Liquid Dispersion Modeling for HNS: Oil and Chemical Trajectory, Fate, and Effects

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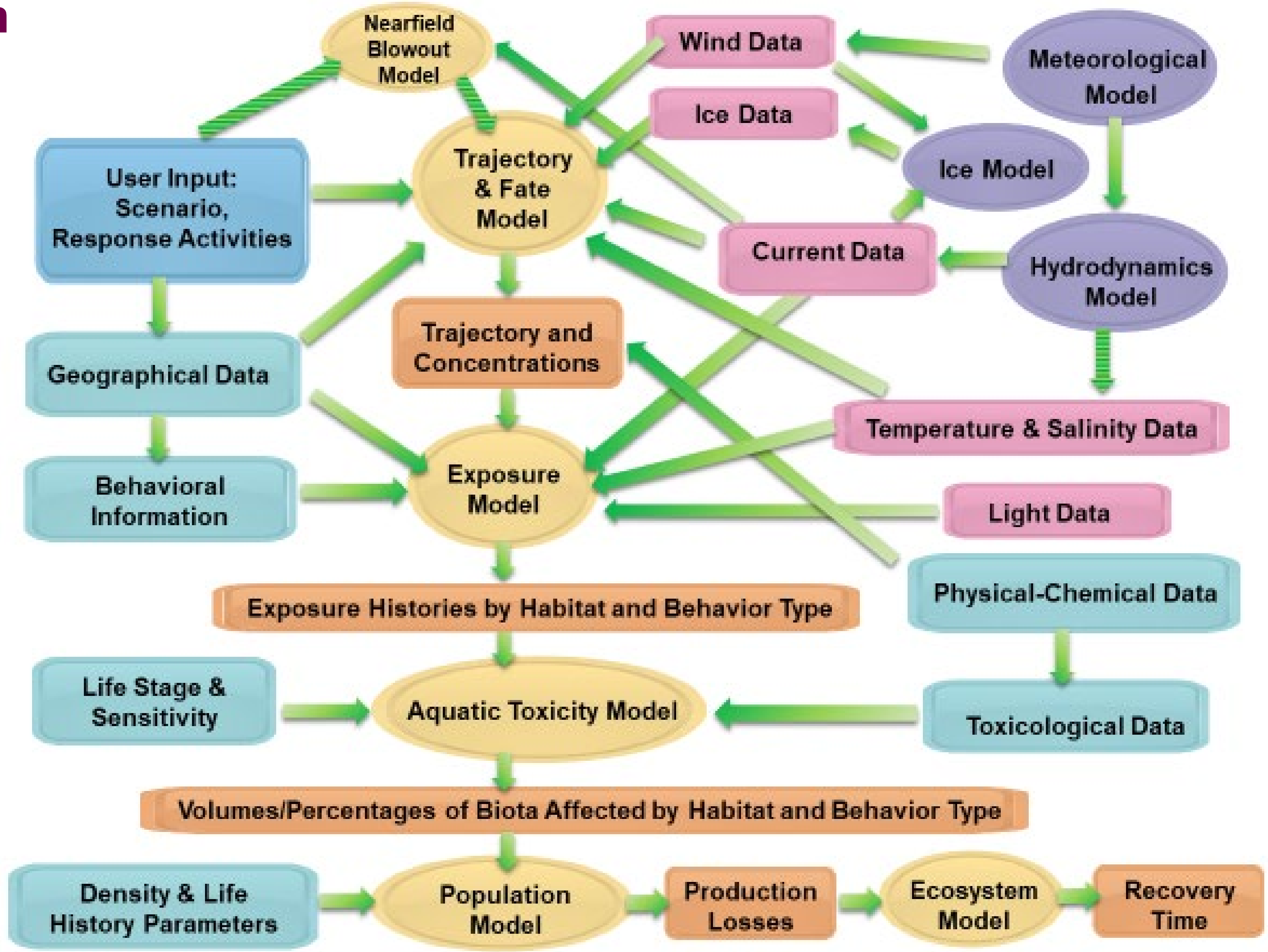
October 2022

RPS' Spill Models: Background

- US CERCLA Law (1980): RPS (formerly ASA) developed "Type A" Natural Resource Damage Assessment Models for US Government Regulations (1984-1996)
  - Estuarine and Marine
  - Great Lakes Environments

- RPS has continued development as
  - OILMAP (OIL Model Application Package) for oil spill response
  - SIMAP (Spill Impact Model Application Package) for oil spill fate and effects modeling
  - CHEMMAP (Chemical Model Application Package) for Hazardous and Noxious Substances

Model System



Model Application: Response vs. Analysis

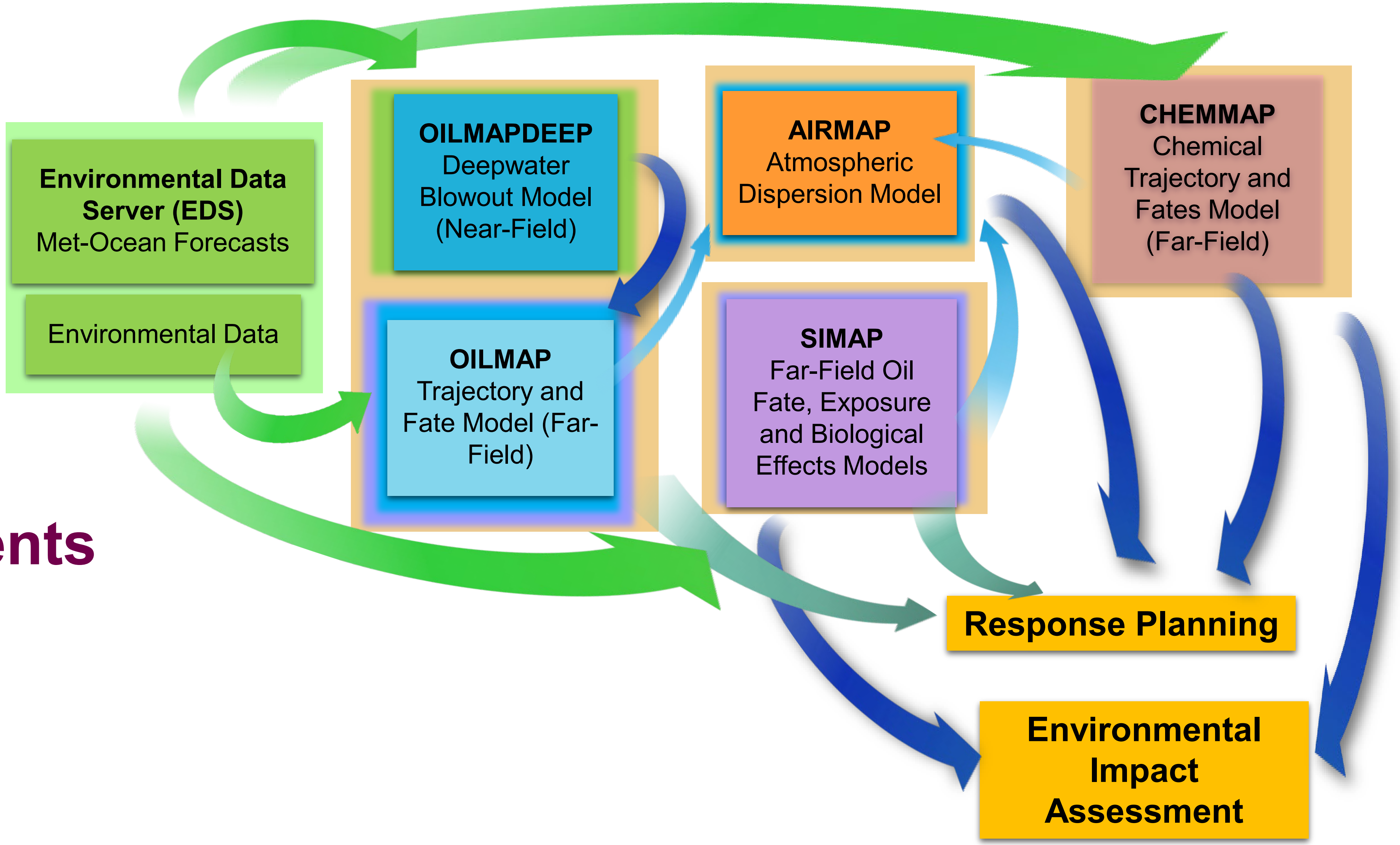
- Emergency Support ↔ Real time
  - Responders need a quick, robust, and reliable modeling system to predict drift (transport) and weathering of oil slicks
  - Integration of available information (pollutant data, availability, and placement of resources, etc.)
  - Met-Ocean input data in near-real-time (Environmental Data Server)
  - To be used during training, drill exercises, and in emergencies

  → ***Deterministic modeling (Trajectory and Fates)***

- Environmental Assessment ↔ Planning and Analysis
  - Impact analyses, on the coastline, ecological consequences, etc.
  - Risk assessment and Contingency Planning
  - Large datasets, combination of several models to evaluate the environment, the pollutant source, and human activities

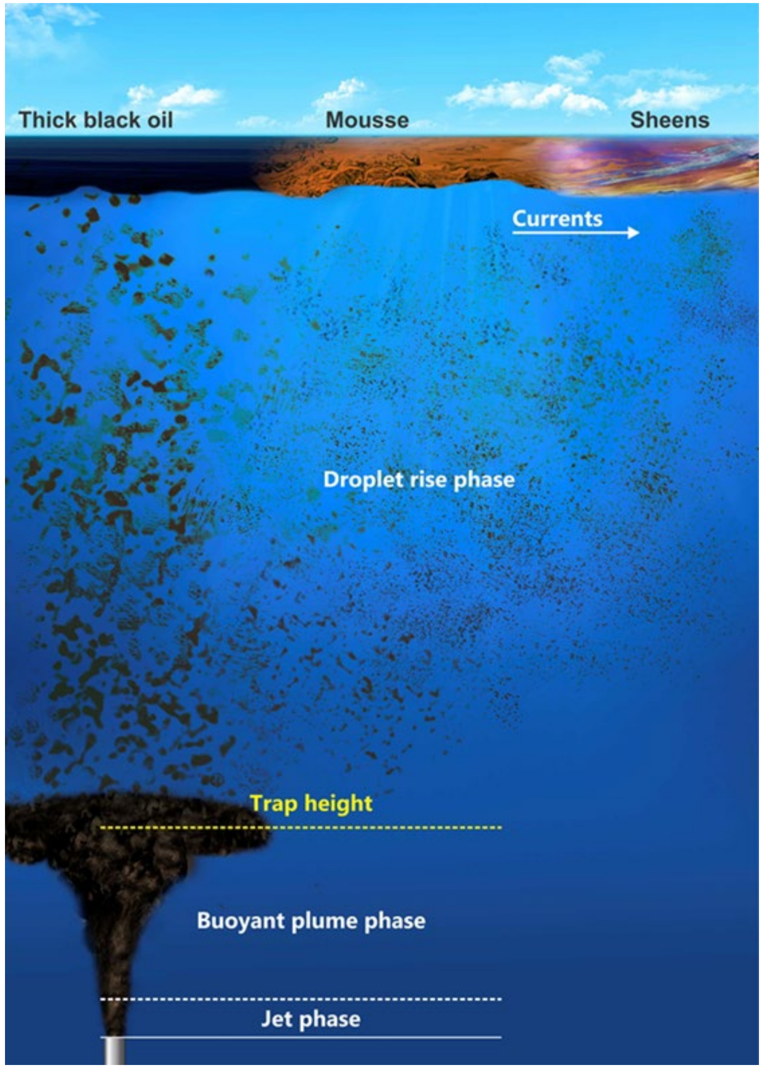
  → ***Multiple or ensemble simulations (Stochastic Modeling)***

RPS Models for Spills into Aquatic Environments

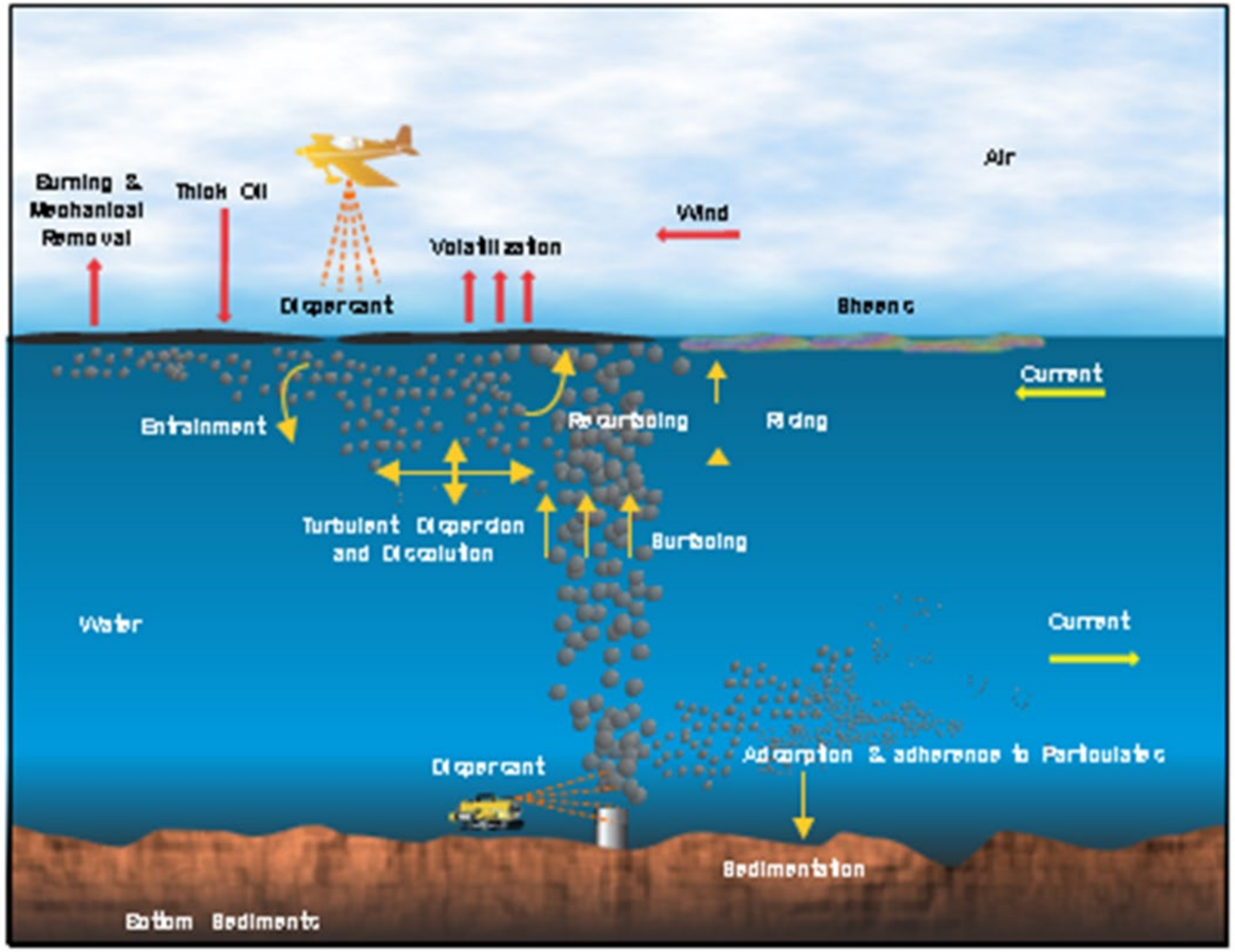


Oil Spill Modeling Considerations: Location and Release Conditions

- **Water surface**
  - Spills at water surface
    - Initialized as floating slicks
- **Low pressure release from subsea pipeline or wreck**
    - Low energy
    - Initialized as large droplets
    - Oil surfaces rapidly to form slicks
- **Uncontrolled blowout**
    - High energy
    - Gas content
    - Range of initial droplet sizes depend on conditions & orifice size
    - Oil droplet size key to oil fate



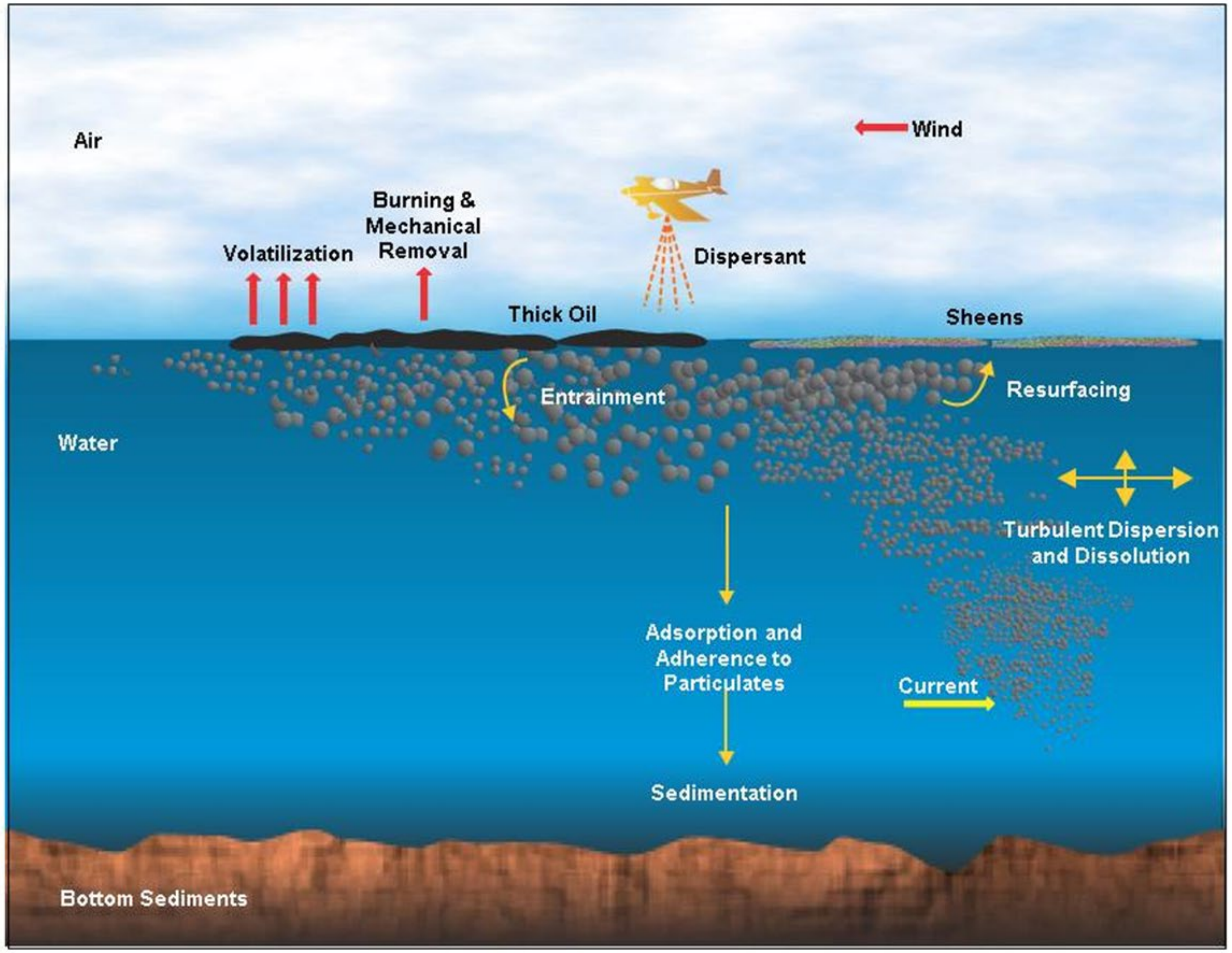
Important Processes Determining Amount of Surfacing Oil Mass and Exposure



- Droplets >500 µm surface in hours

- Droplets <100 µm unlikely to ever surface

Important Processes
Floating Oil and Exposure in Surface Waters

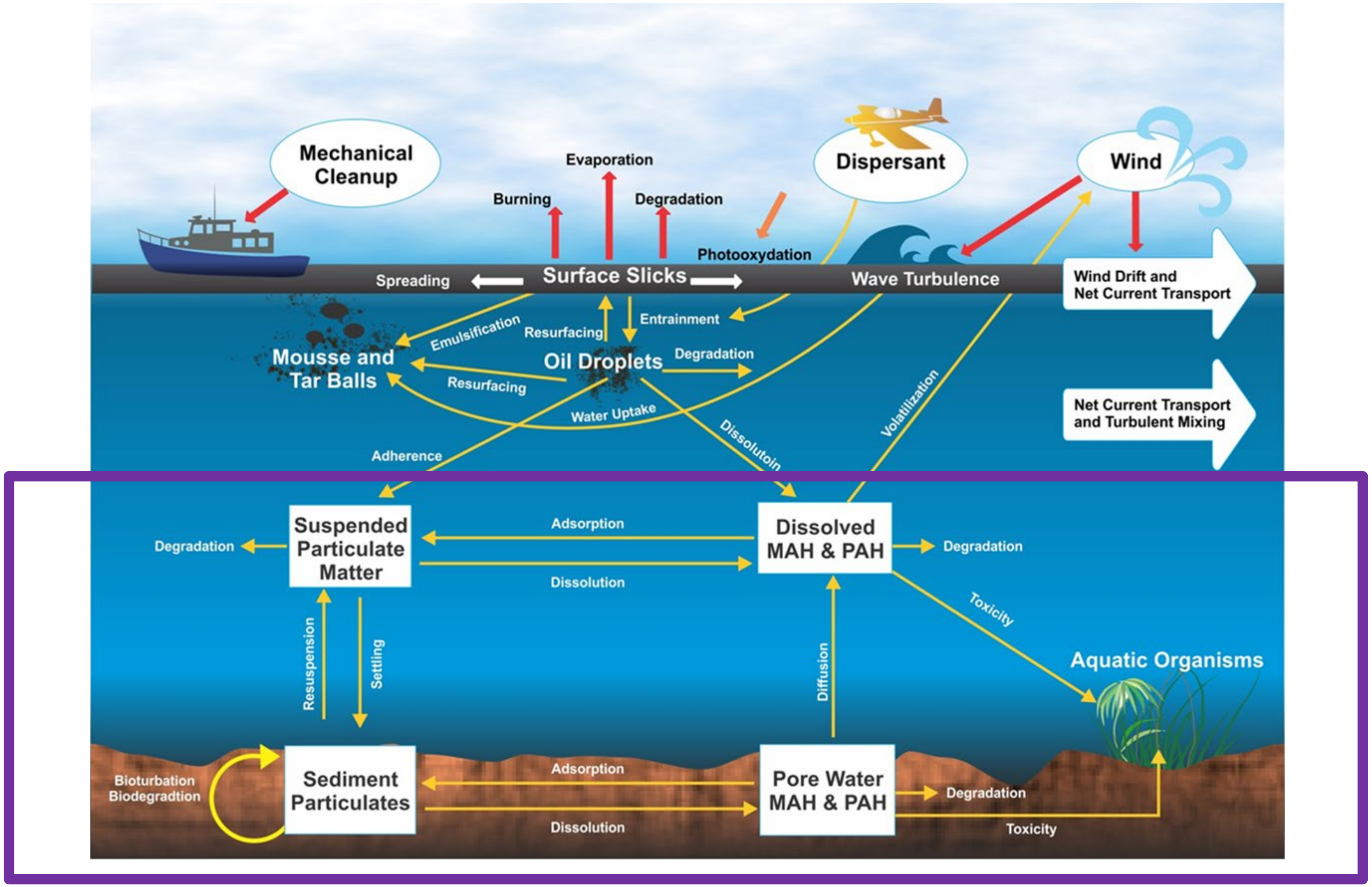


- Droplets sizes are related to turbulence levels
- More exposure in water column with higher turbulence entraining smaller droplets

OILMAP and SIMAP: Trajectory and Fate Models

OILMAP & SIMAP

SIMAP



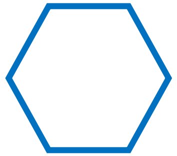
Volatile Components of Oil Modeled Separately

OILMAP: Aromatics are not separately tracked

C-C-C-C-C-C

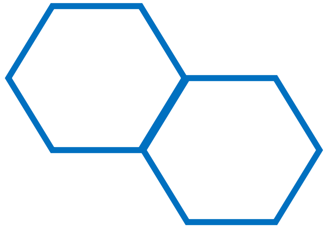
Aliphatics:
- Alkanes – C11-C23 – volatile, negligible solubility
- Alkanes ≤ C10 & Cyclics – volatile & soluble

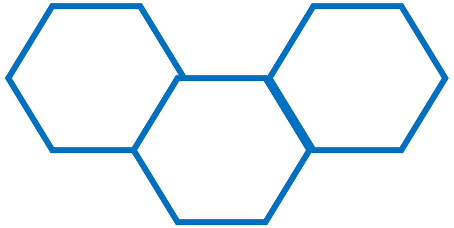
Non-soluble volatiles grouped by boiling range



Monoaromatic Hydrocarbons (MAHs)
- Benzene, Toluene, Ethylbenzene and Xylenes = BTEX – highly soluble, highly volatile, moderately toxic
- Alkyl-substituted Benzenes – soluble, less volatile, more toxic

Solubles & Semi-solubles grouped by log(Kow)





Polynuclear Aromatic Hydrocarbons (PAHs) & Heterocycles
- Naphthalenes (2-ring PAHs)
  - soluble, less volatile, more toxic
  - with more alkyl chains, less soluble but more toxic
- Decalins
- 3 ring PACs – semi-soluble, most toxic fractions
  - Phenanthrenes
  - Fluorenes
  - Dibenzothiophenes
- 4-ring PAHs – fluoranthenes, pyrenes, chrysenes
- larger PAHs insoluble

What Properties Matter to Behavior?

- Oil density
- Oil viscosity
- Emulsion formation and maximum water content

- Volatile and semi-volatile content
  - Soluble and semi-soluble content

- The rest don't vary much among oils

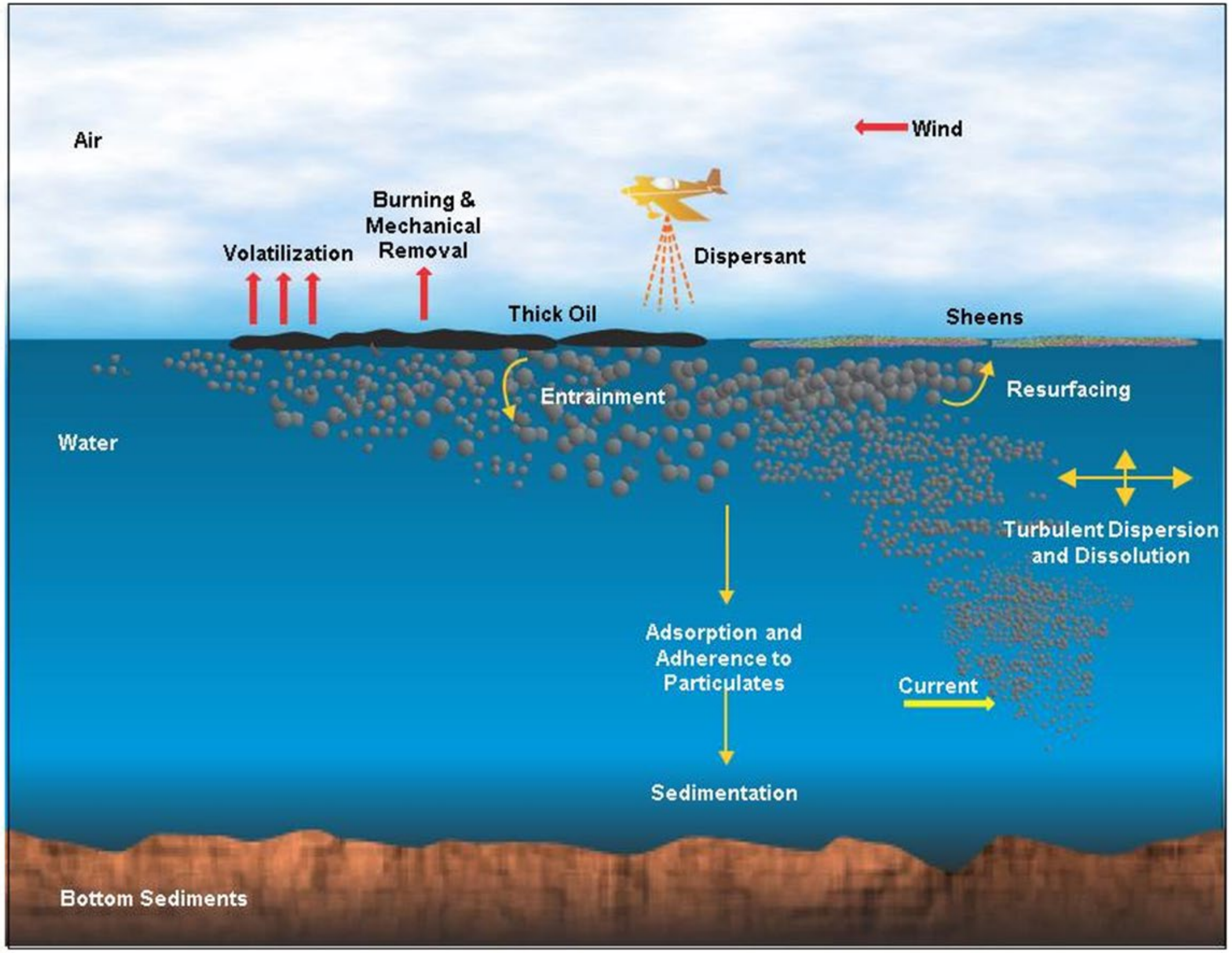
Response Model

- Model accounts for
  - Dispersant application at water surface
  - Booming
  - Mechanical removal (off water and shorelines)
  - In situ burning
- User specifies
  - Location of response actions (GIS polygon)
  - Time window
  - Efficiency/Amount per time
  - Failure thresholds (wind, waves, minimum thickness)

Important Processes – Related to Viscosity
Floating Oil Fate and Exposure in Surface Waters

Options and Time Windows for Response:

- Removal
  - Techniques vary with viscosity
  - Water in emulsions increases collection volume
- Burning – water content affects
- Dispersants less effective when oil more viscous



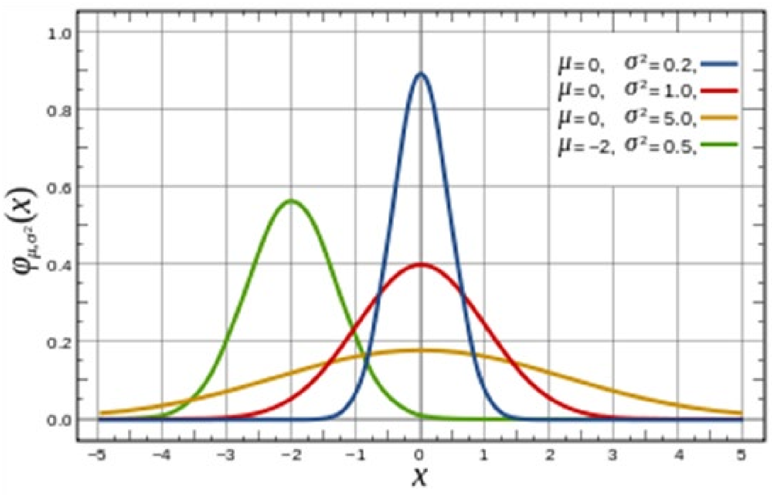
Impact:

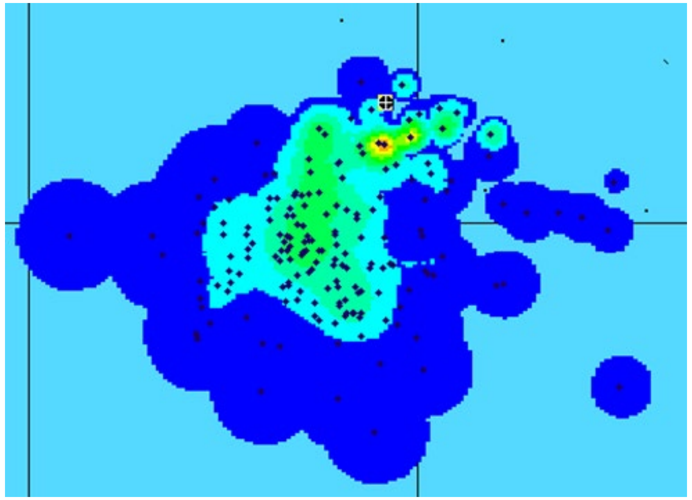
- Oil more viscous:
  - Lasts longer on water surface
  - More coating of biota and habitats
- Water column:
  - Droplets sizes are related to viscosity and turbulence levels
  - More exposure in water column with lower viscosity and higher turbulence entraining smaller droplets

Lagrangian (“Particle”) Model

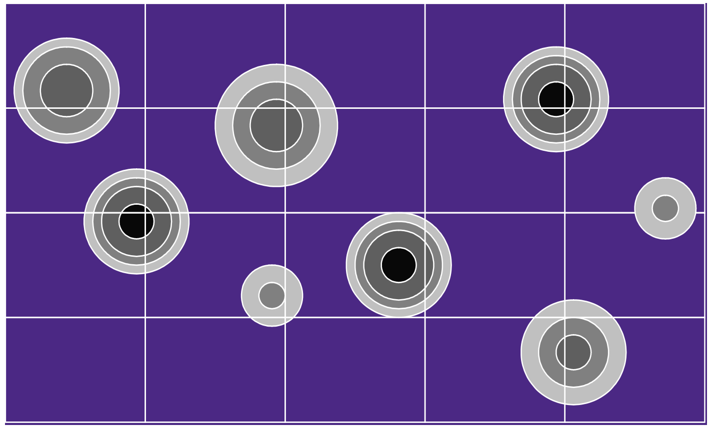
- Released mass is partitioned into sublots = Lagrangian elements (“spillets”)
- Spillets are tracked as they move with winds, currents, natural dispersion, and settling.
- 3d Dispersion – Gaussian around spillet center (better resolution with fewer spillets)
- Fate processes are calculated for each individual spillet.

- **Classify each spillet**
  - on the surface (floating)
  - particulate in the water column
  - dissolved in the water column
  - on bottom sediments
  - stranded on shoreline

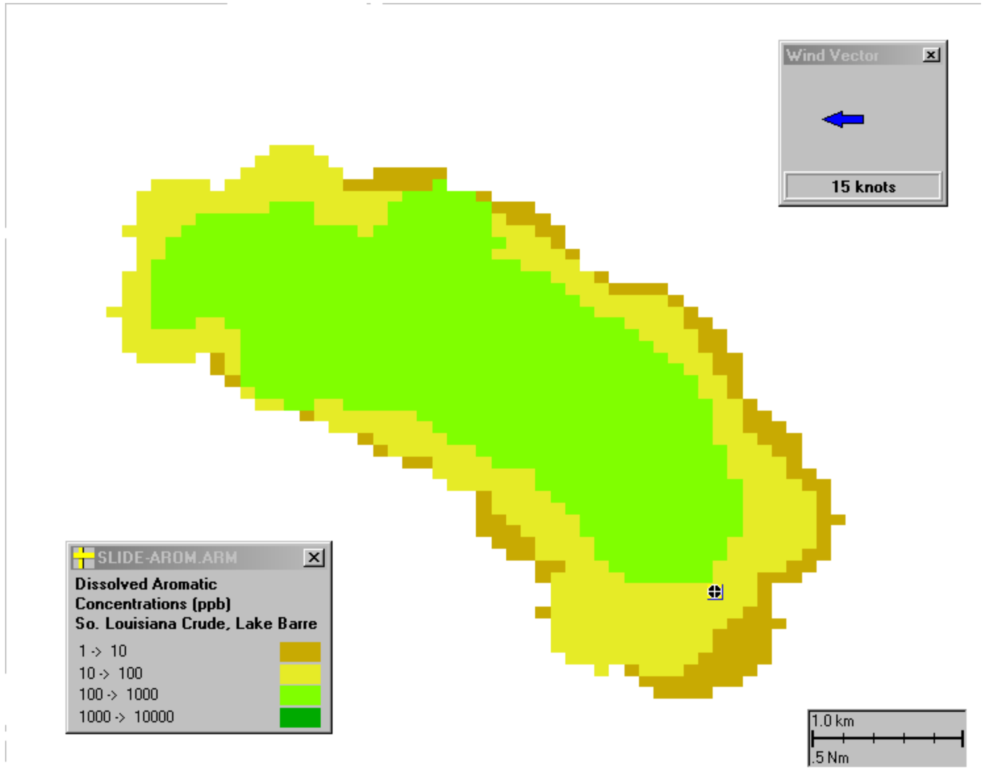




Concentrations



Horizontal cross section of LEs with Gaussian distributions of mass, projected into a grid



SIMAP Model Validation

- Developed over 3 decades, several in-depth peer reviews, validation studies – model design, algorithms and assumptions are published
- Derived from NRDA models: CERCLA Type A model (French et al. 1996); also referred to in OPA 90 NRDA regulations
- *Exxon Valdez* Oil Spill (French McCay 2004; Mar Poll Bull)
- *North Cape* Oil Spill (French McCay 2003; Mar Poll Bull)
- 20 spills (French McCay and Rowe, 2004)
- Test spills designed to verify algorithms (French and Rines 1997; French et al. 1997; Payne et al. 2007; French McCay et al. 2007)
- Deepwater Horizon (DWH) oil spill
  - in support of the Natural Resource Damage Assessment (NRDA) – NOAA (Spaulding et al. 2015, 2017; French McCay et al. 2015, 2016, 2018)
  - as part of validation study for BOEM risk assessment project (French McCay et al., 2018a,b,c)
  - Recent publications and ongoing work

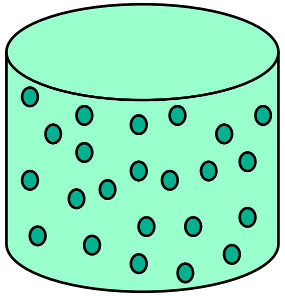
Spills where water chemistry data available to validate modeling

CHEMMAP Model Design - Track a Single Substance

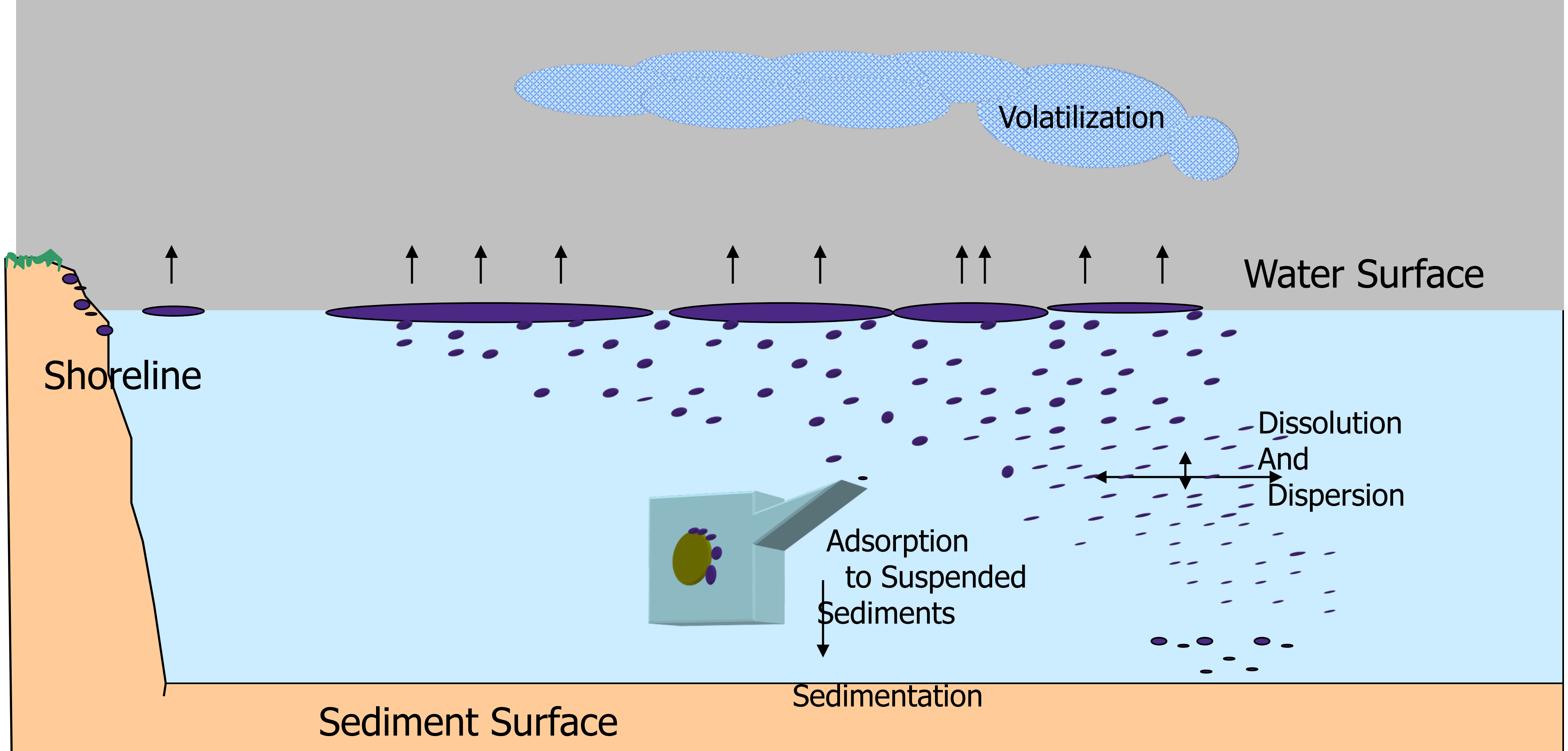
- **Classify each spillet by chemical characteristics and spill conditions**
  - on the surface (floating)
  - particulate in the water column (solid, liquid droplet or bubble)
  - dissolved in the water column
  - adsorbed to particulate in the water column
  - on bottom sediments
  - stranded on shoreline
  - in atmosphere

HNS Substance State When Spilled

- Pure Chemicals
  - Solid, powder
  - Solid, pellet
  - Solid, block
  - Liquid
  - Gas
- In Mixtures
  - Dissolved in aqueous solution
  - Particulate suspended in aqueous solution
  - Dissolved in hydrophobic solvent
  - Dissolved in and/or adsorbed to hydrophobic material suspended in aqueous solution
- Non-changing (“conservative”) substances, e.g.:
  - Plastic
  - Drifting objects
- Pathogens



HNS



Physical/Chemical Processes

Transport
Spreading
Entrainment
Dispersion

Dissolution
Volatilization
Adsorption
Buffering (pH)

Settling
Sediment mixing and partitioning
Degradation (reaction or transformed to non-toxic substance)

Classification Systems

- Hazard classifications
  - International Maritime Dangerous Goods (IMDG) code classifies HNS by their potential hazards relative to transportation
  - Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) - HNS shipped in bulk; potential to enter the marine environment and cause hazards to both human and marine environment
  - Atlantic Regions' Coastal Pollution Response (ARCOPOL) programme of 2012 - parameters determining the fate, behavior, and weathering of select bulk HNS in the European region (Cunha et al. 2015)
- Classification by Physical Behaviour in Water
  - European Union: Standard European Behavior Classification (SEBC) – describe dominant behaviors in water
    - Bonn Agreement Counter Pollution Manual for HNS
    - HNS-MS project (Legrand et al. 2017)
  - RPS (ASA) CHEMMAP Model and Assessments – properties determining fate and exposure

EU Standard European Behavior Classification (SEBC)

Category	Behavior Class	Density (kg/m^3)	Vapour Pressure (kPa)	Solubility (mg/L, for applicable states)
Gases	Gases (G)	< 1023	> 3	≤ 10 for gas
	Dissolving Gases (DG)		> 3	> 10 for gas
Evaporators	Evaporators (E)		> 3	≤ 1 for liquids
	Dissolving Evaporator (DE)		> 3	> 1 for liquids
Floaters	Floaters (F)		< 0.3	≤ 0.1 for liquids; ≤10 for solids
	Floating Evaporators (FE)		0.3 – 3	≤ 0.1 for liquids
	Floating Evaporating Dissolvers (FED)		0.3 – 3	0.1 – 5 for liquids
	Floating Dissolvers (FD)		< 0.3	0.1 – 5 for liquids; > 10 for solids
Dissolver	Dissolvers (D)		≤ 10	> 5 for liquids; > 99 for solids
	Dissolving Evaporators (DE)		> 10	> 5 for liquids
Sinkers	Sinkers (S)	> 1023	(not applicable)	≤ 0.1 for liquids; ≤ 10 for solids
	Sinking Dissolvers (SD)		(not applicable)	> 0.1 for liquids; > 10 for solids

RPA/ASA HNS Classification

Density Relative to Water (g/cm^3)	Solubility (ppm)	Volatility – Vapor Pressure
Floater: $\rho < 1.0$	Highly soluble: > 1000	Highly volatile: $> 10^{-3}$ atm
Neutral: $1.01 < \rho < 1.03$	Soluble: 100 - 1000	Semi-volatile: 10^{-7} - 10^{-3} atm
Sinker: $\rho > 1.03$	Semi-soluble: 1 - 100	Non-volatile: $< 10^{-7}$ atm
	Insoluble: < 1	

RPS/ASA HNS Classification

#	Buoyancy in Water	Solubility Behavior	Volatility	Example Modeled	Others in Category
1	floater	highly soluble	highly volatile	Benzene, Methyl Ethyl Ketone (MEK)	Acetaldehyde, ammonia, ethylenediamine, methanol, isopropanol, triethylamine
2	floater	semi-soluble	highly volatile	Styrene	Cyclohexane, toluene, ethylbenzene, xylenes
3	sinker	highly soluble	highly volatile	Trichloroethylene (TCE)	Chloroform, Furfural, Hydrochloric acid
4	sinker	highly soluble	semi-volatile	Ethylene Glycol	Phenol
5	sinker	soluble	highly volatile	Carbon Tetrachloride	Chlorobenzene
6	sinker	semi-soluble	semi-volatile	Naphthalene	Tetraethyl Lead
7	sinker	highly	non-volatile		Sodium Hydroxide
8	Neutrally buoyant	(assumed soluble)	(assumed zero)	Conservative HNS, 10% Aqueous Solution	Aqueous Solutions

Approach for Screening Analysis

- Classified bulk chemicals by physical behavior
- Spill modeling of representative chemicals
  - Determine fate on and in water column
    - Floating, particulate, dissolved fractions
    - Dissolved concentrations
  - Peak exposure concentrations in time
    - Identify threshold of concern
    - Volume exposed > threshold
- Used results from physical behavior class to infer results for other chemicals in class

Effects Thresholds

Aromatic HC	µg/L
Benzene	351
Ethylbenzene	39
Naphthalene	26
Styrene	47
Toluene	102
Xylenes	35

Chemical	µg/L
Acetaldehyde	210
Ammonia	72
Carbon Tetrachloride	20
Chlorobenzene	2
Cyclohexane	240
Ethylene glycol	10,000
Ethylenediamine	1,400
Tetraethyl Lead	2
Trichloroethylene	170

Maximum Volume (million m^3) Above Effects Threshold for 100 m^3 of Chemical Spilled

Threshold (μg/L = ppb)	Light Wind Conditions	Strong Wind Conditions
1	860	5,523
10	559	2,798
100	282	393
1,000	39	40
10,000	6	2
100,000	1	<1

Determinants for Larger Volume Impacted

- More mass spilled
- More soluble
- Floating chemicals → lower concentrations
  - Surface release – more initial spreading and volatilization before dissolves
  - Deep water – dispersing as droplets rise to surface
- Toxicity: lower threshold
- Volatility – if lower, remains longer before volatilizes

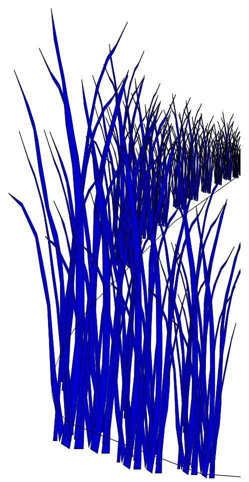
Biological Exposure Pathways

- Oil: Surface smothering/coating exposure
  - Beaches (rocky, gravel, sand)
  - Shoreline habitats (wetlands, mangroves, sea grasses, mud flats)
  - Wildlife (birds, mammals, reptiles, air-breathing stages of amphibians)

- Subsurface toxicity (dissolved components)
  - Fish and invertebrates
  - Aquatic plants

Shoreline and Aquatic Habitats

- Habitats affected by
  - Smothering by oil – shorelines and wetlands
    - Vegetation: 1 kg/m^2
    - Invertebrates: 100 g/m^2
  - Lethal concentrations in water - aquatic habitats
- Sigmoid recovery curve over time from 100% loss to 99% recovery
  - Losses proportional to recovery curve



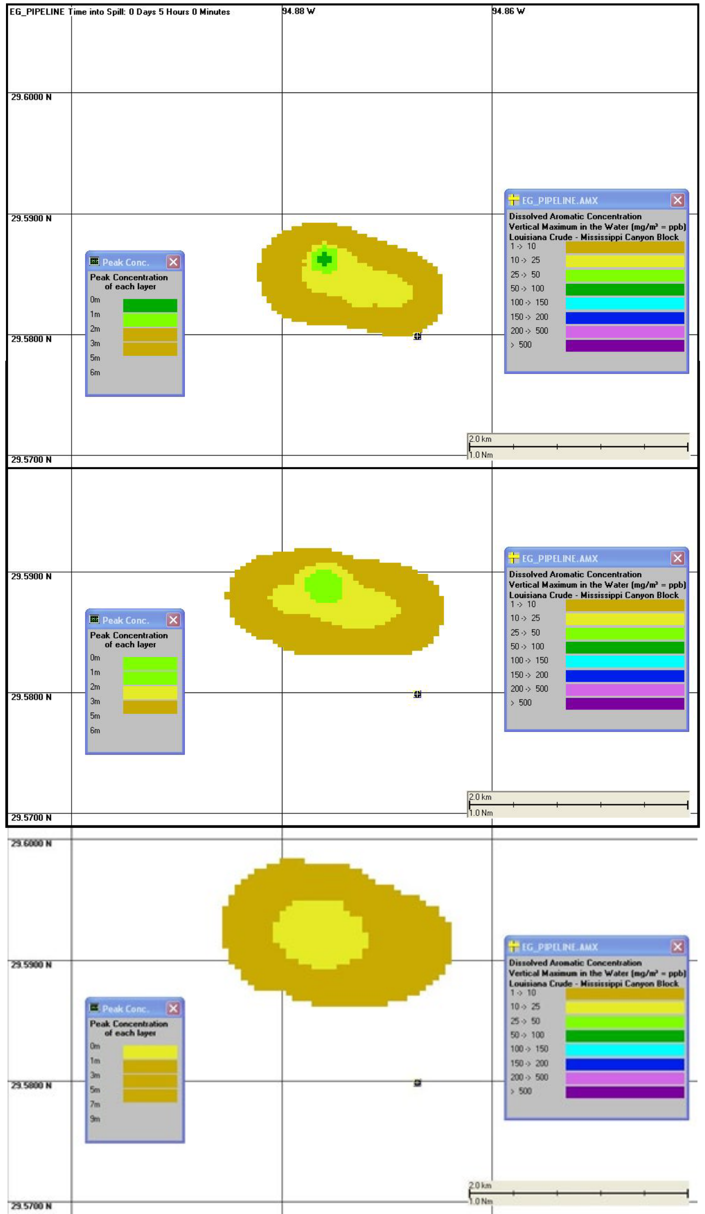
Wildlife Effects Threshold

- Calculate area swept by oil > threshold thickness

- French-McCay (2009, 2016) developed surface oil thickness thresholds:
  - Lethal threshold: 10 g/m^2
  - Sublethal threshold: 1 g/m^2
- Basis
  - Experimental & field observations (few) suggest
    - ~10 g/m^2 as lethal threshold
    - ~1 g/m2 sublethal threshold
  - DWH NRDA – Lethal and reproductive effects on dolphins in areas exposed to >10 g/m^2 floating oil

Quantification of Exposure and Toxicity for Aquatic Biota

- **Complications**
  - **High spatial and temporal variability of**
    - **In-water concentrations**
    - **Oil composition changes with weathering**
  - **Movements and patchiness**
    - **Planktonic**
    - **Active swimming**
    - **Stationary**
  - **Sensitivity varies (species, life stage, physiological status)**
- **Modeling Solutions**
  - **Traditional quasi-steady state over-simplified**
  - **Dynamic fate models and concentrations, but exposure and toxicity treated as if constant using spatial maximum or average concentration**
  - **Dynamic fate, *exposure and toxicity* modeling – most realistic**

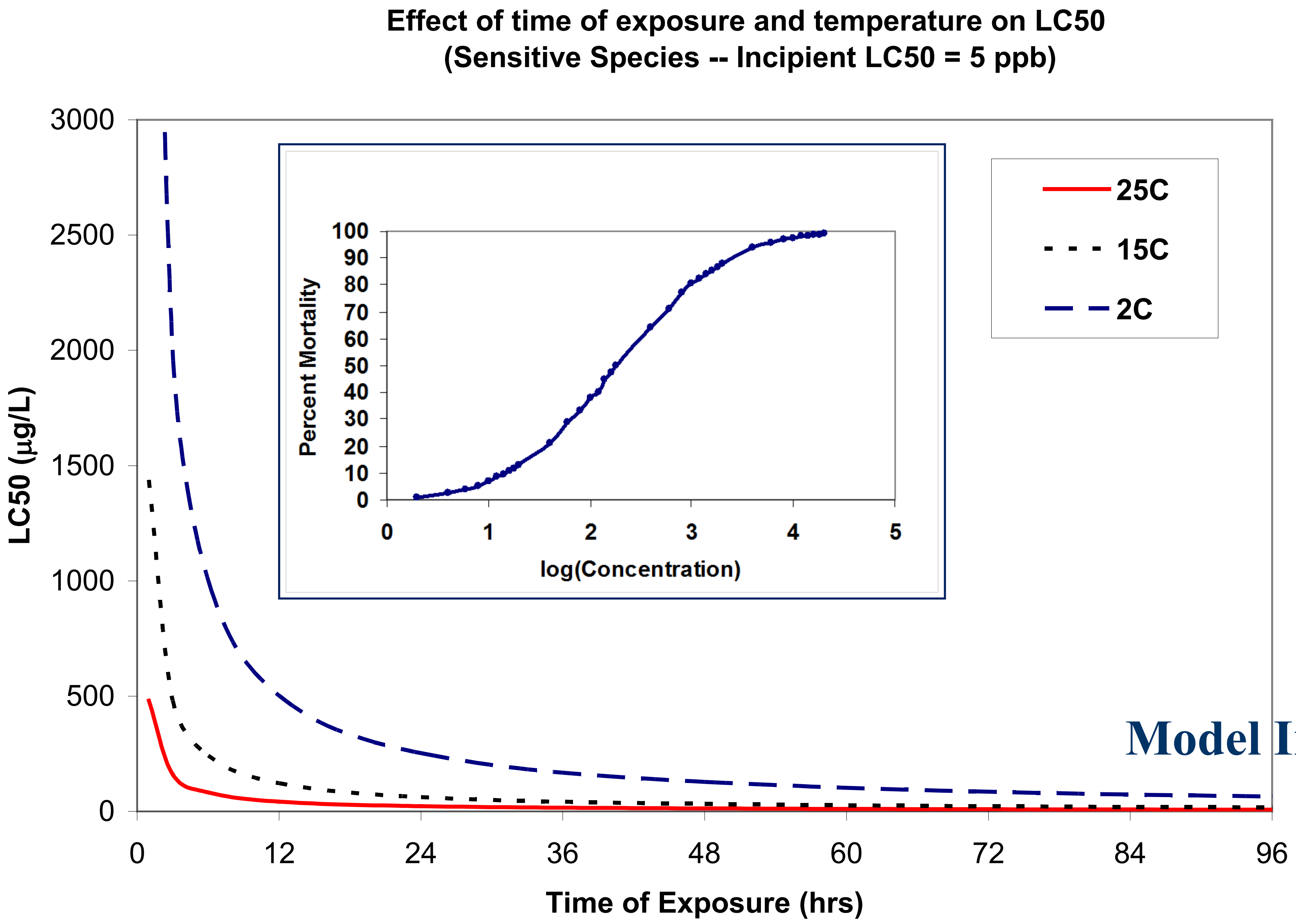


Activity-Based Exposure Model: Fish and Invertebrates

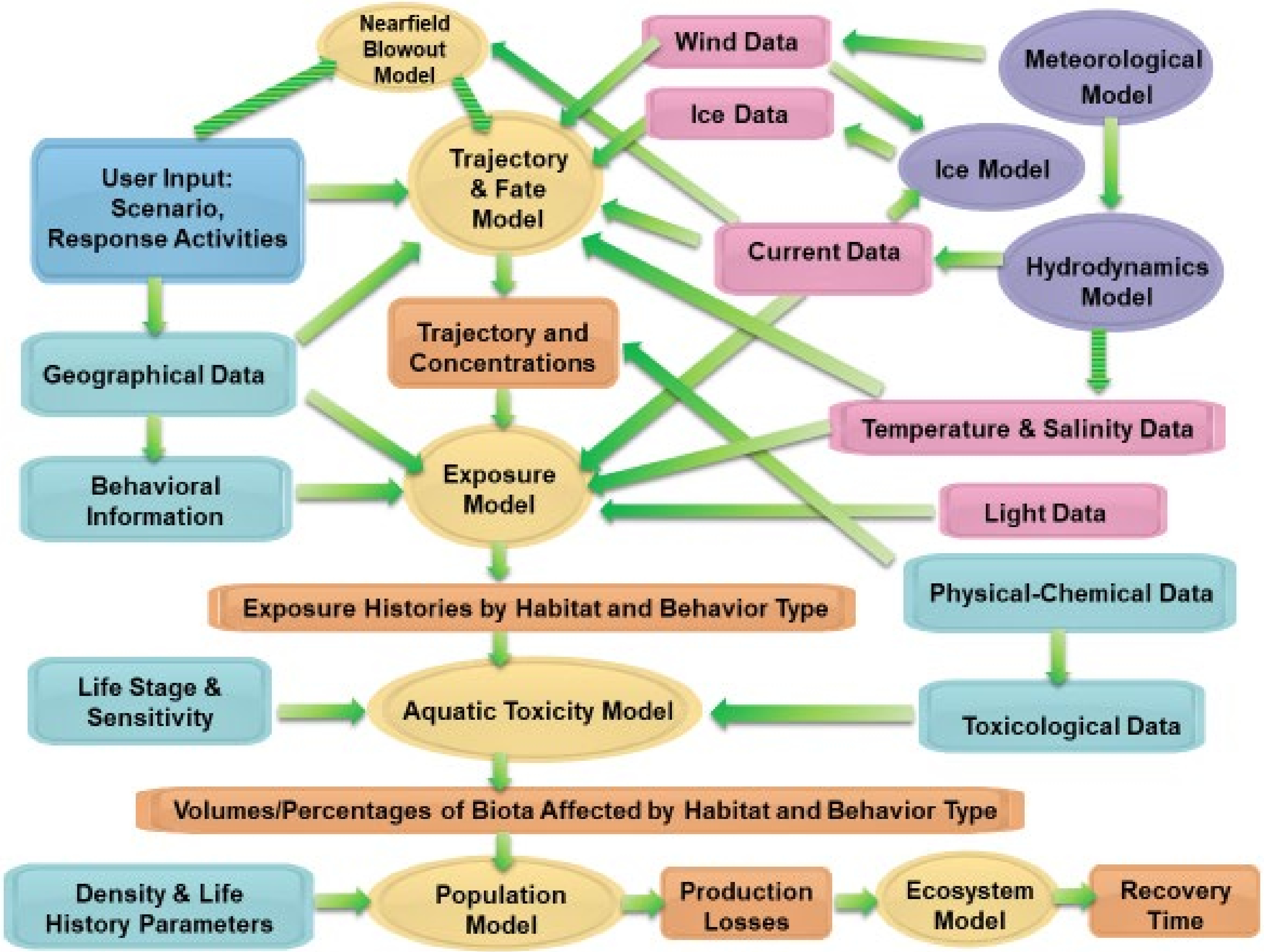
- Movements of organisms are tracked using Lagrangian Elements (LEs) to calculate and track exposure of individuals
  - External concentrations of each pseudo-component
  - Body burden
  - Light, temperature
- Organisms classified by behavior
  - Swimming
  - Drift with currents
  - Stationary (benthic)
- Define behavior inputs
  - Swim speed
  - Vertical zone
  - Diel migration

- Acute toxic effects
  - Exposure duration – while total concentration > threshold
  - Mean concentration of each pseudo-component during exposure duration
  - Oils: Additive effects of mixture
- Dose-response: use LC50 (or EC50) adjusted for
  - Oils: Mixture composition
  - LC50 or EC50 of each component
  - Duration of exposure
  - Temperature
  - Light exposure (phototoxicity)

Model Corrects LC50 for Duration and Temperature of Exposure



Model Input = $LC50_{\infty}$


Nearfield Blowout Model
Wind Data
Meteorological Model
Ice Data
Trajectory & Fate Model
User Input: Scenario, Response Activities
Ice Model
Current Data
Hydrodynamics Model
Trajectory and Concentrations
Geographical Data
Temperature & Salinity Data
Exposure Model
Behavioral Information
Light Data
Physical-Chemical Data
Exposure Histories by Habitat and Behavior Type
Life Stage & Sensitivity
Aquatic Toxicity Model
Toxicological Data
Volumes/Percentages of Biota Affected by Habitat and Behavior Type
Density & Life History Parameters
Population Model
Production Losses
Ecosystem Model
Recovery Time

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Deepwater Horizon Spill – Technical Reports and Publications

Near-field

- Spaulding, M. Z. Li, D. Mendelsohn, D. Crowley, D. French-McCay, and A. Bird, 2017. Application of an Integrated Blowout Model System, OILMAP DEEP, to the Deepwater Horizon (DWH) Spill. Marine Pollution Bulletin 120: 37-50.

Far-field

- French-McCay, D.P, K. Jayko, Z. Li, M. Horn, Y. Kim, T. Isaji, D. Crowley, M. Spaulding, L. Decker, C. Turner, S. Zamorski, J. Fontenault, R. Shmookler, and J.J. Rowe, 2015. Technical Reports for Deepwater Horizon Water Column Injury Assessment – WC_TR14: Modeling Oil Fate and Exposure Concentrations in the Deepwater Plume and Cone of Rising Oil Resulting from the Deepwater Horizon Oil Spill.
- French-McCay, D., M. Horn, Z. Li, K. Jayko, M. Spaulding, D. Crowley, and D. Mendelsohn, 2018. Modeling Distribution, Fate, and Concentrations of Deepwater Horizon Oil in Subsurface Waters of the Gulf of Mexico. Chapter 31 in: S.A. Stout and Z. Wang (eds.) Case Studies in Oil Spill Environmental Forensics. Elsevier, ISBN: 978-O-12-804434-6, pp. 683-736.
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