

*Environmental Fate of Low Vapor
Pressure – Volatile Organic Compounds
from Consumer Products:
A Modeling Approach*

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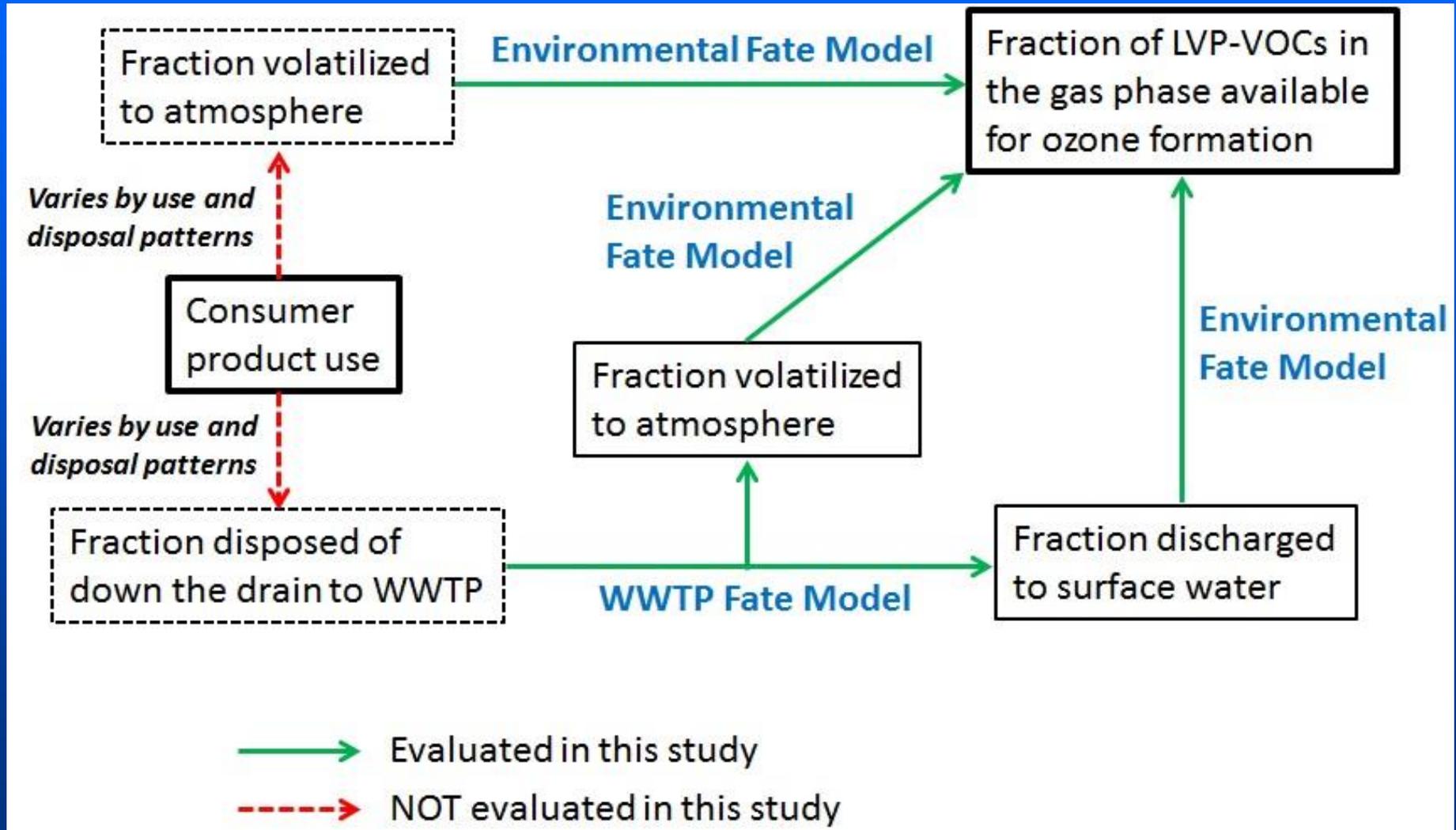
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Objectives

Develop and evaluate environmental modeling tools to determine

1. what portion of a LVP-VOC volatilized to air from consumer product use will remain in the urban air gas phase to form ozone
2. what portion of a LVP-VOC disposed down the drain from consumer product use will be emitted to air and subsequently form ozone

Scope of this Study



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- This study did not estimate the fraction that would make it to outdoor air (red dotted arrows in a previous slide)
 - The environmental fate modeling for this project started with LVP-VOCs that have already made it into the outdoor air
- This study only predicts the fraction of what reaches outdoor air that may react with the OH radicals
 - More complex atmospheric photochemical models such as the U.S. EPA Community Multi-scale Air Quality Model (CMAQ) are needed to simulate how much ozone will be formed in the atmosphere.

Project Tasks

1. Evaluate existing wastewater emission models, select one, and estimate the atmospheric availability of LVP-VOCs disposed down the drain
2. Evaluate existing multimedia fate models that are suitable for simulating the fate and transport of LVP-VOCs in an urban multimedia environment and select one
3. Evaluate the need to integrate additional complexities into a basic multimedia model, specifically, a dynamic or multi-box spatial model
4. Provide an integrated model and final model results to ARB
5. Publish a paper on findings

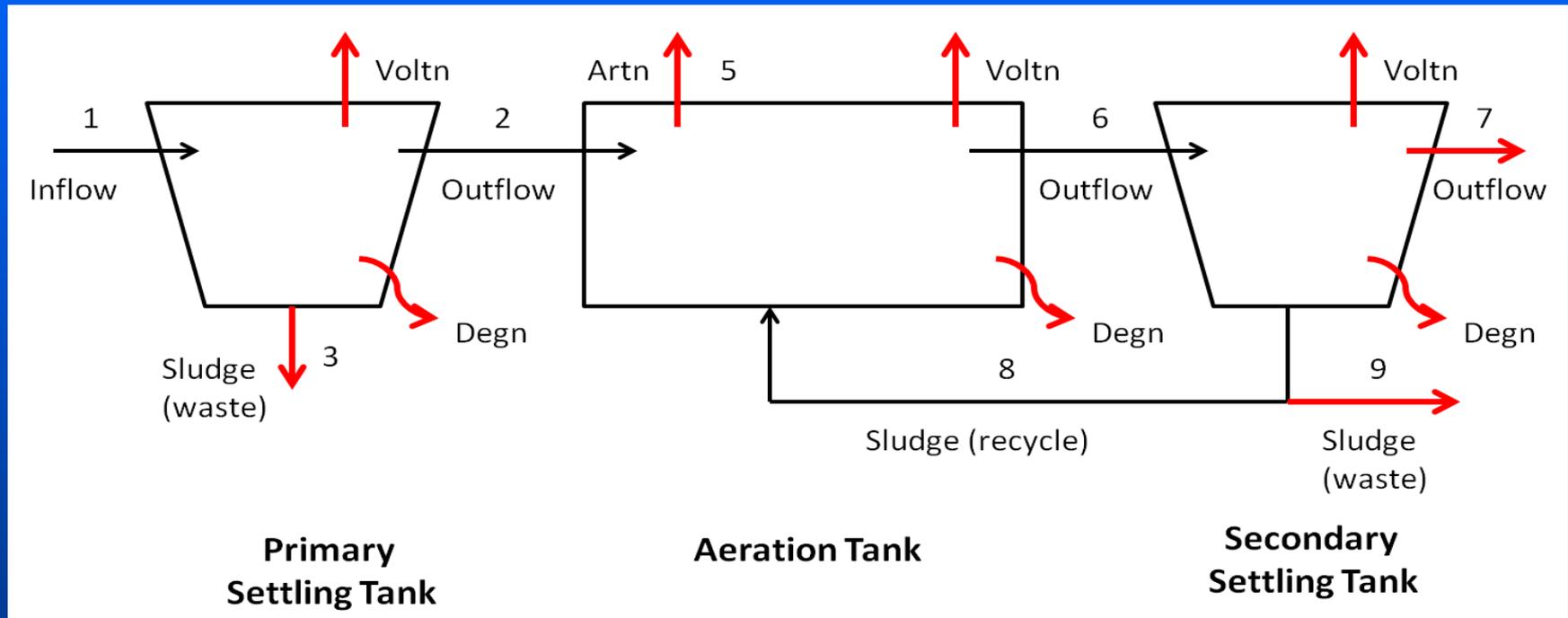
Selected LVP-VOCs

- A total of **32** compounds and mixtures was selected by ARB with input from stakeholders.
- According to the U.S. EPA's Chemical and Product Categories (CPCat) database, many of the selected compounds are commonly used in a variety of consumer products including laundry detergents, fabric softeners, dishwashing detergents, and other laundry products.
- In this presentation, we sometimes focused on the results of **23** high production volume chemicals. Note that these 23 compounds were selected because they have a single CAS number which allows us to obtain chemical properties from chemical properties estimation programs (e.g., EPA EPI Suite).
- The results for 32 compounds/mixtures are available in the final report.

WWTP Emission Models

- Goal: understand how LVP-VOCs that are disposed down the drain and enter a wastewater treatment plant (WWTP) are treated in typical wastewater treatment processes
- Three major removal processes and their associated key chemical properties
 - Volatilization to air – *Henry's law constant*
 - Biodegradation – *biodegradation half-life*
 - Sorption to sludge – *octanol-water partition coefficient*

Processes in a Typical Activated Sludge-type WWTP



Voltn = volatilization
Artn = aeration loss
Degn = degradation

→ Removal pathways

Excerpt from Seth et al. 2008

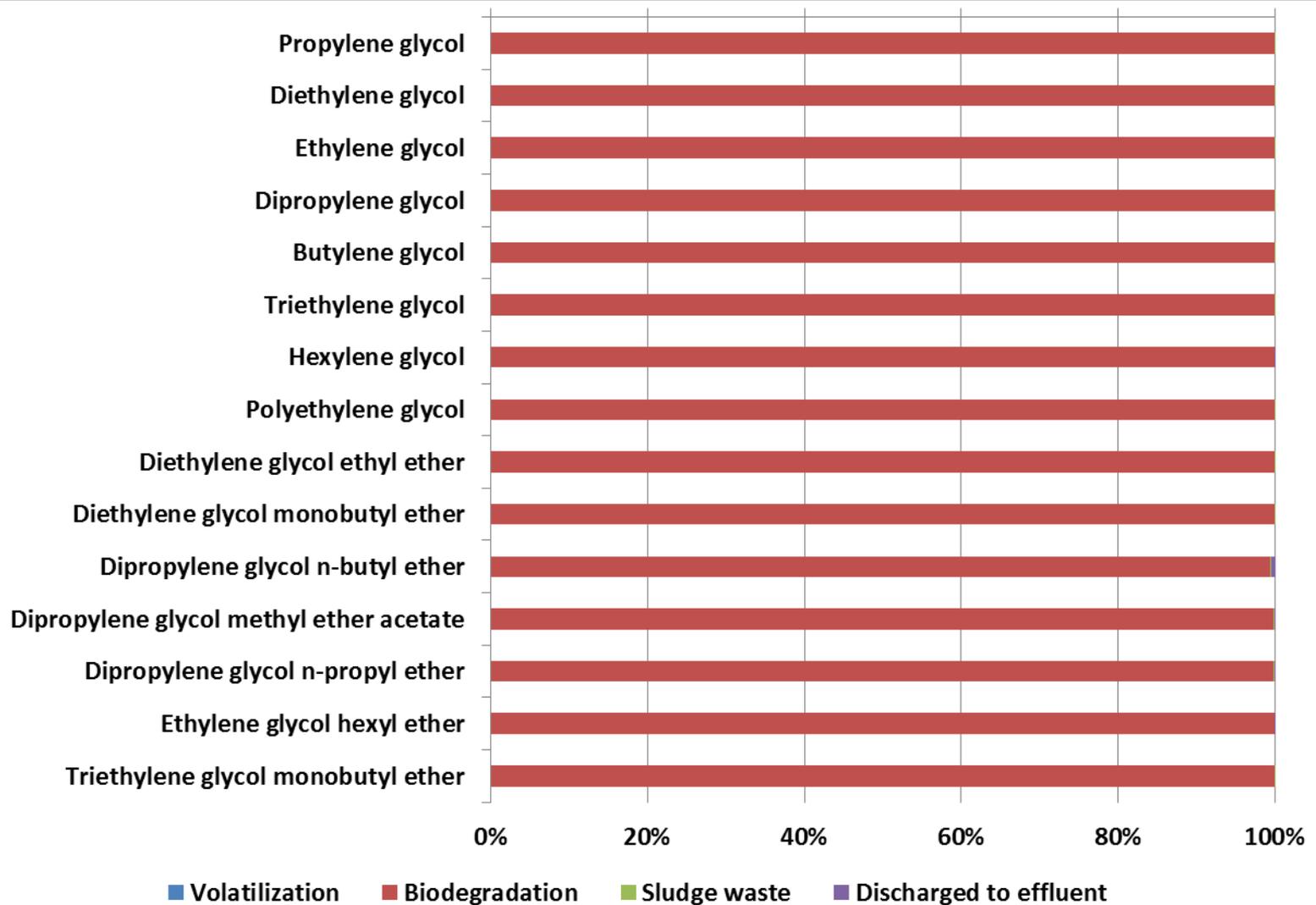
Selected Models and Findings

- Selected models
 - Namkung and Rittmann model (1987): conventional concentration-based
 - Clark et al. model (1995): fugacity-based, with updates in Seth et al. model (2008)
- Findings
 - All other models developed after these two models were published are descendants of each of these models
 - More features of removal mechanisms and handling various types of compounds are added to later models to improve model predictions. For some of the models with updates to Namkung and Rittmann, the model results are not replicable
 - After model comparison, Clark et al. model is considered to be more appropriate than Namkung and Rittmann model for our study purpose

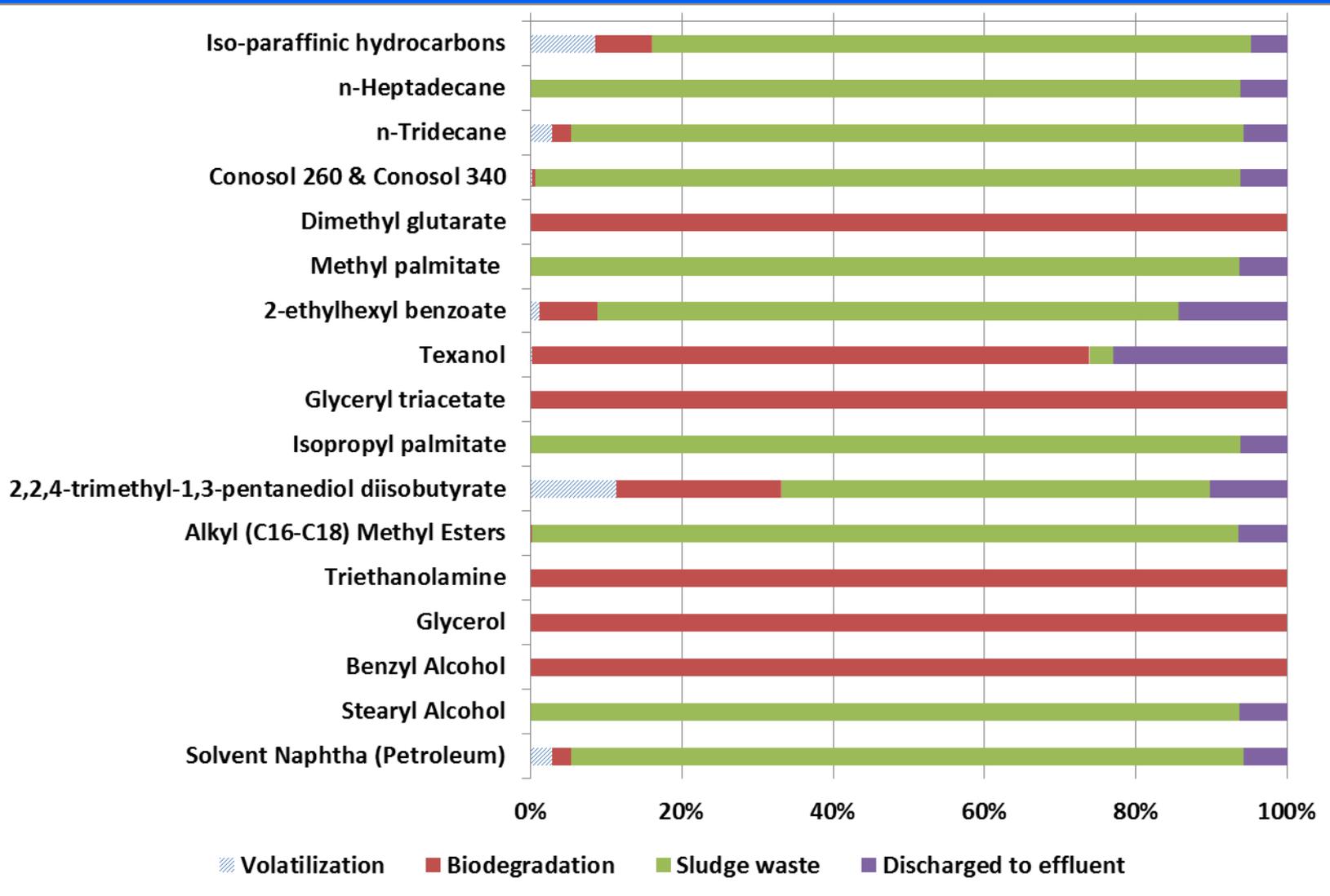
Key Input Parameters

- Directly obtained for each chemical from the U.S. EPA EPI Suite™
 - Henry's law constant (H)
 - Octanol-water partition coefficient (K_{ow})
 - Biodegradation half-life in wastewater ($t_{1/2_WW}$)
- Biodegradation rate constant
 - Data are not available
 - Derived using $t_{1/2_WW}$, the composition of biomass, and partitioning between water and solids

Fate of LVP-VOCs in a WWTP



Fate of LVP-VOCs in a WWTP



Summary of Findings

- The biodegradation half-life in wastewater is the most uncertain input variable during sewage treatment processes among other input parameters
- Loss by volatilization in a WWTP is negligible for most compounds, confirming that losses by biodegradation or sorption to sludge are major loss mechanisms

Sensitivity Analysis on $t_{1/2_WW}$

- Roughly estimated (e.g., 1, 10, 30 days)
 - the most uncertain input variable during sewage treatment processes
- Method:
 - increased and decreased the initially assigned half-lives by a factor of 10 and ran our model.

Findings from Sensitivity Analysis

- Iso-paraffinic hydrocarbons, a complex mixture of many compounds, and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate are most sensitive
 - the volatilization fraction is sensitive (7% and 15% changes, respectively) to the selection of the half-lives
- For the remaining compounds
 - the changes in the half-lives did not influence significantly (<2%) the results on volatilization
- The majority of the change relates to whether the compound is biodegraded or removed with the sludge

Evaluation of Multimedia Models

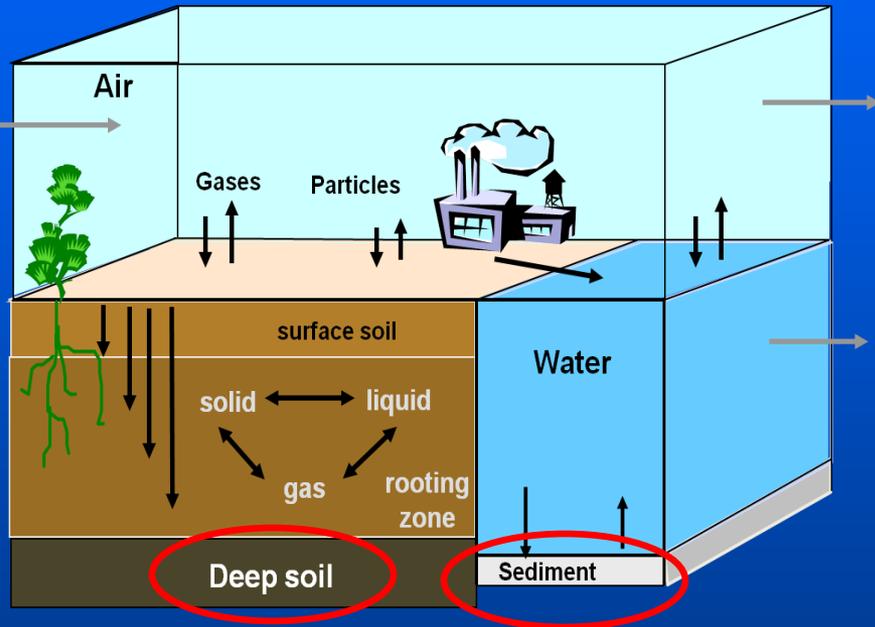
1. Reviewed existing models (N=2)
2. Replicated results of the selected models
3. Compared results to determine model differences
4. Obtained or estimated key model parameters
5. Applied LVP-VOCs to the selected models

CalTOX Model

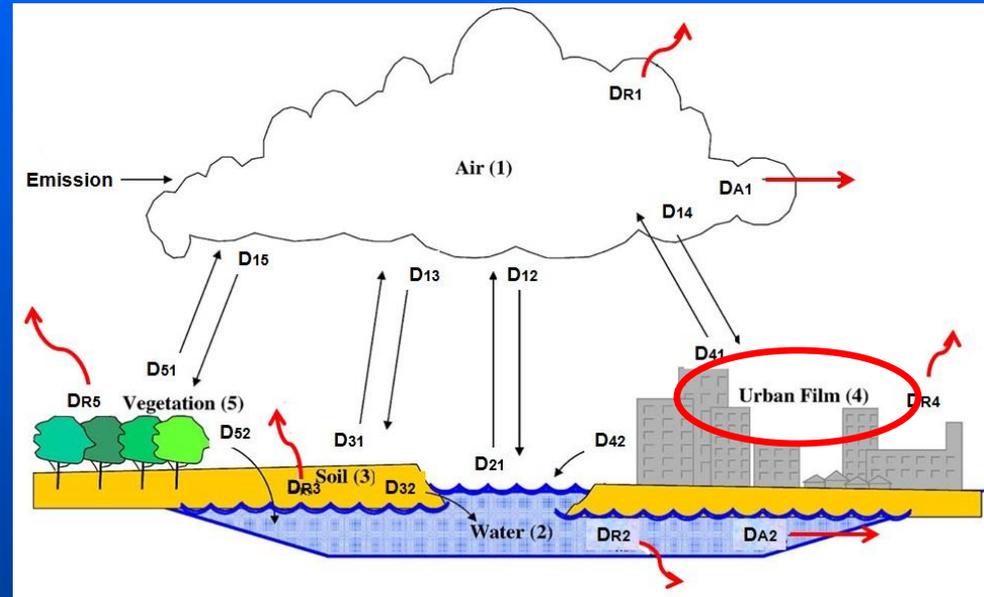
- A mature and widely used multimedia fate and transport model – with an extensive history of model evaluation exercises and case studies
- Determine competing processes by which chemicals
 - a) accumulate within the compartment of origin
 - b) are physically, chemically, or biologically transformed within a compartment (e.g., hydrolysis, oxidation, etc.)
 - c) are transported to other compartments by cross-media transfers that involve dispersion or advection (e.g., volatilization, precipitation, etc.)

Compartments in Both Models

CalTOX



Foster et al.



 : Extra model compartments

Model Comparison

- Similarities
 - Use fugacity concept
 - Level III multimedia partitioning model
 - Based on a series of coupled mass transfer equations
- Differences
 - Model compartments/ compartment dimensions
 - Input parameters
 - Fugacity capacity calculation

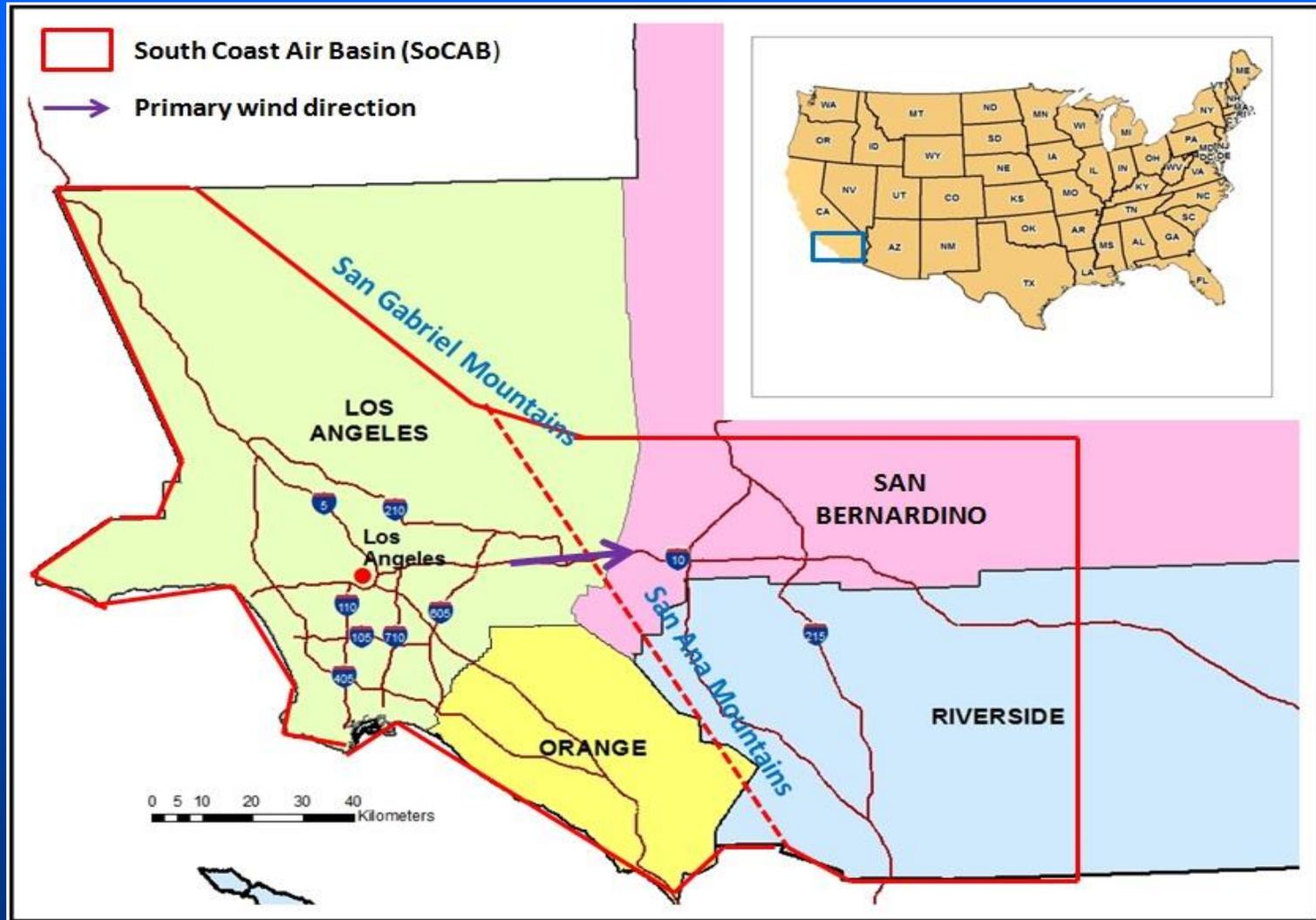
Key Input Parameters

- First-order degradation rate in air (k_R , hour⁻¹)
 - As reaction with OH radicals is the first step toward forming ozone, the fraction of OH reaction in the air is equivalent to the fraction of LVP-VOCs available to form ozone in atmosphere
- Advection loss rate from air (k_A , hour⁻¹)
 - Influences the fraction of LVP-VOCs available for ozone forming reactions in the airshed these compounds are first emitted
- Rain events
 - Influences the mass distribution of LVP-VOCs because compounds with a low H value are likely to have favorable partitioning in the water phase

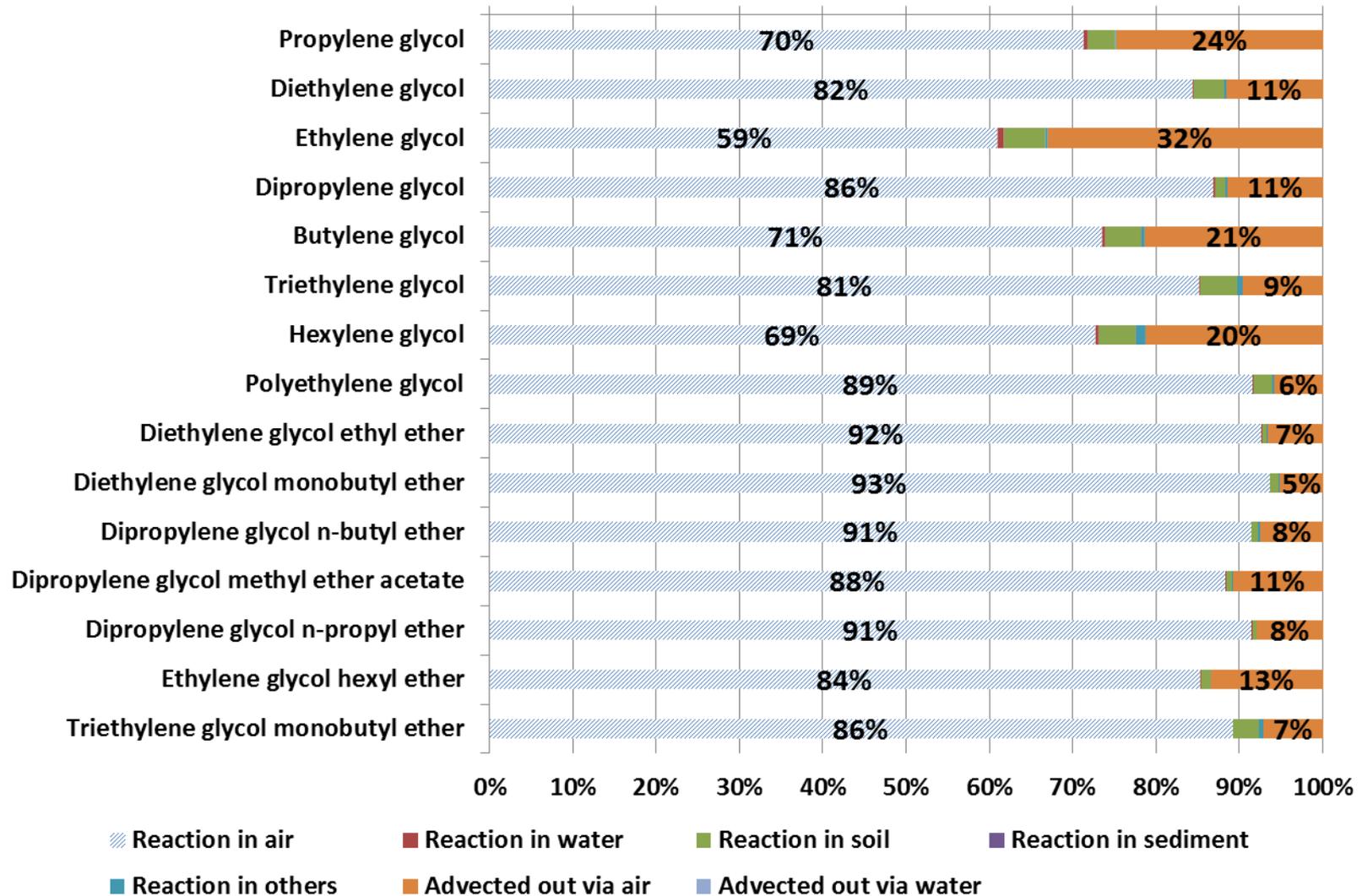
Case Study

- South Coast Air Basin (SoCAB)
 - Extreme status with regard to ozone non-attainment
 - The San Gabriel Mountains and the Santa Ana Mountains form an East-West wall through the SoCAB
 - Higher concentrations of ozone are measured and predicted in downwind areas of the SoCAB (i.e., less densely populated Riverside and San Bernardino Counties) than the upwind areas of the SoCAB (i.e., more densely populated Los Angeles and Orange Counties)
 - Ideal for evaluating two-box airshed models

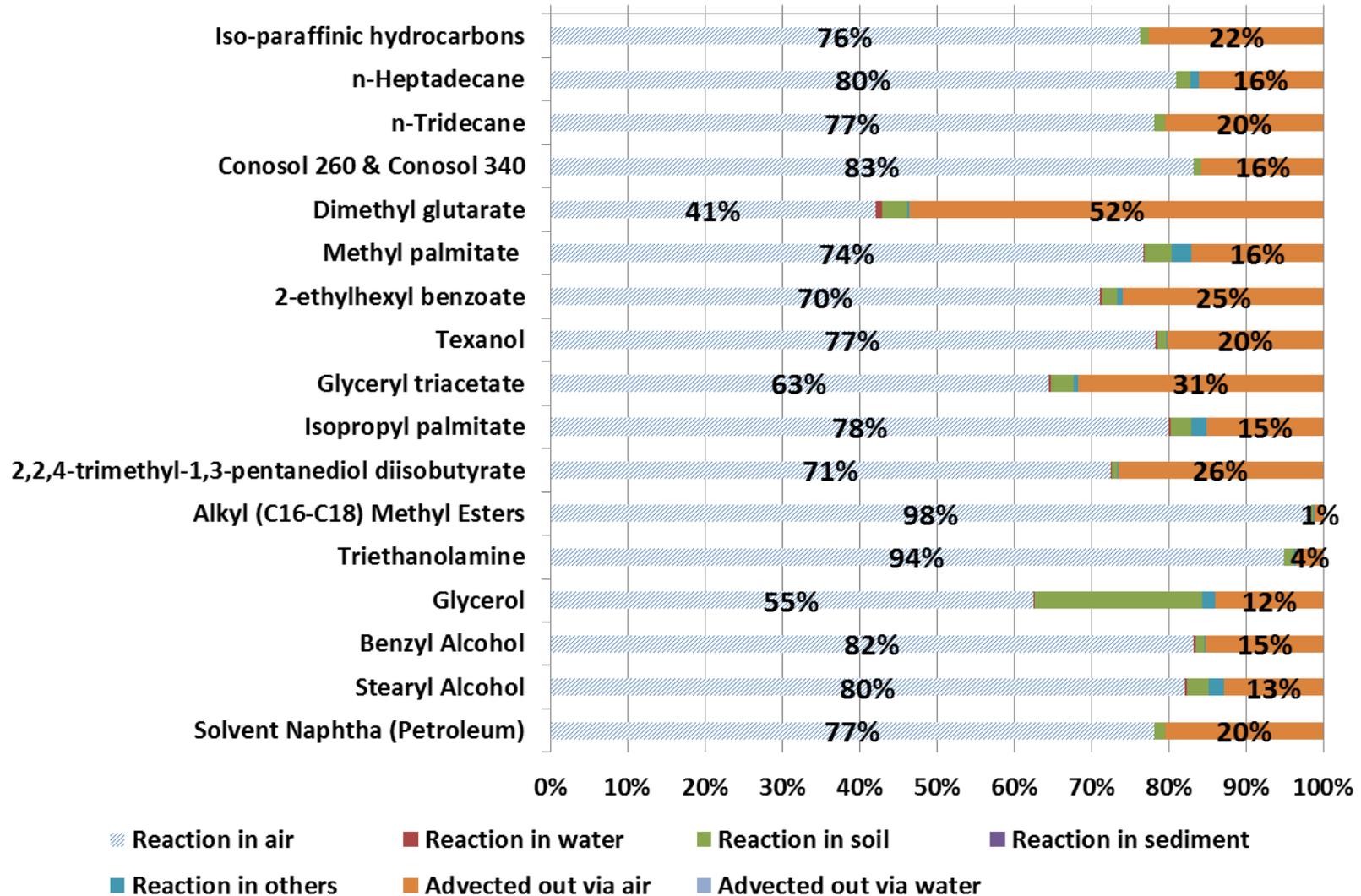
Study Area



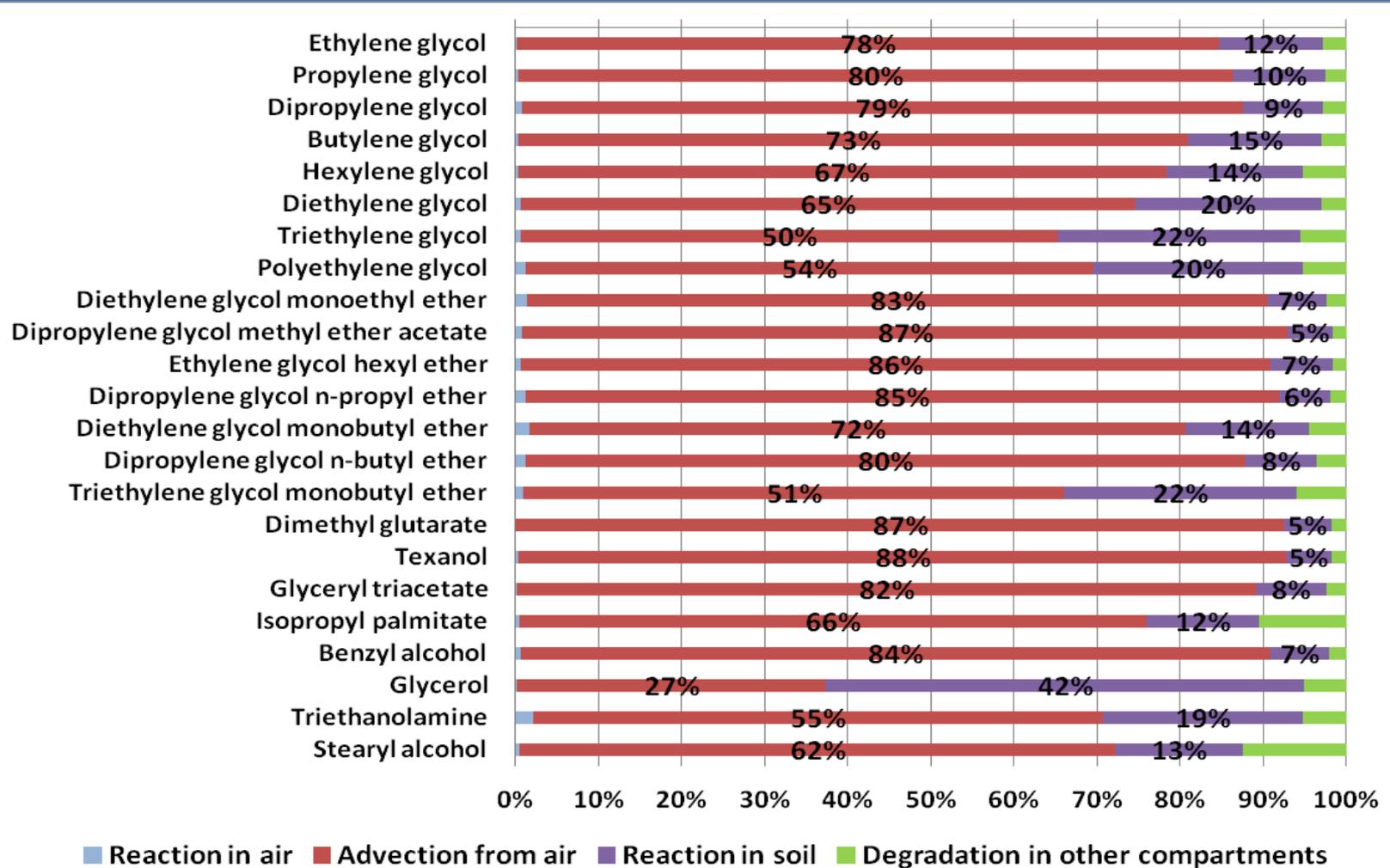
Fate of LVP-VOCs in an Outdoor Environment during the Day



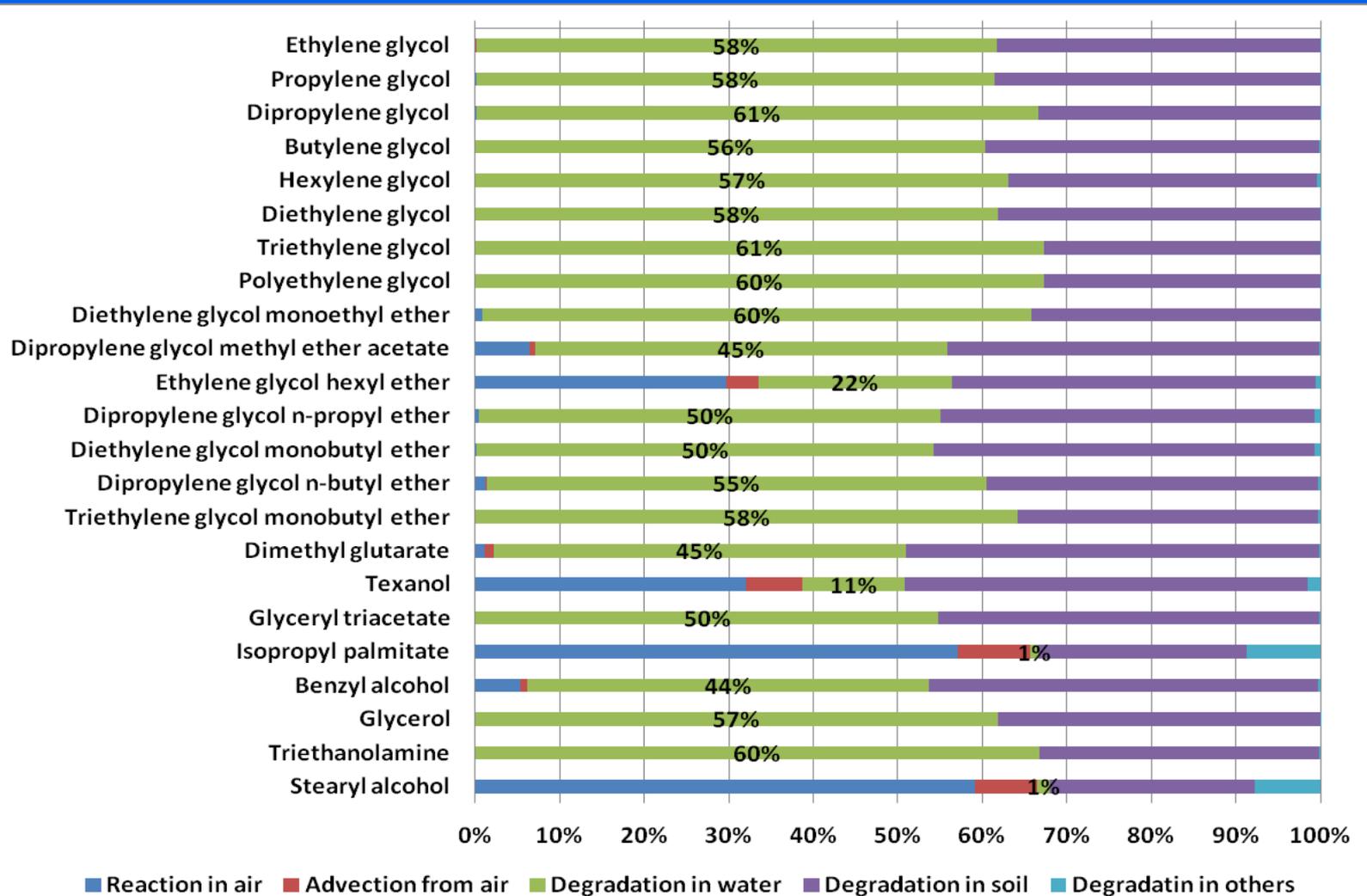
Fate of LVP-VOCs in an Outdoor Environment during the Day



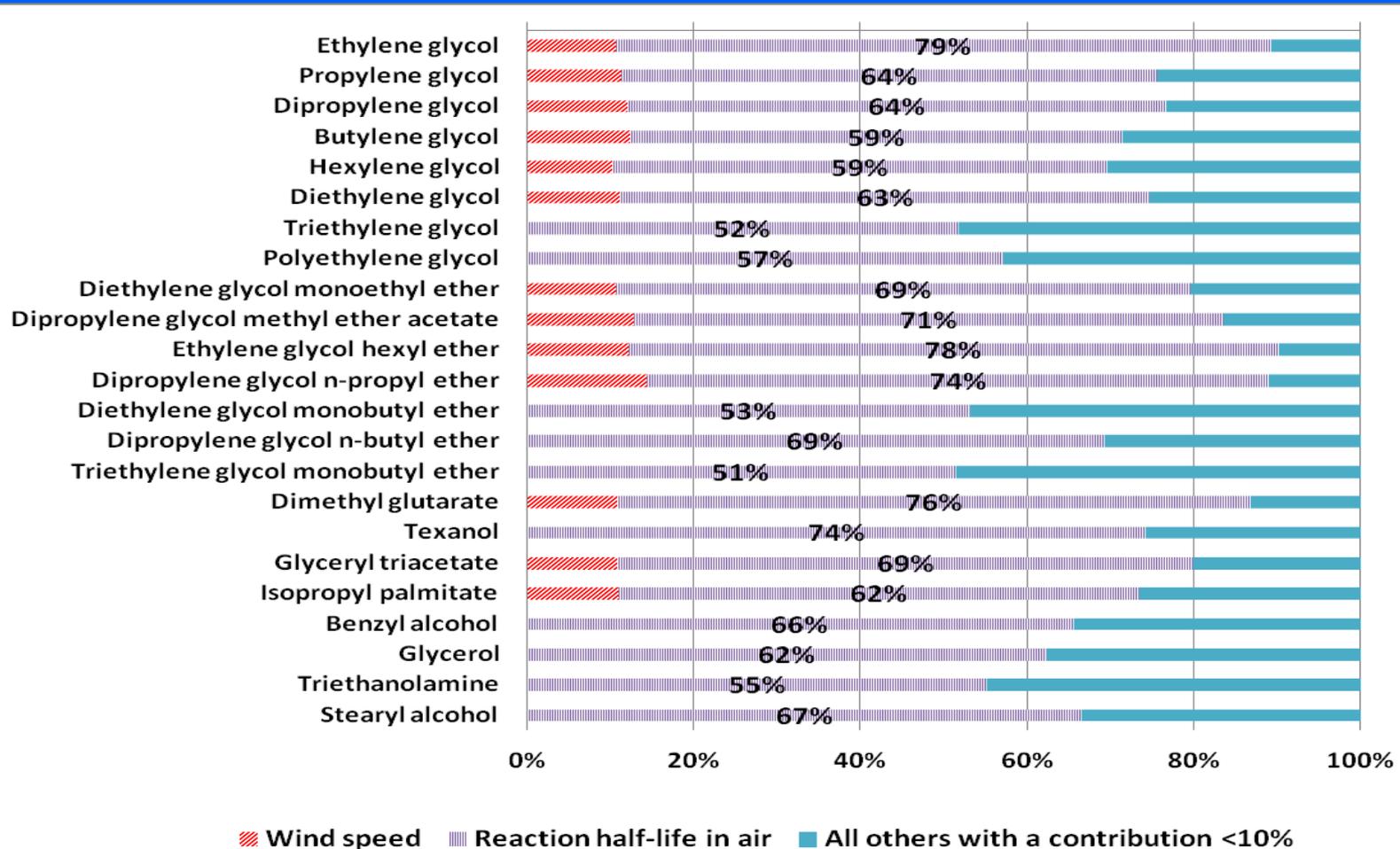
Fate of LVP-VOCs in an Outdoor Environment during the Night



Fate of LVP-VOCs with a Continuous Rainfall Scenario



Uncertainty Analysis: Percent contribution of model inputs to the output uncertainty



Findings from Multimedia Modeling

1. During the daytime, both models predict that compounds are primarily either degraded in air due to the reaction with OH radicals or transported out of the air basin by air advection
2. During the nighttime, loss by reaction in air with OH radicals is negligible (<7%) for all chemicals for both models, due to the small OH radical concentration during the night
3. Loss by reaction in other compartments such as soil, vegetation, and urban surface film is negligible for most compounds
4. From the Monte Carlo uncertainty analysis, wind speed and the reaction half-life in air are the two most influential parameters on the overall fraction available for ozone formation

Findings from Dynamic Conditions

- Ran the Foster model in a dynamic condition (Level IV version)
- Even if the model runs with dynamic conditions, concentration changes over the entire period are within a factor of 2 or 3 of the mean concentration
 - The overall fraction of LVP-VOCs for ozone formation from the Level IV version is similar to that from the Level III version

Findings from Two-box Models

- Loss by degradation from other environmental compartments is much smaller than loss by reaction due to OH radical reaction and advection from air
- Except glycerol, more than 90% of LVP-VOCs in the ARB list will be available for ozone forming reactions in air during the day either in the air basin that has releases or in the adjacent air basin which receives advective flows during day and night
 - For those air basins which are located downwind of highly populated urban area such as Riverside and San Bernardino Counties, additional inflow of chemicals needs to be considered in multi-compartment models

Findings from VOC Runs

- To compare the fate of LVP-VOCs with that of VOCs, we ran both the Foster and CalTOX models for 6 VOCs recommended by ARB.
 - acetone, ethyl acetate, methyl ethyl ketone, toluene, 2-butoxyethanol, and isopropyl alcohol
- For acetone, ethyl acetate, and methyl ethyl ketone,
 - The half-lives in air are 1170, 160, and 223 hours, respectively, which are far greater than the longest half-life (i.e., 78 hours for dimethyl glutarate) of the evaluated LVP-VOCs
 - The results for these VOCs are influenced by the magnitude of OH radical rate constants rather than compound's volatility.
 - Thus, percent loss by reaction with OH radicals for these VOCs is less than 30% from both models

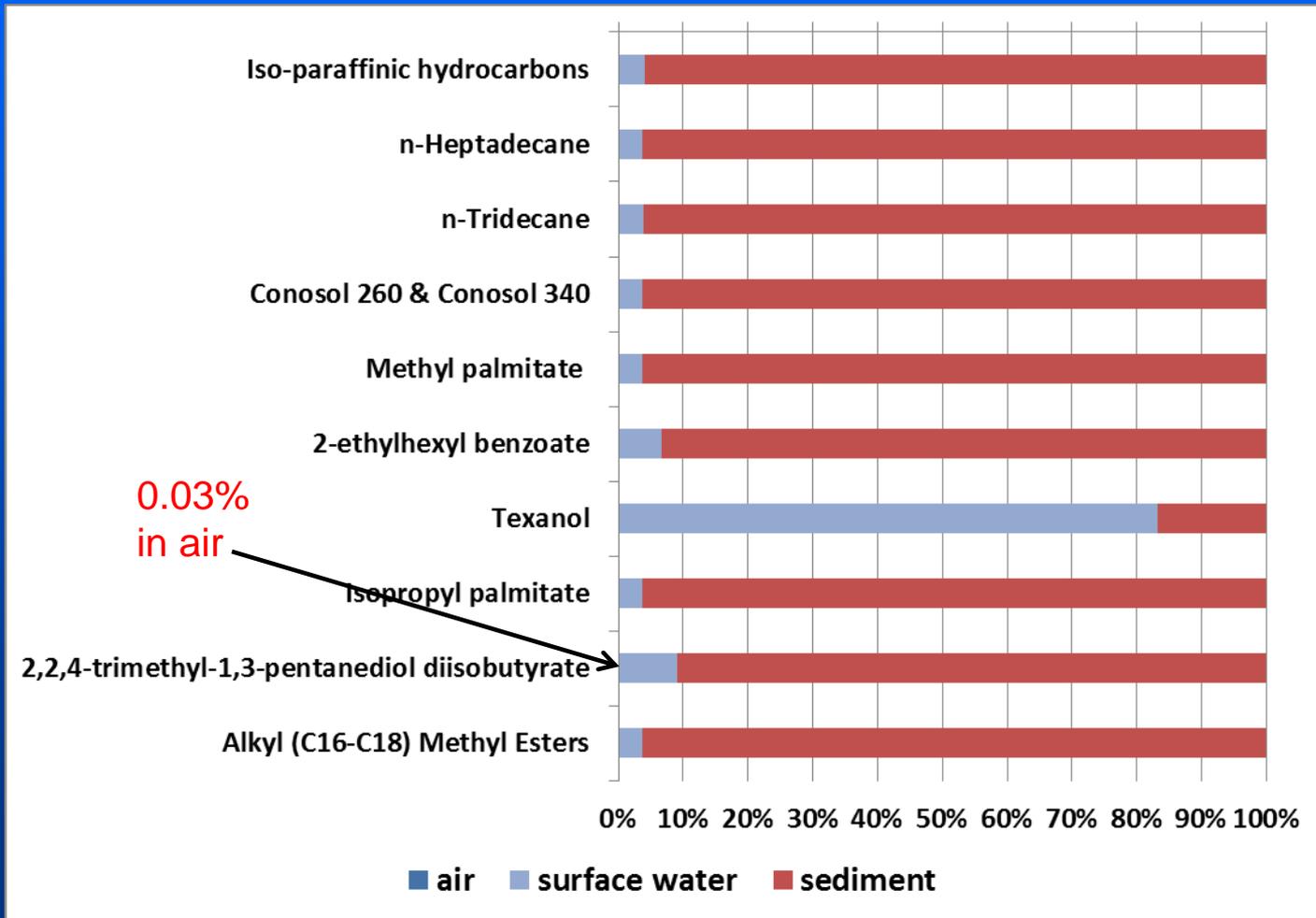
Implications of Results for SoCAB vs. Other States

- For LVP-VOCs with small Henry's law constant
 - Model conditions such as precipitation rate and the fraction of the horizontal area that is surface water implemented in this study (i.e., Southern California during the dry, hot summer season) differ from those that would be implemented in other states.
 - Therefore, the studies of other states in U.S. with different landscape and climate factors would have very different results.
 - However, the vast majority of the population of California lives in a region with a dry summer and little surface water, and therefore results are expected to be similar.

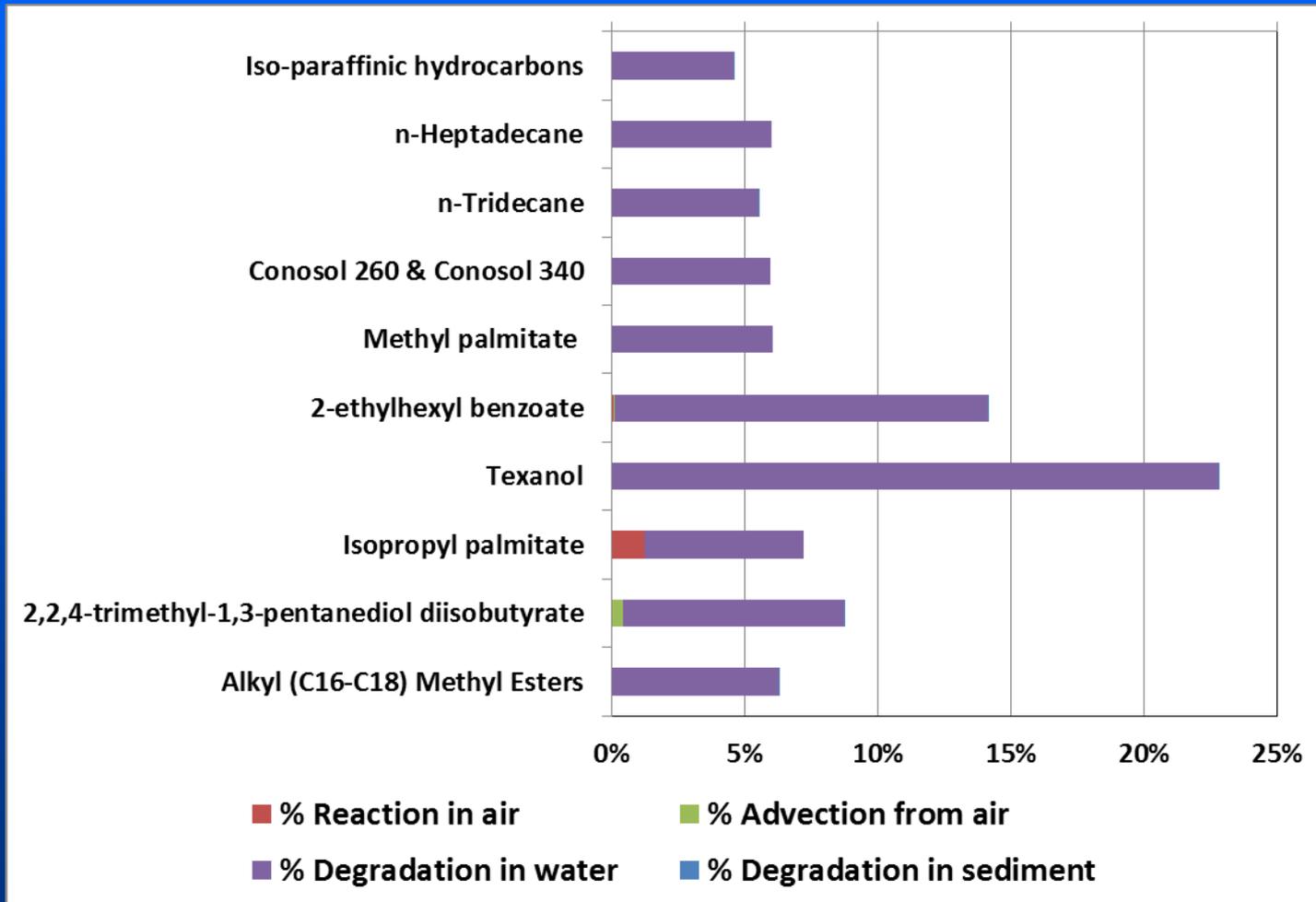
Model Integration

- Once a chemical goes into the waste water treatment facility, 3 options
 1. A portion is removed by biodegradation or sludge removal
 2. A portion is volatilized → input to multimedia model
 3. A portion is discharged with the effluent → input to multimedia model

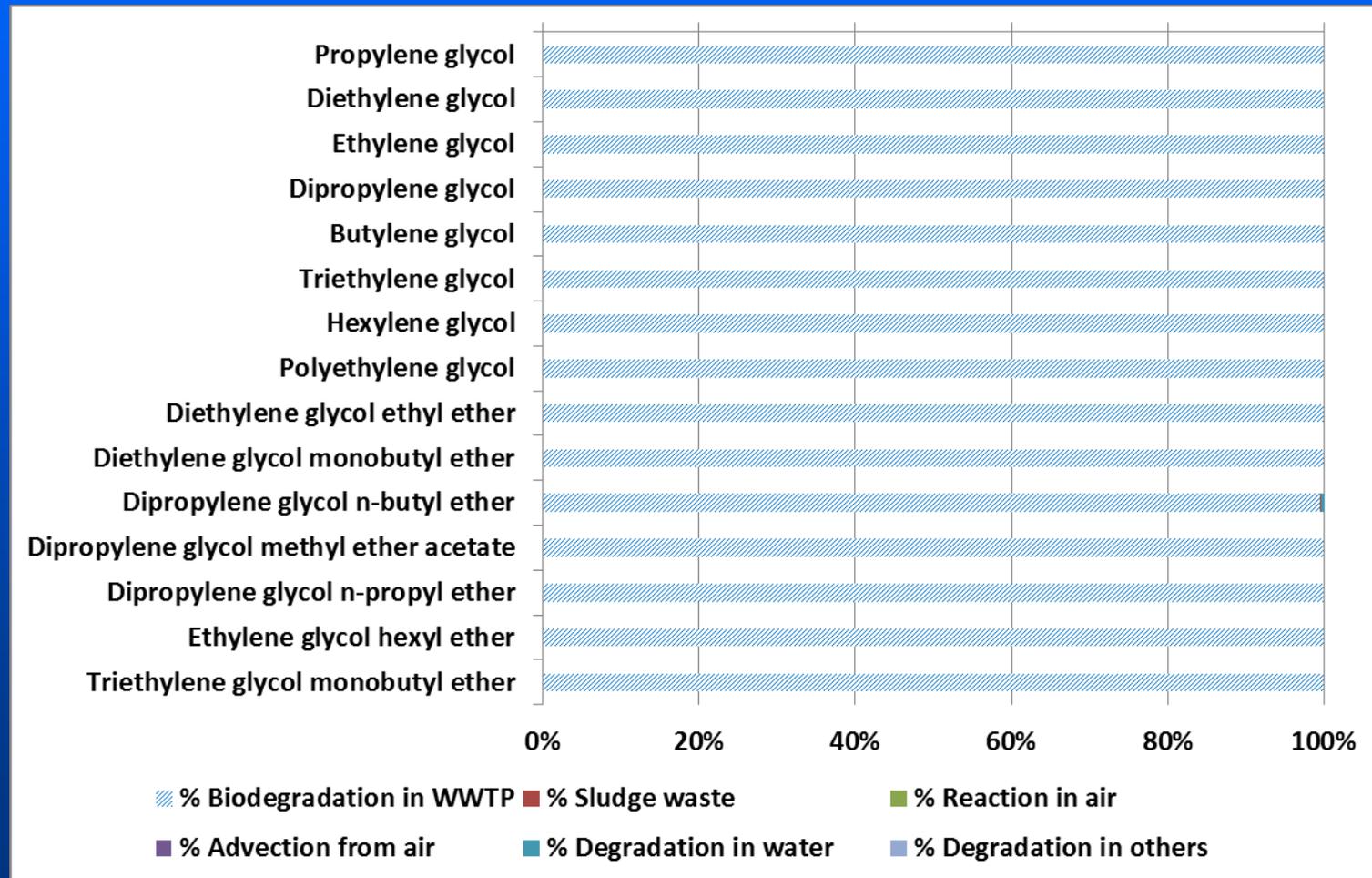
Distribution of 10 LVP-VOCs in a Surface Water Release



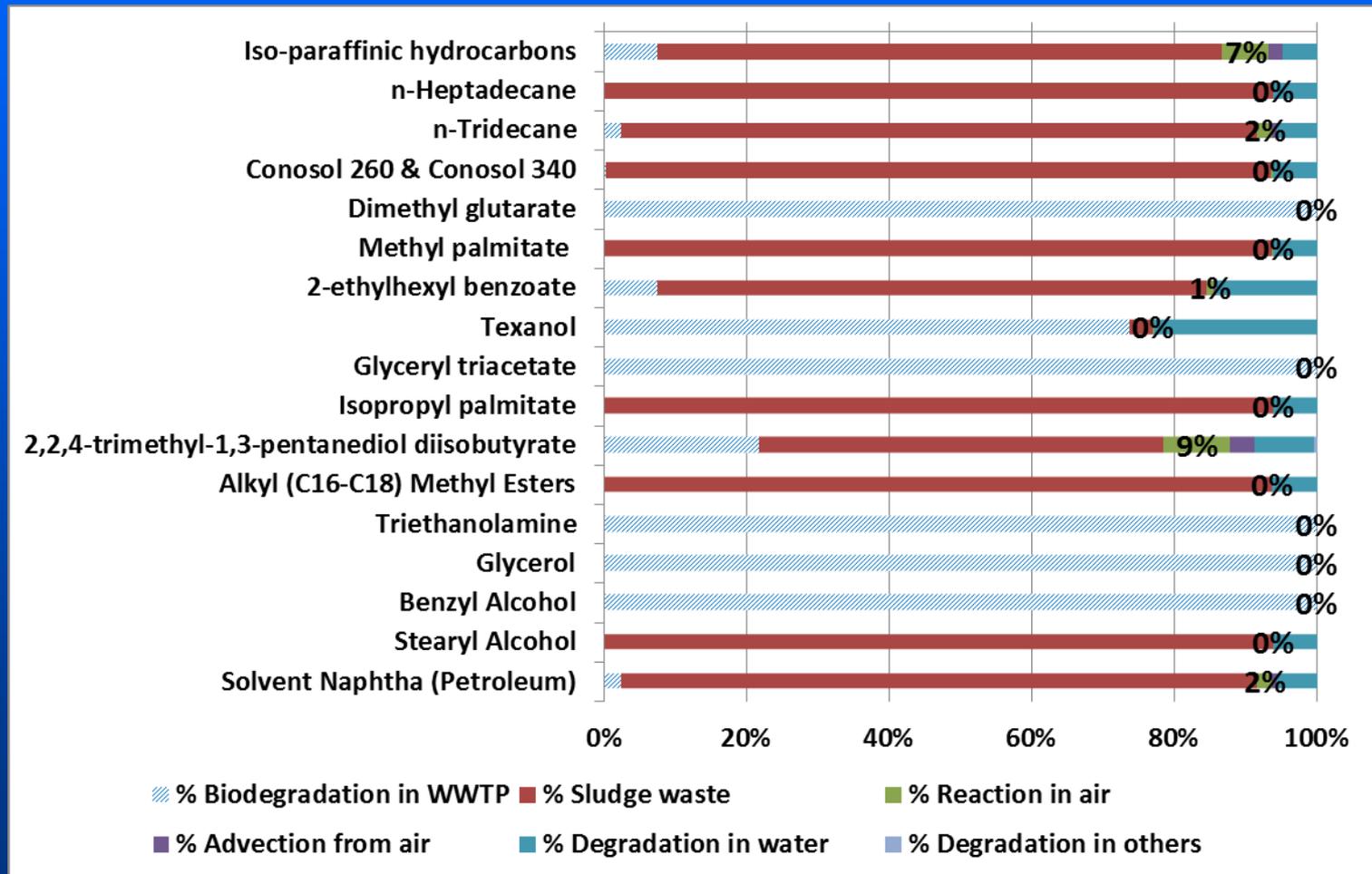
Removal of 10 down-the-drain LVP-VOCs discharged from WWTP



Final percent going to each for LVP-VOCs going down the drain



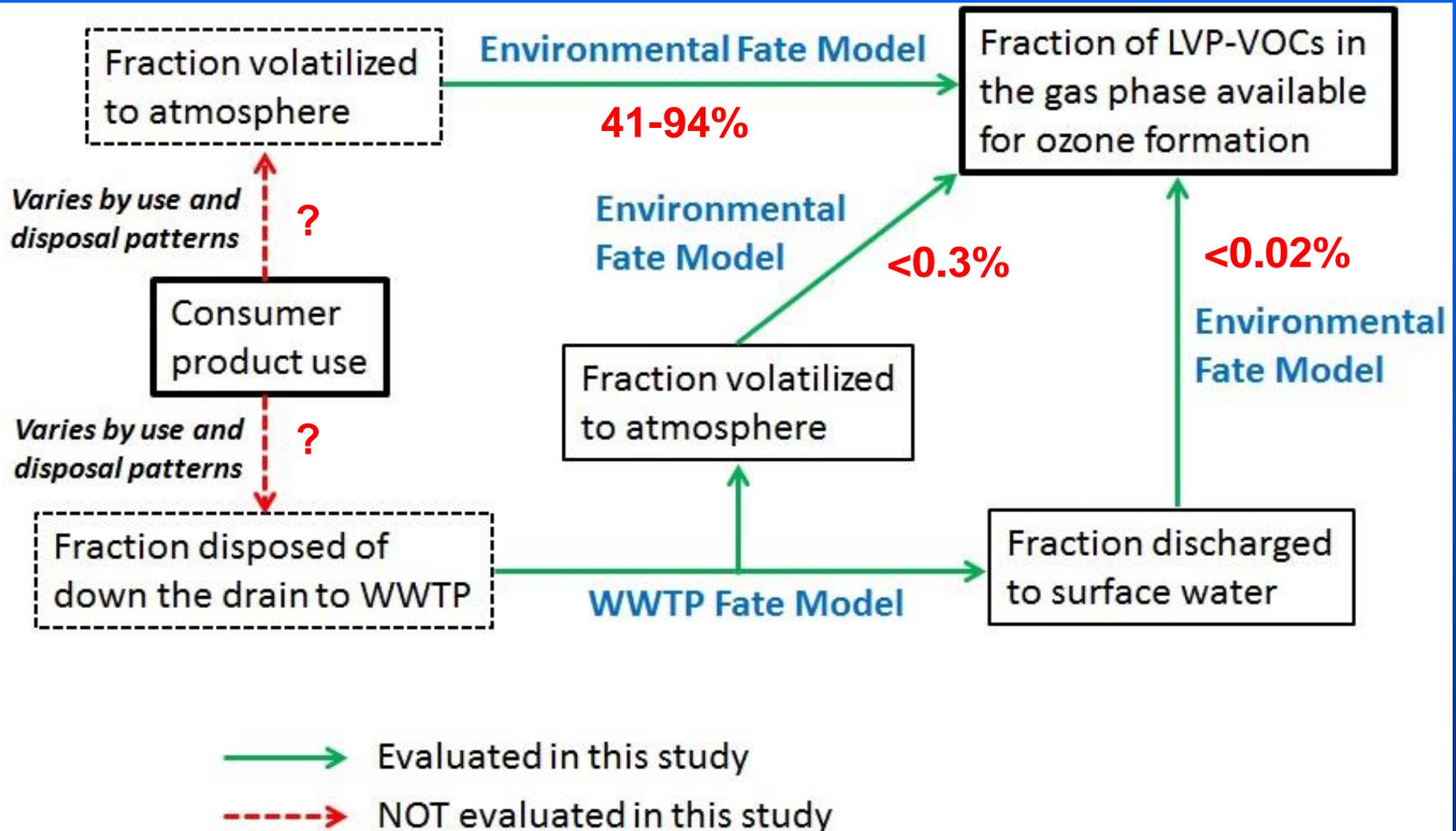
Final percent going to each for LVP-VOCs going down the drain



Format of Integrated Model

- **Instruction:** describes each sheet & provides general instructions for using the spreadsheet
- **ChemProp:** lists chemical properties necessary for running WWTP and CalTOX models
- **WWTP:** programs a wastewater treatment plant (WWTP) fate model
- **CalTOX_air:** programs a CalTOX model for an outdoor air release scenario
- **CalTOX_water:** programs a CalTOX model for a surface water release scenario
- **WWTP+CalTOX:** presents integrated model results for the fate of down-the-drain compounds

Findings from Model Integration



Limitations

- Many of the compounds have estimated OH radical rate constants and half-lives in each compartment are not directly measured, but estimated based on its chemical structure
- We are unable to estimate what fraction is emitted into air and transferred to the outdoor air and the distribution through the airshed
- There could be processes not included in these models
- The results of this study had not been evaluated with measured real-world data