant	Negative	No data
Isooctane	Practically non-toxic	Practically non-toxic	Non-toxicant	Negative	5
Toluene	Slightly toxic	Practically non-toxic	Toxicant	Negative	4
1-Hexene	Practically non-toxic	Practically non-toxic	Non-toxicant	Negative	No data

[a] Based on categorization used in the EPA pesticide registration program. Acute toxicity data from the public domain (median lethal dose or LD_{50}) were compared to the EPA's categorization scheme in 40 CFR 152.62 (EPA 2018b).

[b] Categorization based on chronic study No Observed Adverse Effect Levels (NOAELs), which are measures of chronic exposure toxicity. NOAELs were categorized with the scheme proposed by Ruishalme (2018).

[c] Based on structural activity relationships developed using EPA's Toxicity Estimation Software Tool (T.E.S.T) (EPA 2016c). These are derived from quantitative structure–activity relationship models (QSARs), which are predictors of biological activity based on physico-chemical properties or theoretical molecular descriptors of chemicals. These results should be used as indicators and not necessarily as predicators of biological activity. The database from which these results were extrapolated is nearly all animal or microbial systems, and the administered dosages may not be reflective of the exposure humans would likely receive.

[d] Categorization based on ranking American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (2018).

[e] Benzene is recognized as a human carcinogen (EPA 2002). Note there is generally a distinction between chronic toxicity as evaluated by NOAELs (note b) and carcinogenicity.

Note: These metrics represent a partial compendium of human exposure and toxicology indicators. They are intended as indicative and not definitive gauges of the potential risks associated with the candidate blendstock chemicals.

Inspection of Table 5 indicates:

- **Acute Toxicity** – Overall, none of the Co-Optima blendstocks exhibits particularly notable acute human toxicity. The two furans (2,5-dimethyl and 2-methyl) are categorized as moderately toxic.
- **Chronic Toxicity** – Overall, none of the Co-Optima blendstocks exhibits notable chronic human toxicity. Benzene, one of two baseline compounds, while categorized as slightly toxic in the No Observed Adverse Effect Levels (NOAELs) scheme, is considered carcinogenic.
- **Developmental Toxicity** – Of the Co-Optima blendstocks, only ethanol was categorized as a nontoxicant. The other Co-Optima blendstocks exhibited evidence of developmental toxicity (defined as whether or not a chemical causes developmental toxicity effects in humans and animals). Of the baseline compounds and gasoline surrogate compounds, only benzene and toluene were categorized as developmental toxicants. Note that these binary results were generated from structural activity relationship modeling and are more indicative than deterministic.
- **Mutagenicity** – None of the blendstocks exhibit Ames positive mutagenicity based on the quantitative structure–activity relationship model (QSAR) results.
- **Occupational Exposure Risk** – None of the blendstocks for which ACGIH threshold limit values were available exhibits particularly significant risk with the exception of benzene. All of the Co-Optima blendstock chemicals, baseline compounds, and gasoline surrogates, including benzene, are safely used in the workplace using conventional control technologies.

Notwithstanding the potential carcinogenic properties associated with benzene and potential development characteristics, none of the Co-Optima blendstocks or gasoline surrogates stands out as posing a significant risk to human health. It should be noted that the assumption is based on extrapolated results from animals and/or microbial systems and any impact to human health is a best, and conservative, estimate.

For perspective, it should be noted that benzene is commonly found in urban air (0.8 to 5.3 parts per billion [ppb] in San Francisco, California) as well as some rural settings (0.02 to 0.85 ppb northwest of Denver, Colorado) (U.S. Department of Health and Human Services 2007). The Department of Health and Human Services has set a minimum risk level concentration of 3 ppb for long-term chronic inhalation exposure to benzene (2007). Interpretation of the QSAR-based developmental determination requires caution. Many chemicals exhibit mutagenic characteristics —common examples that are regularly consumed include vanillin and caffeine.

California Proposition 65 (P-65) requires businesses to notify the public if potential exposure exists to certain chemicals that cause cancer, birth defects, or reproductive harm (California Office of Environmental Health Hazard Assessment 2018). While gasoline exhaust as a mixture is listed, gasoline is not. None of the Co-Optima blendstocks is listed in P-65. Of the baseline chemicals and gasoline surrogates in this study, only benzene and toluene are listed by P-65. The

P-65 list is dynamic and is reviewed annually; new chemicals may be added or subtracted (delisted) over time.

3.6. Ecological Exposure

The potential for adverse impacts to ecological receptors is also an important consideration when evaluating the consequences of selecting a blendstock chemical. Table 6 lists some common indicators of potential ecological impact, including acute freshwater toxicity, bioconcentration, persistence and bioaccumulation tendency, and freshwater receptor chronic toxicity. These metrics were gathered from common public domain sources and are intended to provide additional insight into the environmental impact of these compounds.

The acute freshwater aquatic toxicity reveals notable ecological toxicity risk for DIB, the only Co-Optima blendstock with a significant effect. Similarly, isooctane also has a notable ecological toxicity risk. The categorization scheme is relative between chemicals and is not necessarily indicative of absolute toxicity risk and hazard. As with previous metrics, DIB exhibits different behavior than the other proposed Co-Optima blendstocks, showing notable ecological toxicity risk, even compared to other gasoline surrogate blendstock chemicals such as toluene and 1-hexene.

The potential to bioaccumulate measures the likelihood that a chemical will be consumed through the food chain and concentrate in tissues of higher animals. None of the chemicals analyzed in this study exhibit particularly notable bioconcentration factors (BCFs). It is noted that these are aquatic BCFs and most of the blendstock chemicals are relatively water soluble. Generally, bioconcentration is inversely related to water solubility. DIB and isooctane exhibit a medium potential for long persistence and bioaccumulation.

There is little information on chronic freshwater aquatic toxicity of the blendstock chemicals. Information used by EPA to initially screen concentrations indexed to their potential chronic (long-term) adverse impacts on freshwater biota were found for four of the chemicals studied. Information was only available for ethanol and isopropanol on the Co-Optima blendstocks and only for benzene and MTBE for the baseline compounds. As indicated, the range is great (over three orders of magnitude) and not intuitive. As the analysis shows, the chronic screening value for MTBE is ten times that for ethanol, which is three times as high as benzene.

Table 6. Ecological Exposure Results

Chemical	Ecological Acute Risk Index *Daphnia magna* [a], 1 (High) to 5 (Low)	Bioconcentration Factor (BCF) [b]	Persistence and Potential to Bioaccumulative Category [c]	EPA Freshwater Chronic Screening Values [d], mg/L
Ethanol	5	1.28	Low	1.4
N-Propanol	4	2.5	Low	-
Isopropanol	4	1.28	Low	0.0075
Isobutanol	4	2.2	Low	-
Cyclopentanone	2	2.5	Low	-
DIB	1	311.27	Medium	-
2,5-Dimethylfuran	2	7.75	Low	-
2-Methylfuran	3	6.39	Low	-
Benzene	3	30.78	Low	0.37
MTBE	3	3.49	Low	11.07
Isooctane	1	761.89	Medium	-
Toluene	2	48.88	Low	0.002
1-Hexene	2	93.55	Low	-

[a] *Daphnia magna* lethal concentration$_{50}$ (LC_{50}) represents that concentration in water that kills half of the *D. magna* (a water flea) in 48 hours. It is a common ecological screening test. The risk index is an order of magnitude categorization test whose results are generated by T.E.S.T (EPA 2016c) to compare the chemicals. For perspective, the LC_{50} for dichlorodiphenyltrichloroethane (DDT) for *D. magna* is two orders of magnitude lower (more toxic) than for DIB, 1,3,5-trimethyl benzene, and isooctane and seven orders of magnitude lower than ethanol.

[b] The bioconcentration factor (BCF) is the ratio of the concentration of a chemical in biotic tissue to the concentration in an exposure medium: $BCF = C_{biota}/C_{water}$. There are numerous sources of BCFs in the public domain. These were derived with T.E.S.T. (EPA 2016c) for consistency.

[c] Categorization comes from EPA (2018d). For context, DDT has a reported BCF of 4,026.08 and would be categorized as having a “high” potential to bioaccumulate.

[d] Select freshwater concentration screening criteria used by EPA Region 3 to evaluate the long-term risks posed by chemicals. Note: “—” indicates no screening value (Oak Ridge National Laboratory 2019).

Note: These metrics represent a partial compendium of ecological exposure and impact indicators. They are focused more on the water column than other compartments. As with human health metrics provided in Table 5, they are intended as indicative and not definitive gauges of the potential risks associated with the candidate blendstock chemicals.

4. Discussion

The information provided here should be used as a framework, not an absolute answer to the question of the environmental impacts of the novel Co-Optima blendstocks. The fields of toxicology and biodegradability depend heavily on perspective and context. As an example, the use of *Daphnia magna* as an indicator of ecological risk is common due to its ease of growth, use, and reproduction. However, *D. magna* are also large enough to be a source of food for fish and only naturally occur in bodies of water without these predators. Thus, there has been speculation in the literature about the utility of this species as a representative of ecological toxicity (Koivisto 1995). However, for the time being, this indicator remains useful, simply due to the wealth of data previously collected.

Many of the indicators presented here are also based on chronic doses, when in reality, accidental environmental releases may not be as immediately fatal to aquatic life. Norberg and Mount (1985) show that a subchronic toxicity test provides a reasonable estimate of chronic toxicity. The BCFs also provide a good indication of how subchronic doses can accumulate in aquatic life and migrate through the food chain into higher life forms.

There is significant uncertainly in all but the physical data (e.g., vapor pressures) used in this assessment. In general, there is a paucity of relevant biological/toxicological effects information for many of the blendstocks, surrogates, and baseline chemicals. This is due in part to the circumstance that the environmental toxicology fields, both human health and ecological, are driven by the environmental regulatory arena. Most of the chemicals studied have not been produced in sufficient commercial quantity and subjected to environmental regulations to demand the efforts associated with developing detailed toxicological data to support regulatory policy actions. Much of the regulatory work and requirements are in the area of engine exhaust emissions from combustion of these chemicals in fuels. In addition, the information available on the biological and toxicological effects is largely based on laboratory research studies that may not be fully applicable to real-world exposure situations.

Furthermore, the blendstock chemicals are evaluated as pure constituents when in fact they will be part of a complex mixture. Additive, synergistic, and/or antagonistic effects of the mixture were not considered or addressed. For example, the fact that blendstocks are all hydrocarbons and they will be dissolved in a hydrocarbon fuel mixture will notably affect the effective solubility and vapor pressure and the fate and transport processes associated with those properties. This “effects of the mixture” impacts the biological/toxicological effects, as well where the human or ecological receptor response to exposure to mixture is not known.

Notwithstanding these limitations, the information provided herein is suitable for coarse-scale comparison among chemicals. It is not suitable for predicting human health or ecological receptor impacts.

5. Conclusions

A relative comparison among Co-Optima blendstocks was conducted to evaluate common environmental impact metrics. The intent of this project was not to provide an in-depth environmental evaluation of each blendstock, but to help inform decision makers on potential impacts of these chemicals. Many of these blendstocks have not been produced in sufficient quantities nor used in this manner (as spark-ignited fuels) to allow for detailed environmental and toxicological data to be generated and collected. The overview and assessment provided here are based on three key metrics: environmental transport and fate, environmental and human health toxicity, and environmental regulatory framework.

The results of this work show that all the Co-Optima chemicals evaluated will ultimately end up in the air compartment (cyclopentanone, DIB, 2-methylfuran, 2,5-dimethylfuran) or the water column (ethanol, n-propanol, isopropanol, isobutanol). Typical gasoline compounds, such as benzene, isooctane, and toluene, also end up predominantly in the air compartment, unlike MTBE, which ends up almost completely in the water column; thus, the potential Co-Optima blendstocks do not present an unknown risk using this metric.

None of the Co-Optima blendstocks is particularly toxic to humans, although some pose higher risk than others. Based on structural activity relationships, the following compounds are projected to exhibit some degree of developmental toxicity based on the QSAR and limited animal and/or microbe studies: isobutanol, n-propanol, isopropanol, DIB, 2,5-dimethylfuran, 2-methylfuran, and benzene. None of the blendstocks showed mutagenicity on the Ames test, a common surrogate for carcinogenicity and mutagenicity.

Another key component of the environmental fate of these chemicals is their water solubility and biodegradability. The high mobility of many of these compounds, coupled with both aerobic and anaerobic ready biodegradability, indicates that long-term environmental persistence is not a significant concern. However, it is worth noting that DIB is slightly mobile and not readily biodegradable, meaning the compound would persist in soil and not migrate into the water column.

None of the blendstock chemicals is particularly hazardous from an ecological exposure perspective; however, like the human health hazards, some pose greater risks than others. While DIB and isooctane exhibit notable ecological toxicity risk, this is not necessarily indicative of absolute toxicity risk and hazard.

None of the blendstocks exhibits a particularly notable BCF. DIB and isooctane exhibit a medium potential for long persistence and bioaccumulation. There is limited freshwater chronic toxicity information for the blendstock chemicals. Given the paucity and scatter in these data, caution is appropriate in their allocation.

Overall, based on this assessment, there does not appear to be compelling evidence to eliminate any of the blendstock chemicals from consideration. Using these metrics, DIB stands apart from the other chemicals identified, and potentially additional research should be given to the environmental impact of this chemical when used in higher concentrations in gasoline. Given the lack of available data, much of this information may come from in-use determinations with good engineering judgment to minimize potential risks.

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Appendix A: Environmental Partitioning Illustrations

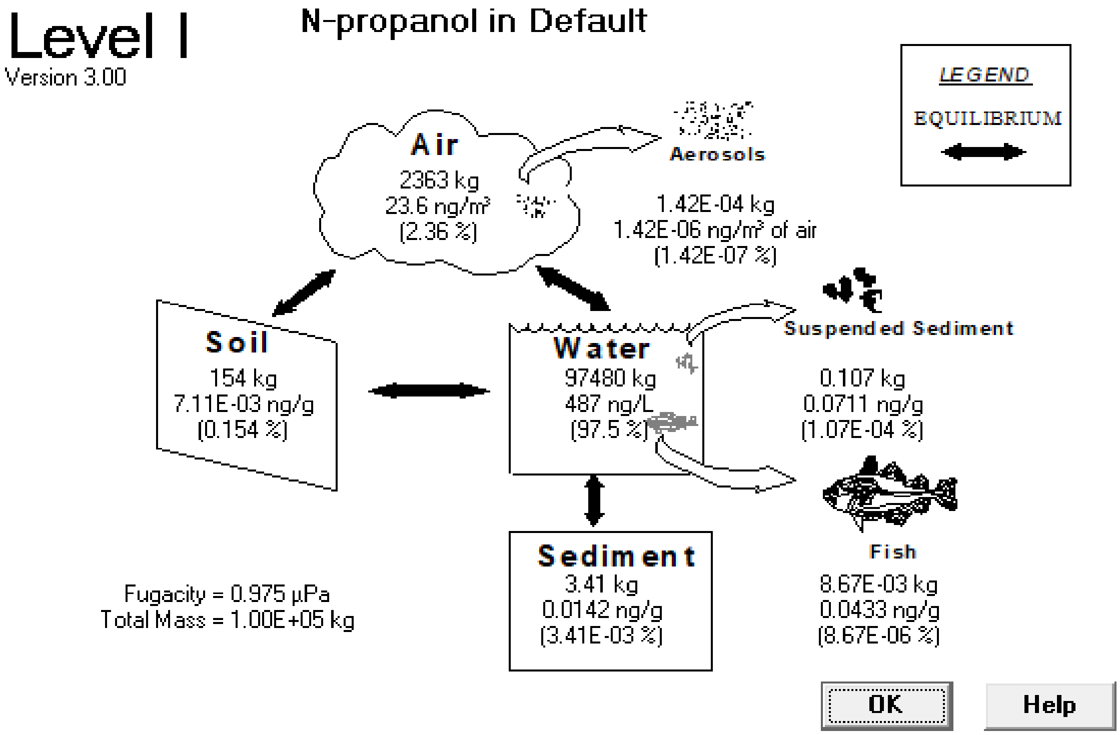


Figure A-1. Environmental partitioning illustration of n-propanol

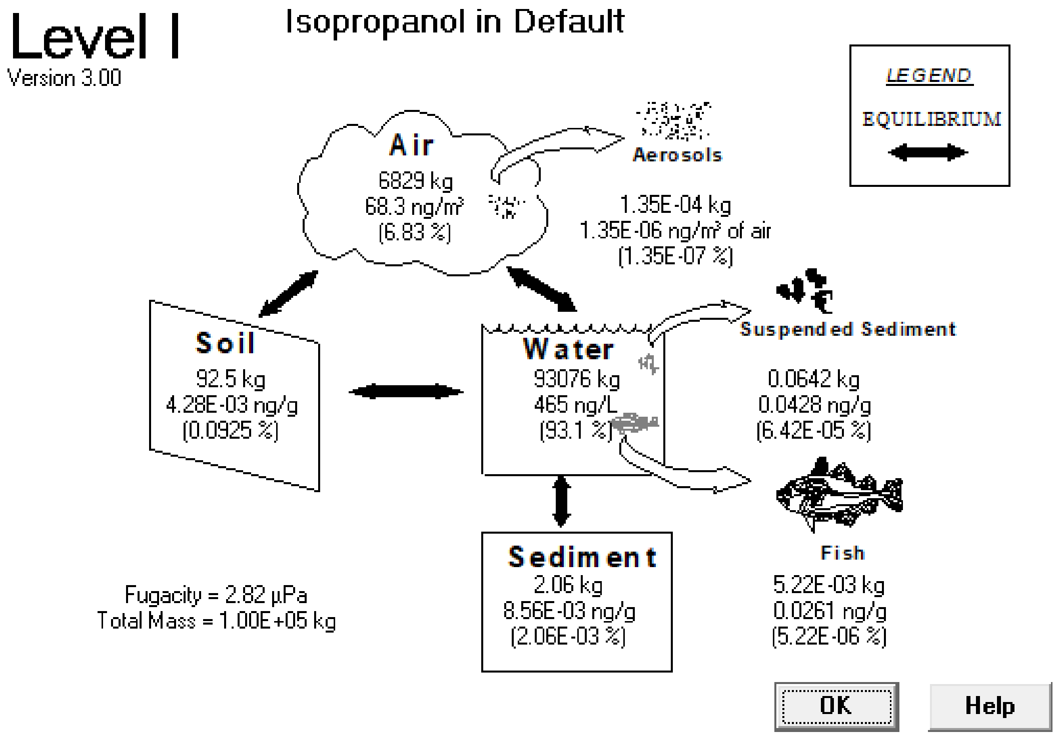


Figure A-2. Environmental partitioning illustration of isopropanol

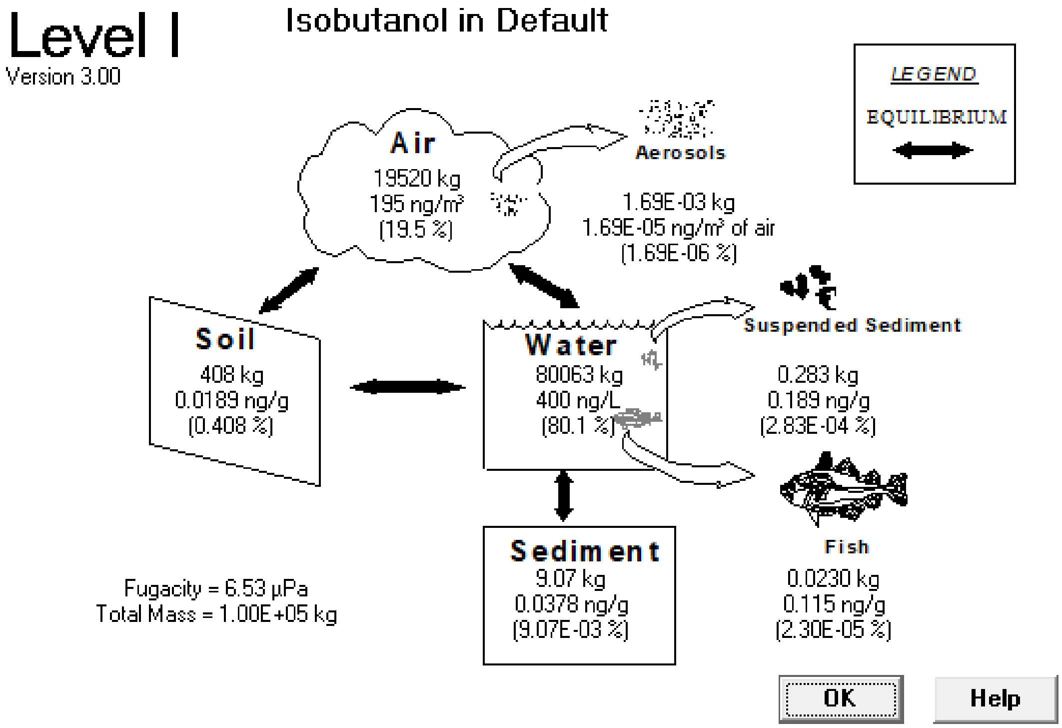


Figure A-3. Environmental partitioning illustration of isobutanol

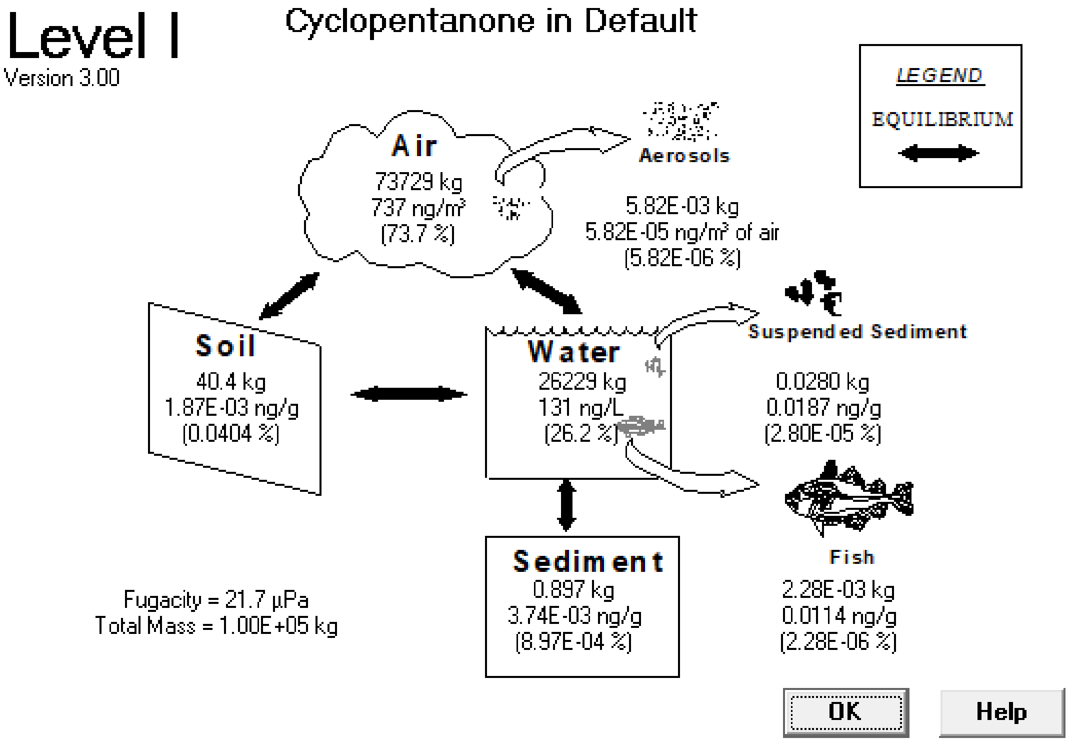


Figure A-4. Environmental partitioning illustration of cyclopentanone

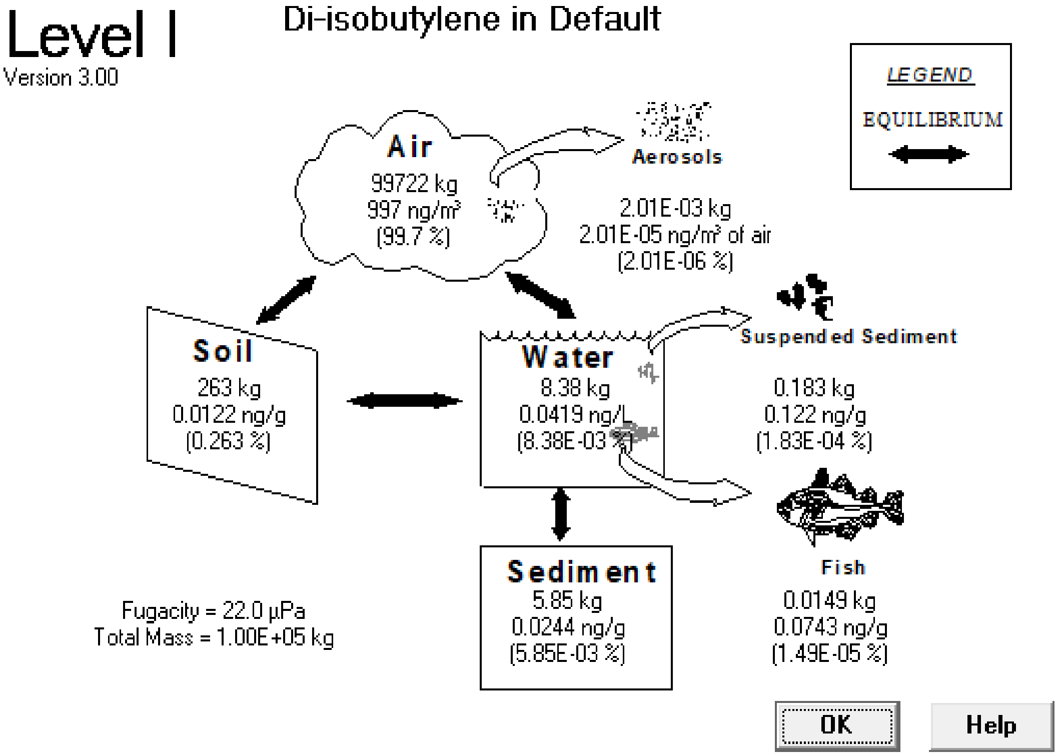
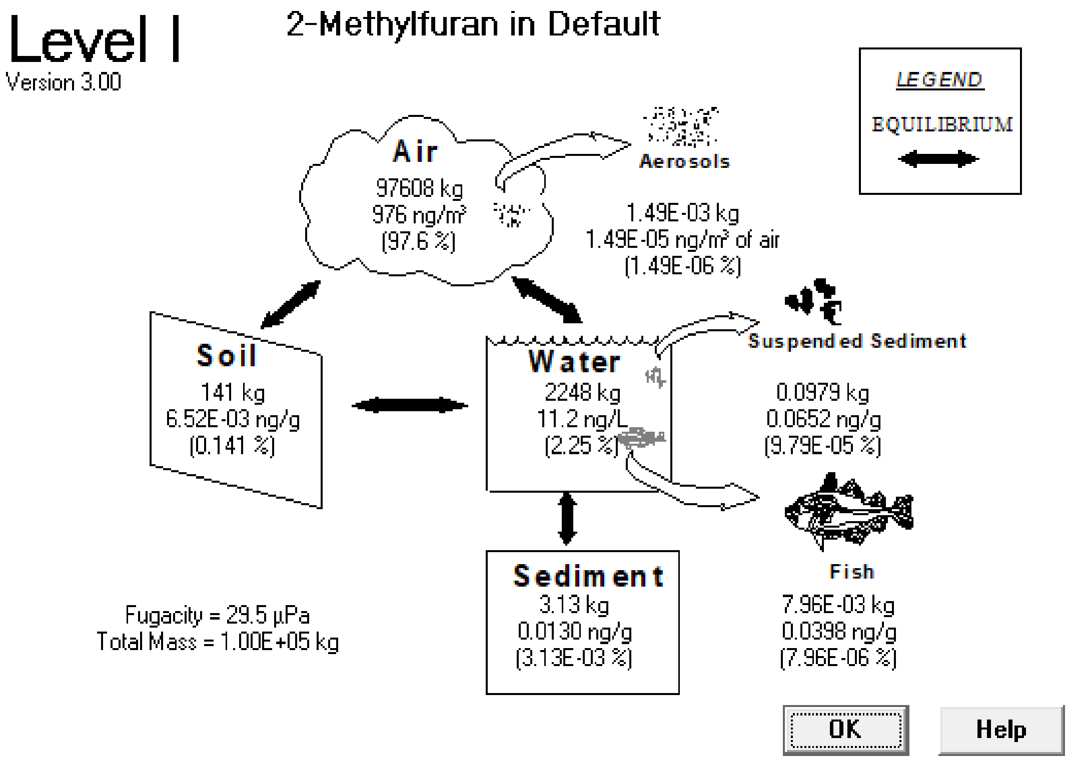


Figure A-5. Environmental partitioning illustration of DIB



Level I
Version 3.00

2-Methylfuran in Default

Air
97608 kg
976 ng/m³
(97.6 %)

Aerosols
1.49E-03 kg
1.49E-05 ng/m³ of air
(1.49E-06 %)

Soil
141 kg
6.52E-03 ng/g
(0.141 %)

Water
2248 kg
11.2 ng/L
(2.25 %)

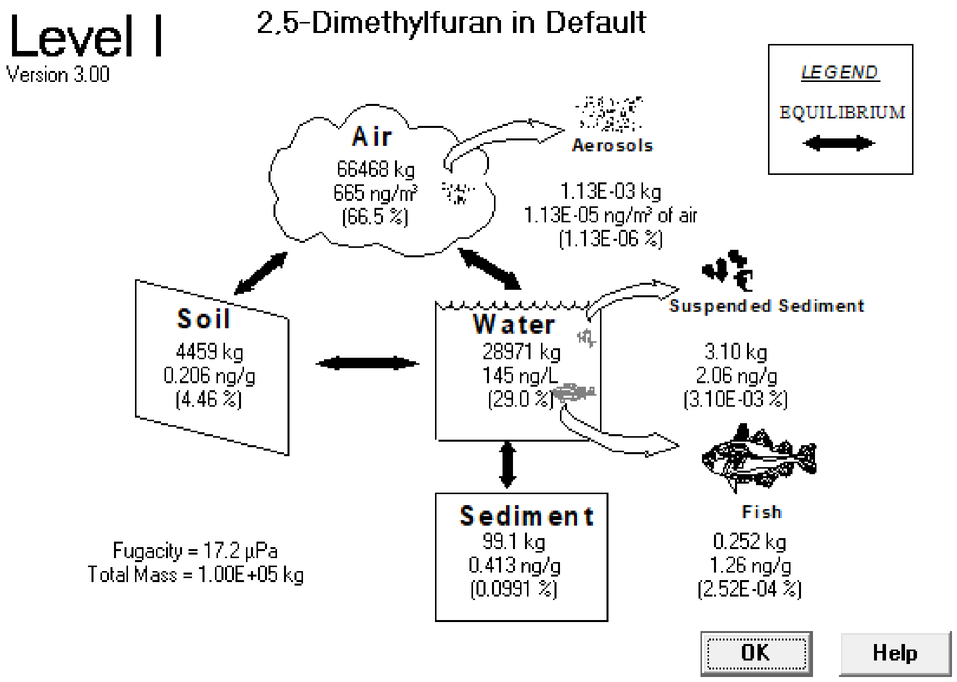
Suspended Sediment
0.0979 kg
0.0652 ng/g
(9.79E-05 %)

Sediment
3.13 kg
0.0130 ng/g
(3.13E-03 %)

Fish
7.96E-03 kg
0.0398 ng/g
(7.96E-06 %)

Fugacity = 29.5 µPa
Total Mass = 1.00E+05 kg

Figure A-6. Environmental partitioning illustration of 2-methylfuran



Level I
Version 3.00

2,5-Dimethylfuran in Default

Air
66468 kg
665 ng/m³
(66.5 %)

Aerosols
1.13E-03 kg
1.13E-05 ng/m³ of air
(1.13E-06 %)

Soil
4459 kg
0.206 ng/g
(4.46 %)

Water
28971 kg
145 ng/L
(29.0 %)

Suspended Sediment
3.10 kg
2.06 ng/g
(3.10E-03 %)

Sediment
99.1 kg
0.413 ng/g
(0.0991 %)

Fish
0.252 kg
1.26 ng/g
(2.52E-04 %)

Fugacity = 17.2 µPa
Total Mass = 1.00E+05 kg

Figure A-7. Environmental partitioning illustration of 2,5-dimethylfuran

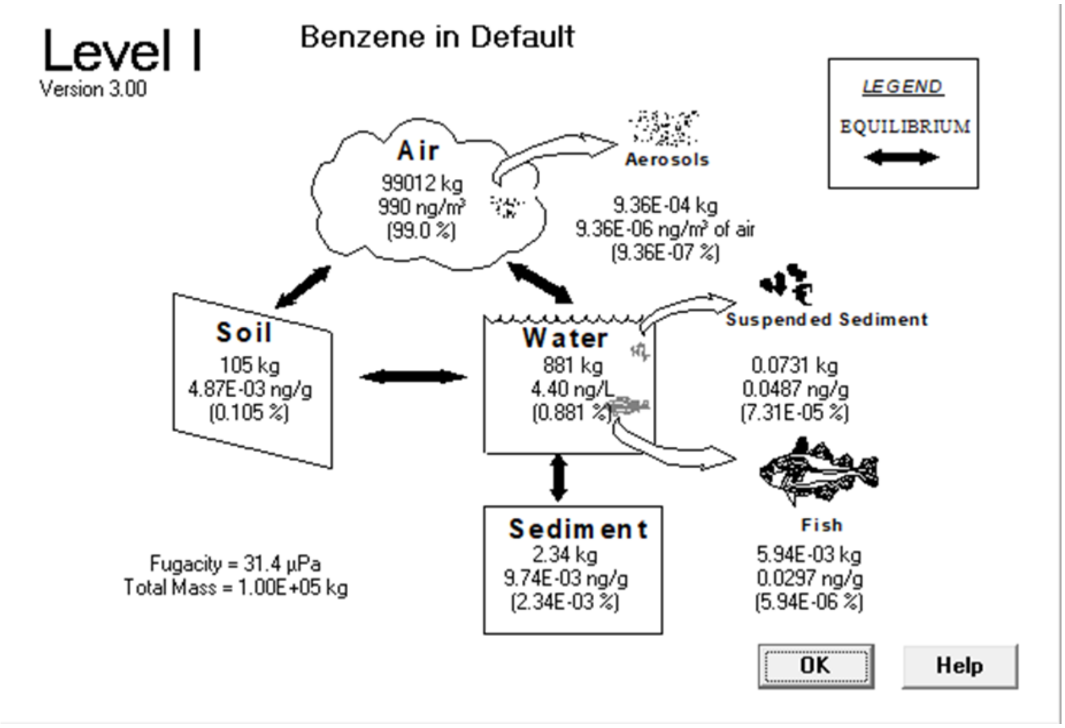


Figure A-8. Environmental partitioning illustration of benzene

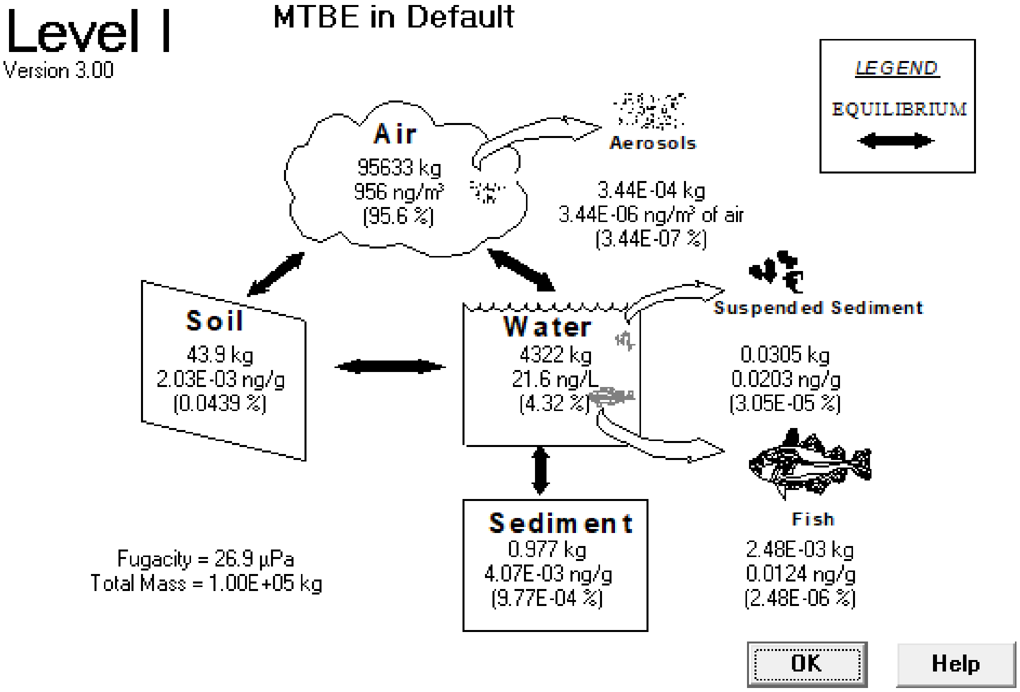


Figure A-9. Environmental partitioning illustration of MTBE

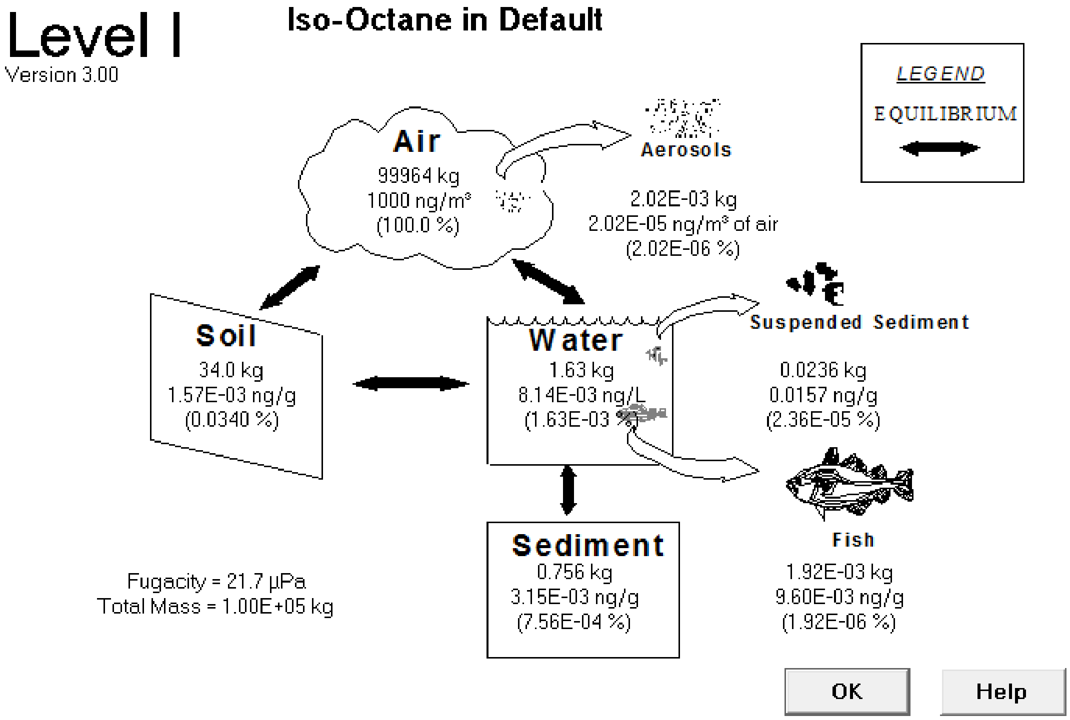


Figure A-10. Environmental partitioning illustration of isooctane

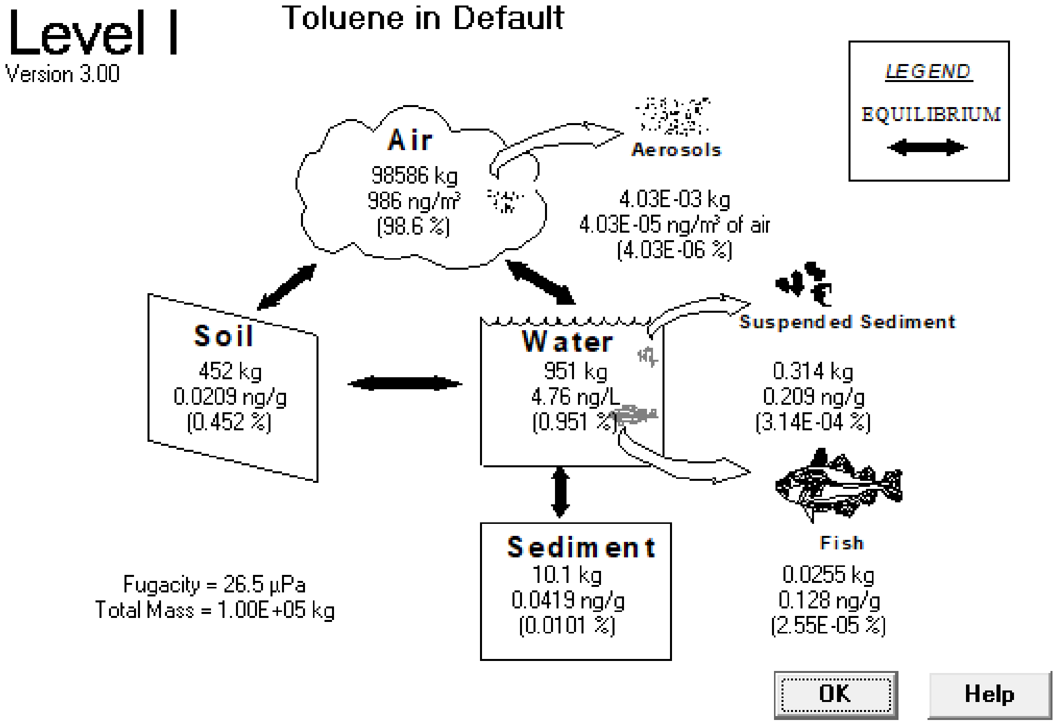


Figure A-11. Environmental partitioning illustration of toluene

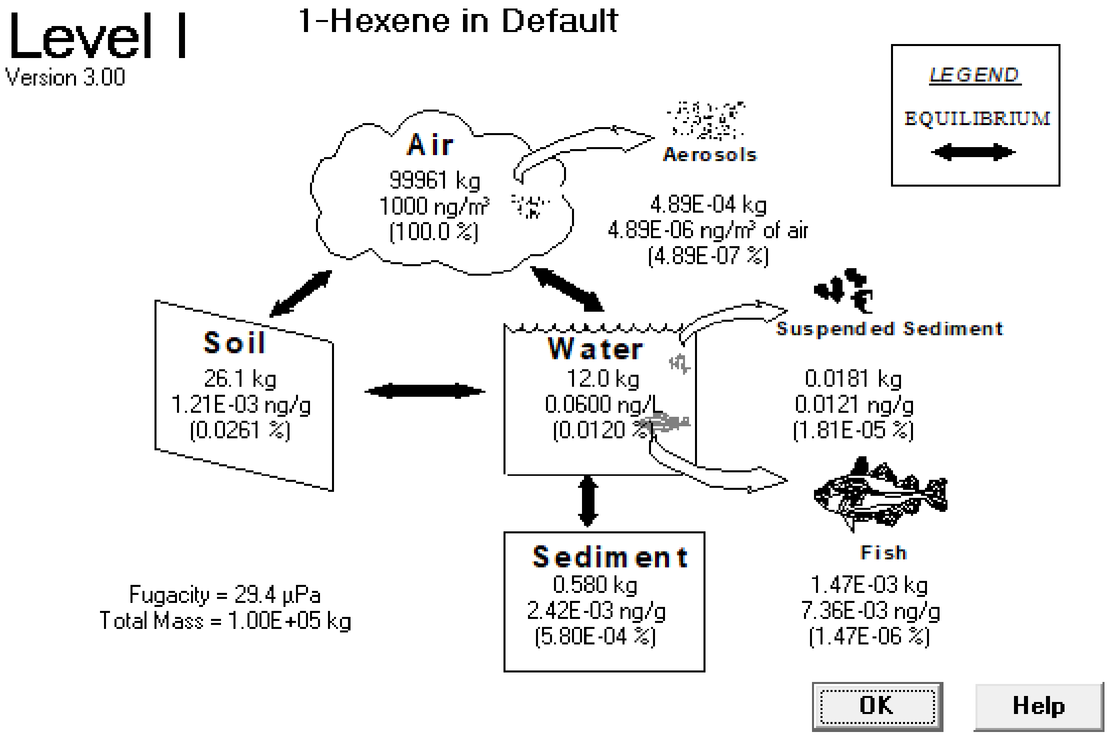


Figure A-12. Environmental partitioning illustration of 1-hexene

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Prepared by National Renewable Energy Laboratory

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