SINTEF

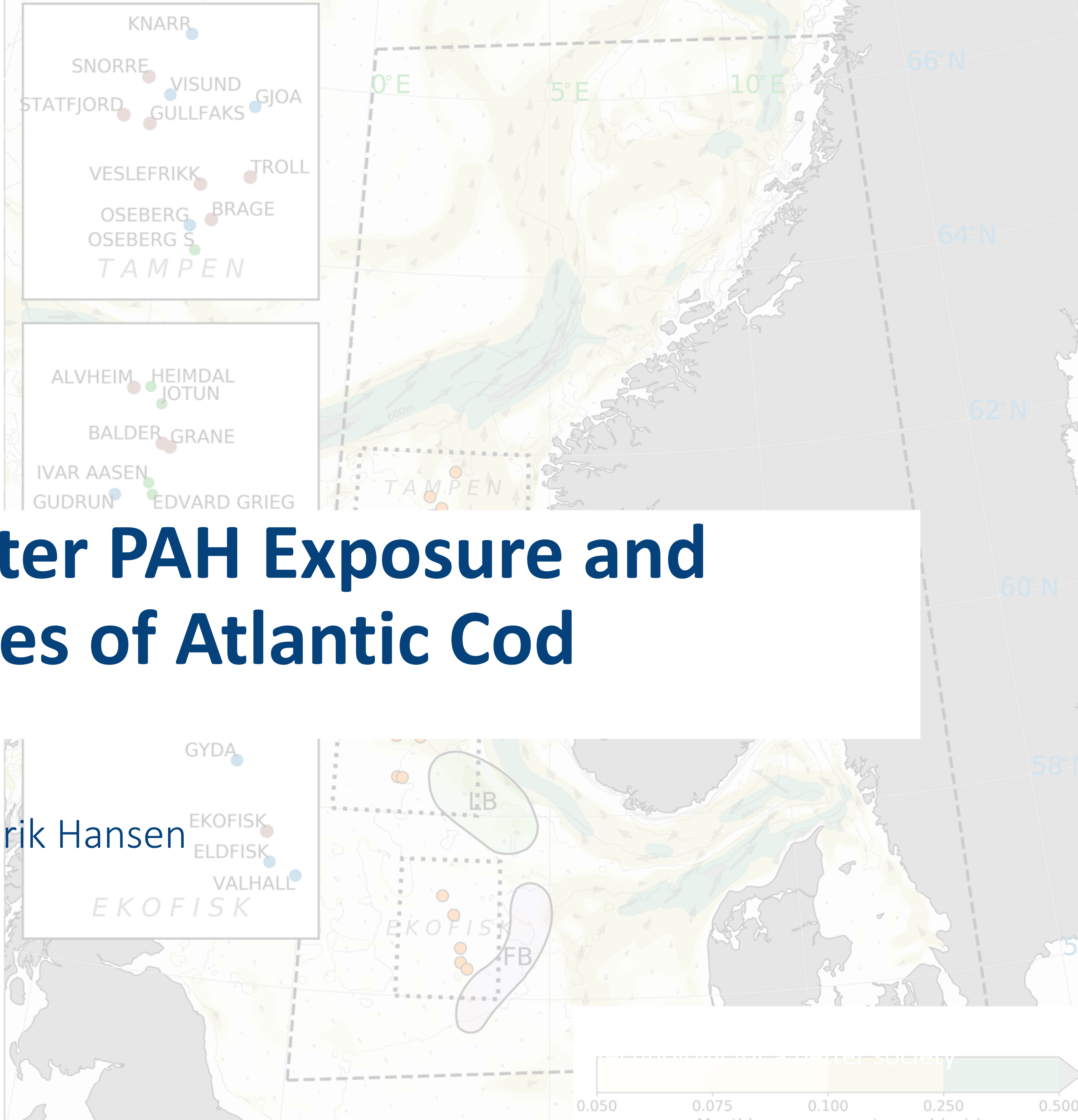
North Sea Produced Water PAH Exposure and Uptake in Early Life Stages of Atlantic Cod

A modelling study

Raymond Nepstad, Jørgen Skancke, Bjørn Henrik Hansen

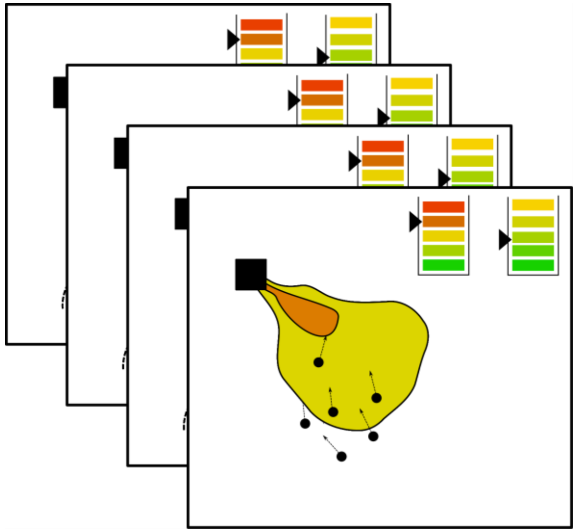
Forum for offshore miljøovervåkning

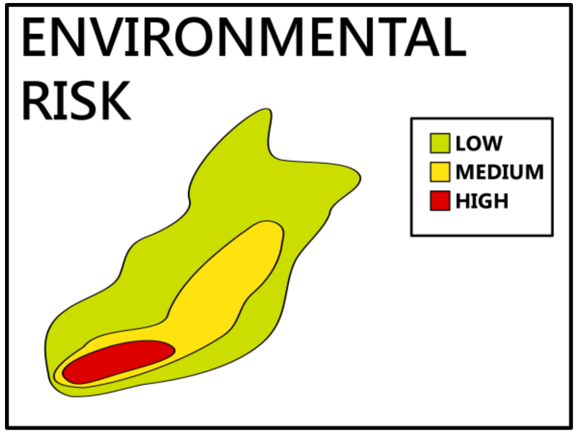
19 October 2021, Oslo



The DREAM-MER project

- Extend the DREAM model: new biology-based tools for environmental impact and risk assessment of produced water discharges
- Project running from 2019 – 2021
- SINTEF Ocean and Akvaplan-niva
- Supported by: AkerBP, Equinor, NOROG, Total, Vår Energi





SINTEF

Akvaplan-niva

Overview

- Paper intro and background
- Model and method
- Results
- Conclusion

SINTEF

Paper

- Coupled fate model with super-individual and toxicokinetic models
- Investigate biological exposure and uptake of PAH components from produced water discharges in the North Sea
  - Atlantic cod early life stages
- Co-authors: Bjørn Henrik Hansen, Jørgen Skancke
- More details in the paper

Marine Environmental Research 163 (2021) 105203

Contents lists available at ScienceDirect

Marine Environmental Research

journal homepage: www.elsevier.com/locate/marenvrev

ELSEVIER

Check for updates

North sea produced water PAH exposure and uptake in early life stages of Atlantic Cod

Raymond Nepstad *, Bjørn Henrik Hansen, Jørgen Skancke

SINTEF Ocean, Trondheim, Norway

ABSTRACT

Produced water discharges from offshore oil and gas platforms represent a significant source of petroleum components such as polycyclic aromatic hydrocarbons (PAHs) released to the ocean. High molecular weight PAHs are persistent in the environment and have a potential for bioaccumulation, and the investigation of their fate and uptake pathways in marine life are relevant when assessing environmental risk of produced water discharges. To study the exposure and uptake of 2–5 ring PAHs in early life stages of Atlantic Cod in the North Sea, we run a coupled fate and individual-based numerical model that includes discharges from 26 platforms. We consider 26 different PAH components in produced water which biodegrade with primary degradation rates; intermediate degradation products are not included. Model simulations are run covering multiple years (2009–2012) to study annual exposure variability, while a one-day time slice of spawning products from the peak spawning season are followed. By covering multiple release points and large spatio-temporal scales, we show how individuals can be exposed to produced water from multiple regions in the North Sea. We find that a combination of oceanic fate processes and toxicokinetics lead to markedly different compositions in the predicted internal concentrations of PAHs compared to discharge concentrations; for instance, naphthalene makes up 30% of the total discharged PAHs, but contributes to at most 1% of internal concentrations. In all simulations we find the predicted total internal PAH concentration (26 components) to be below 1.2 nmol/g, a factor of 1000 less than concentrations commonly associated with acute narcotic effects.

1. Introduction

Produced water (PW) discharges from offshore oil and gas production represent the largest discharge to the marine environment worldwide, with approximately 1.3 x 10^8 m^3 released annually on the Norwegian continental shelf (NCS). PW contains a mixture of formation water, oil, gas, injected fresh/brine water and added production chemicals. The formation water contains a mixture of dissolved inorganic and organic components, and the composition varies between different reservoirs (Neff et al., 2011). Total PW discharges from activities on the NCS in 2017 included 129 tons polycyclic aromatic hydrocarbons (PAHs) (NOROG, 2018). Despite being a small fraction (0.306%) of the total composition of produced water, PAHs are considered a key risk component (Beyer et al., 2020). These PAHs can be dissolved in the water, present in dispersed oil droplets or adsorbed to particulates (Faksness et al., 2004). Different PAHs display varying lifetimes and biological uptake properties in the ocean. In general biodegradation rates tend to decrease with increasing molecular weight of PAHs (Lofthus et al., 2018), and the potential for bioaccumulation (bioconcentration) tend to increase with molecular weight (De Hoop et al., 2013).

The Atlantic cod (*Gadus morhua*) is found throughout the Northern Atlantic Ocean where it has been one of the most commercially important species for centuries (Otterå, 2004). Cod populations in the North Sea have declined (Brander, 2005), and it is labelled vulnerable on the IUCN Red List of Threatened species. Apart from overfishing, recruitment failure is generally believed to be a main contributor to the decline, the causes of which are complex (Huserbråten et al., 2018; Akimova et al., 2019). Important spawning grounds for Atlantic cod in the North and Norwegian Seas are found in vicinity of oil production fields with produced water discharges (see Fig. 1 and Akimova et al., 2019; Sundby et al., 2017). The spawning season for cod in North Sea extends from January to May, with a peak in February and March (Sundby et al., 2017), and the eggs develop over a period of approximately 100 degree-days before hatching (Fraser et al., 1988). After fertilization, eggs are positively buoyant in seawater and are therefore found in the upper water masses. After hatching the larvae drift with ocean currents and perform vertical migration (Vikebø et al., 2007).

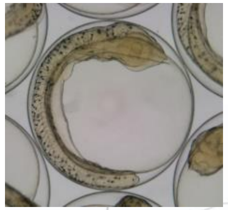
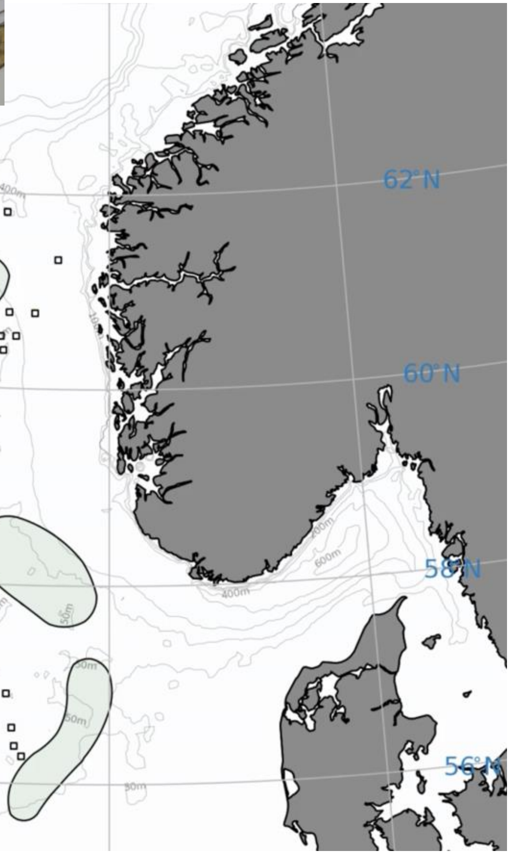
Exposure of early developmental life stages (ELS) to petrogenic compounds has shown to cause acute toxicity as well as a range of sub-lethal effects. Atlantic cod and Atlantic haddock (*Melanogrammus aeglefinus*) embryos exposed to oil dispersions showed craniofacial deformations in hatched larvae. This occurred for exposure concentrations above 0.76 (haddock) and 2.8 (cod) μg TPAH/L, and associated with TPAH internal concentrations of 542 ng/g (wet weight) for cod (Sørensen et al., 2017). In another study, cardiotoxicity and severe craniofacial deformations were observed in cod larvae after embryonic exposure to PW extracts corresponding to 50-500-fold dilutions of PW (ranging 2.5–34 μg TPAH/L) (Hansen et al., 2019). These studies have only measured

* Corresponding author.
E-mail address: raymond.nepstad@sintef.no (R. Nepstad).

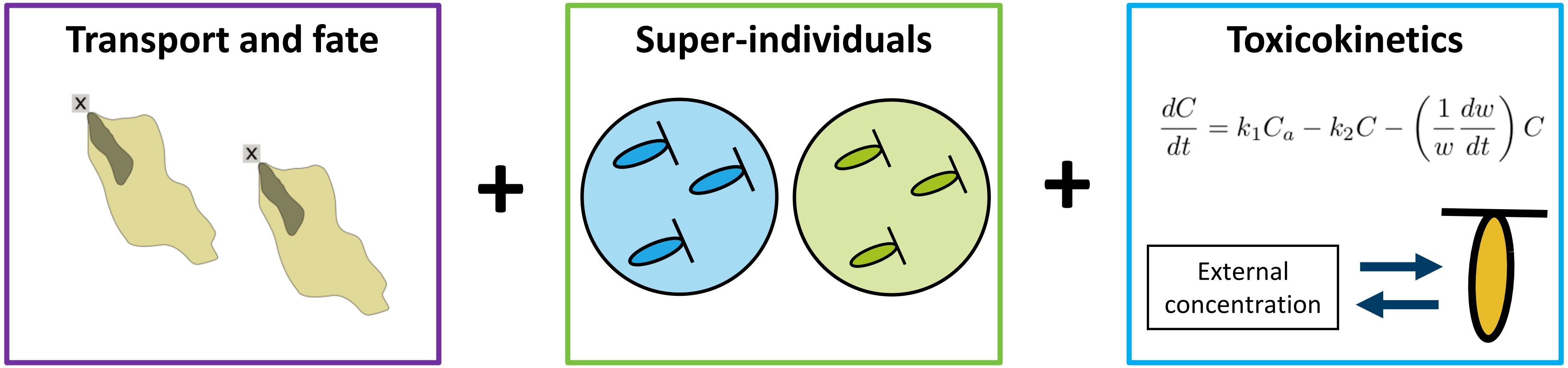
https://doi.org/10.1016/j.marenvres.2020.105203
Received 5 June 2020; Received in revised form 23 October 2020; Accepted 24 October 2020
Available online 27 October 2020

North Atlantic Cod

- Commercially important species
- North Sea population have declined, labeled vulnerable (Brander 2005, Huserbråten 2018)
- Spawning grounds near PW sources in North Sea
- Focus on early life stages (ELS, eggs and larvae)

Model background



Fate model (DREAM)

- Discharge
- Dispersion
- Biodegradation
- Particle model

Super-invididual model

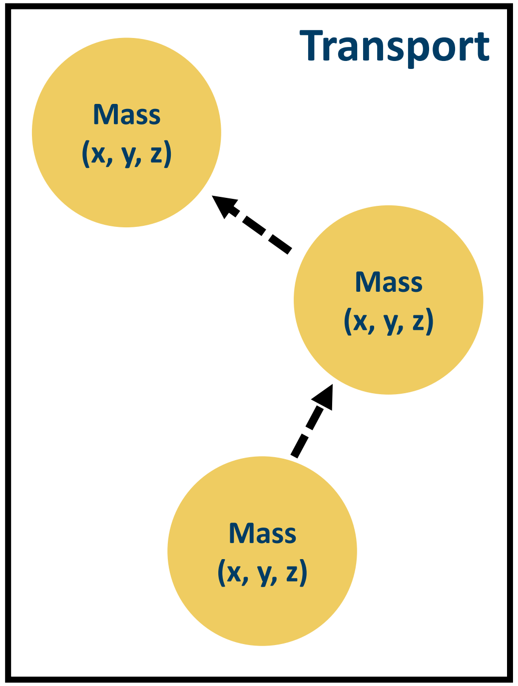
- Biological representation
- Particle transport
- Exposure concentrations from fate model

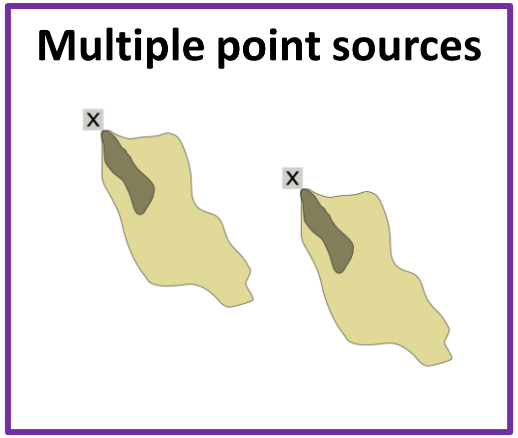
Toxicokinetic model

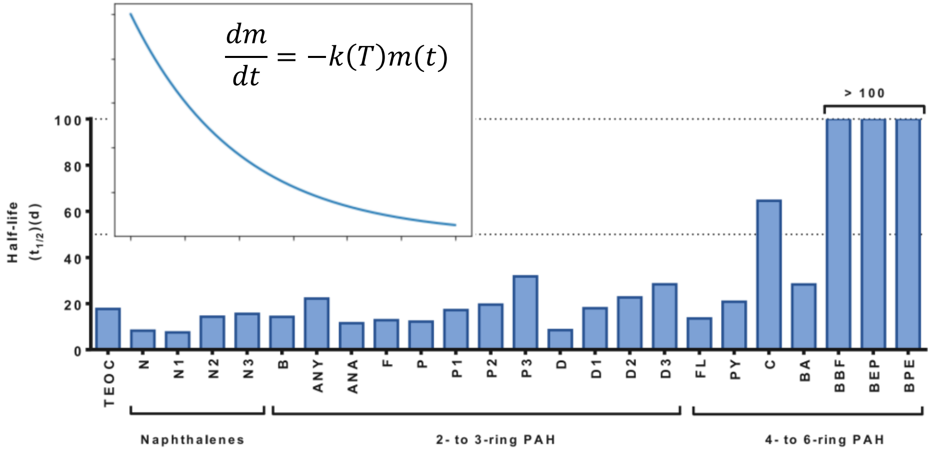
- Translate external to internal concentrations

Fate model

- DREAM: Lagrangian particle model
  - Discharge represented individual particles
  - Particles transported with currents and turbulence
  - Particles -> concentration grids
- Discharge
  - Multiple point sources
  - Multiple components (masses)
- Biodegradation
  - First-order kinetics
  - PAH half-lifes from Lofthus *et al.* 2018







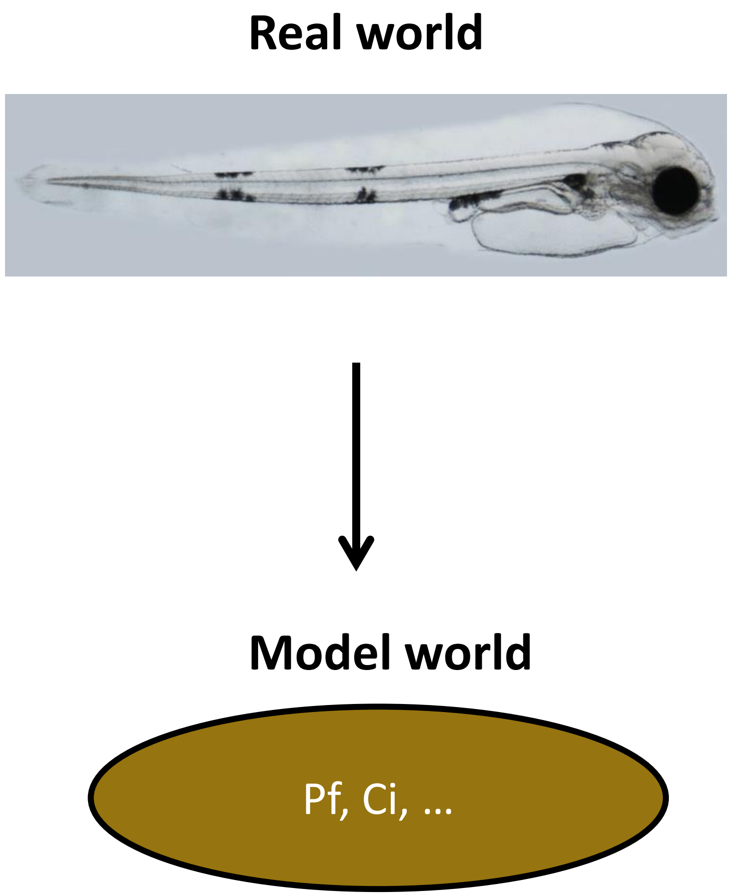
From: Lofthust *et al.* (2018)

SINTEF

Biological representation model

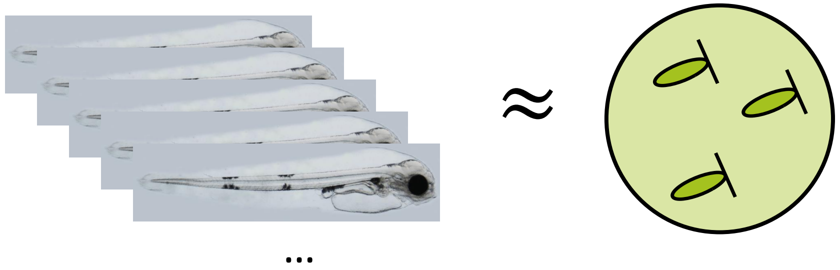
Simplified representations of a complex reality

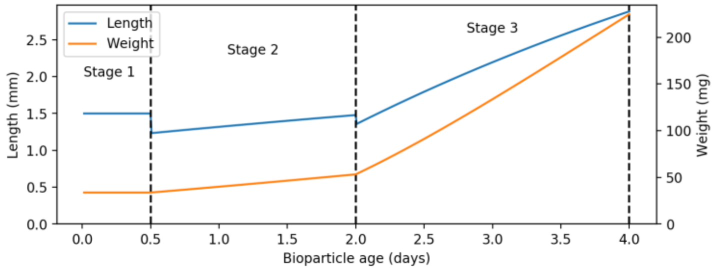
- Balance biological realism, model complexity and flexibility of use
- Focus on exposure -> uptake -> internal concentrations
- Model biological parameters affecting these (e.g. lipid fraction, size/growth, buoyancy, …)
- More than “tracer particles”, but not a bio-energetic or ecosystem model

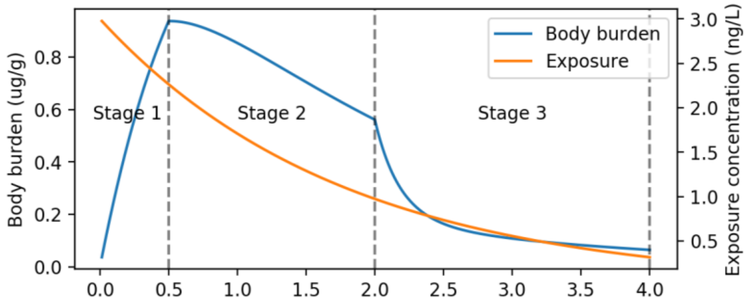


Super-individual model approach

- Each super-individual represents a fraction of a population
  - Multiple identical individuals
- Each super-individual has its own state
  - Dynamic: age, position, stage, weight, internal concentrations
  - Stage-fixed: growth rate, lipid content, behaviour
- Stages changed with age, can have different properties
  - Assumption: Mass conservation on stage change





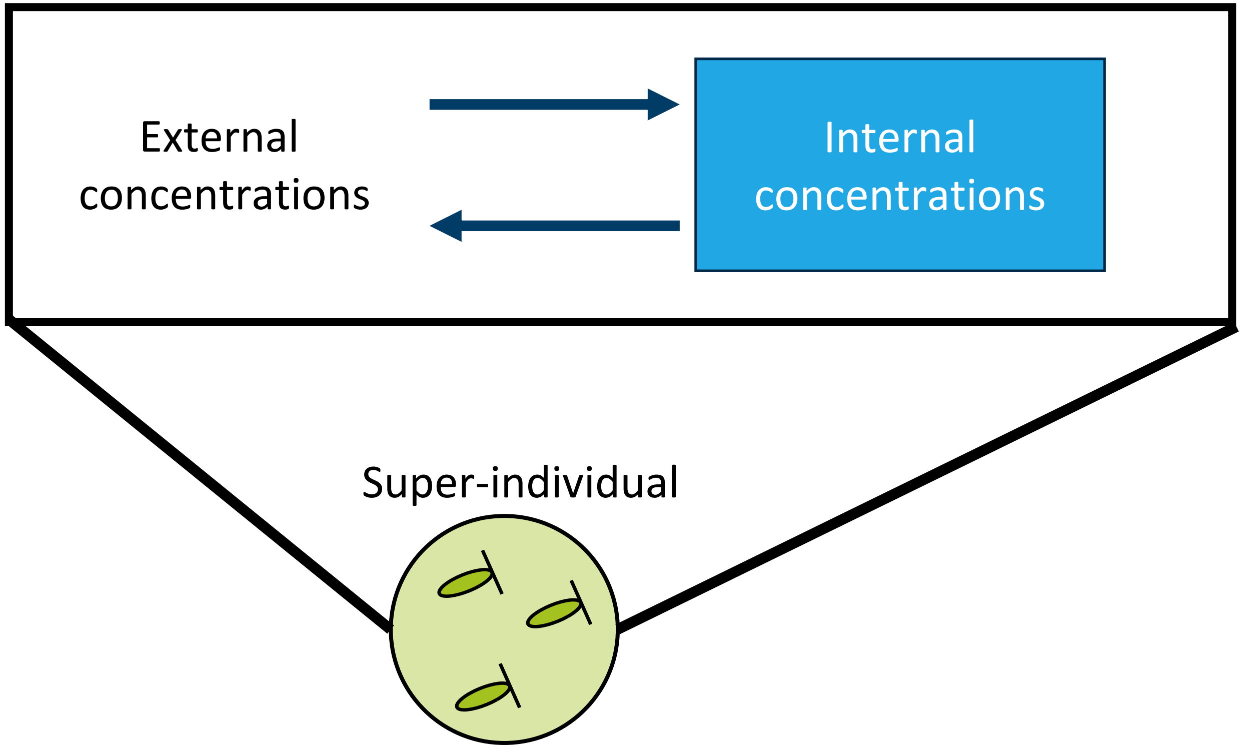


SINTEF

Toxicokinetic model

From fate model (x, y, z, t)

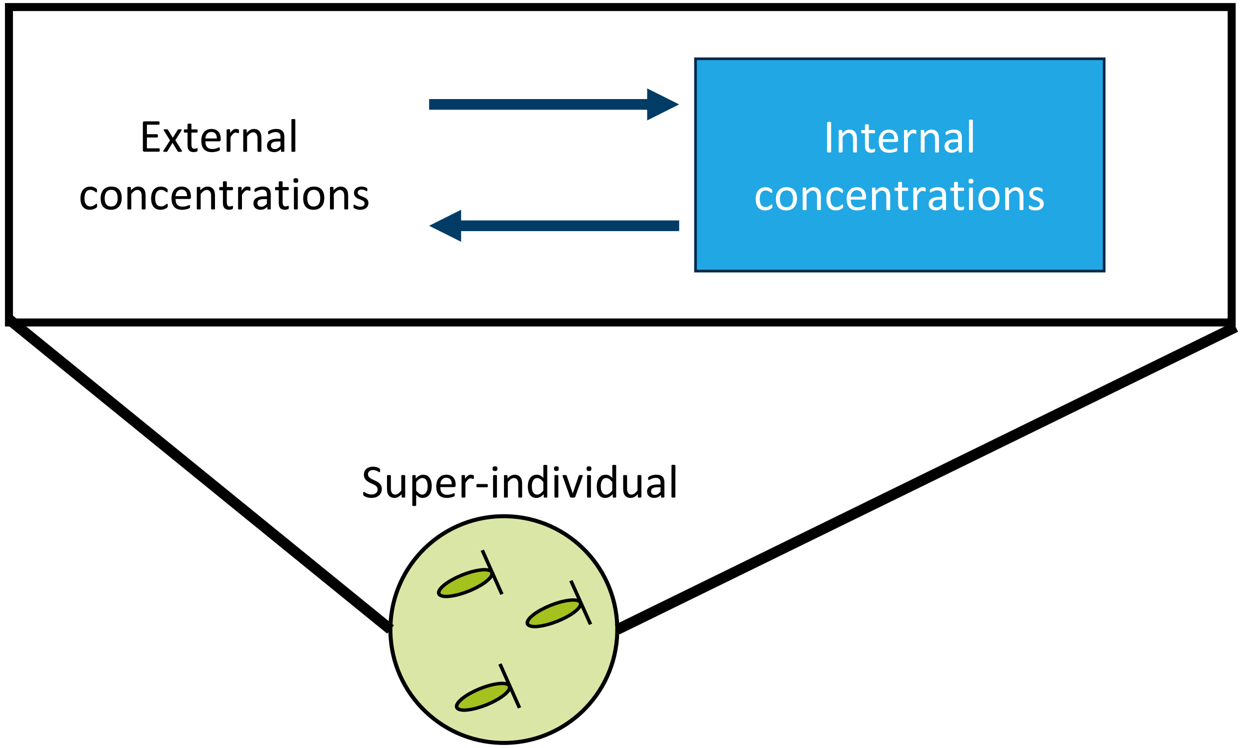
$$\frac{dC}{dt} = k_e(P_{iw}C_a - C) - \frac{1}{w}\frac{dw}{dt}C$$



SINTEF

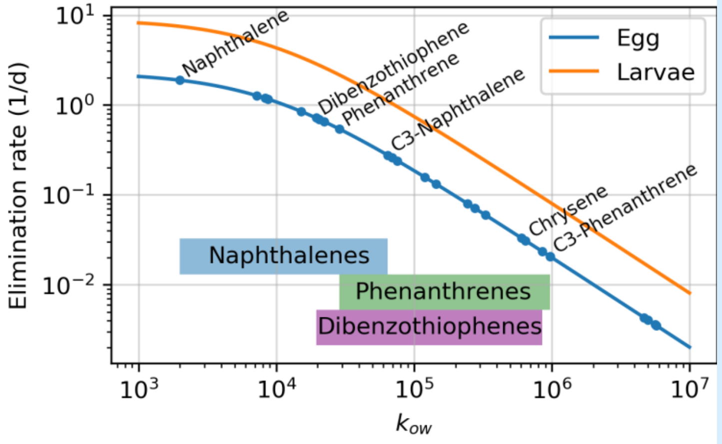
Toxicokinetic model

$$\frac{dC}{dt} = k_e(P_{iw}C_a - C) - \frac{1}{w}\frac{dw}{dt}C$$

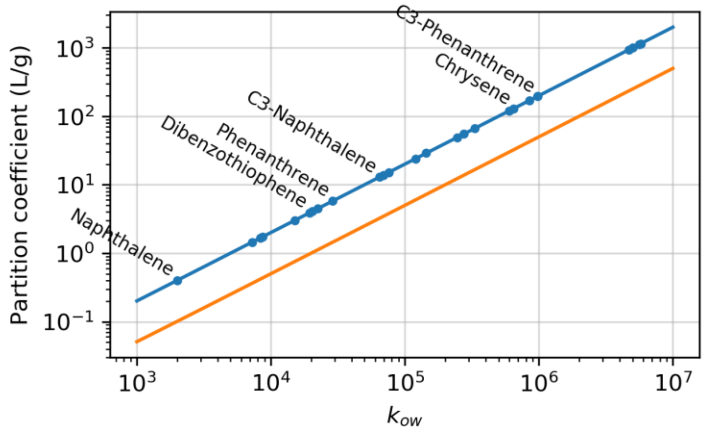


OMEGA model (Hendriks et al 2001)

$$k_e = \frac{w^{-\kappa}}{\rho_0 + \frac{\rho_1}{k_{ow}} + \frac{1}{\gamma_0}} \frac{1}{f_l(k_{ow}-1)+1}$$

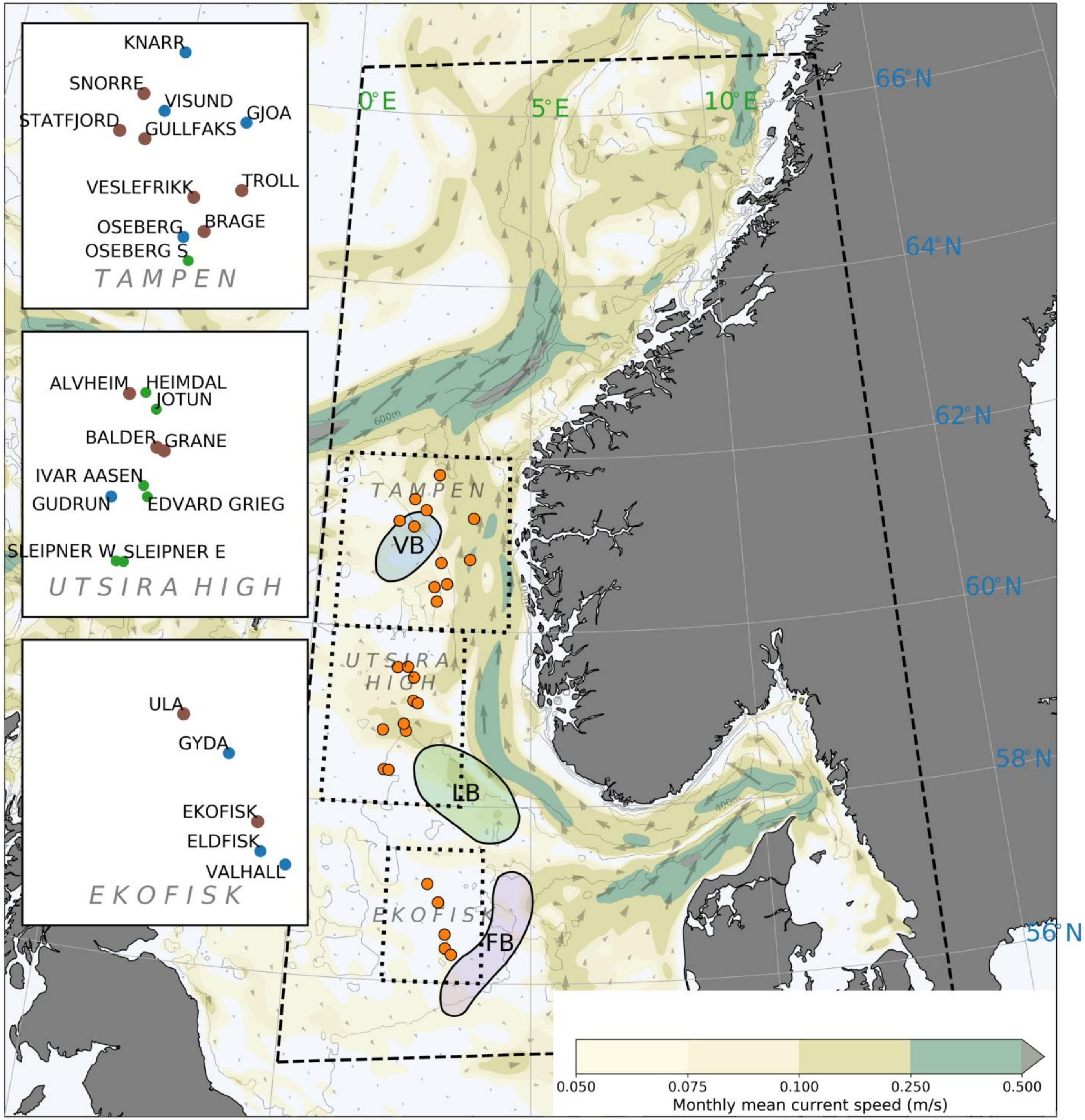


$$P_{iw} = f_l(k_{ow}-1)+1$$



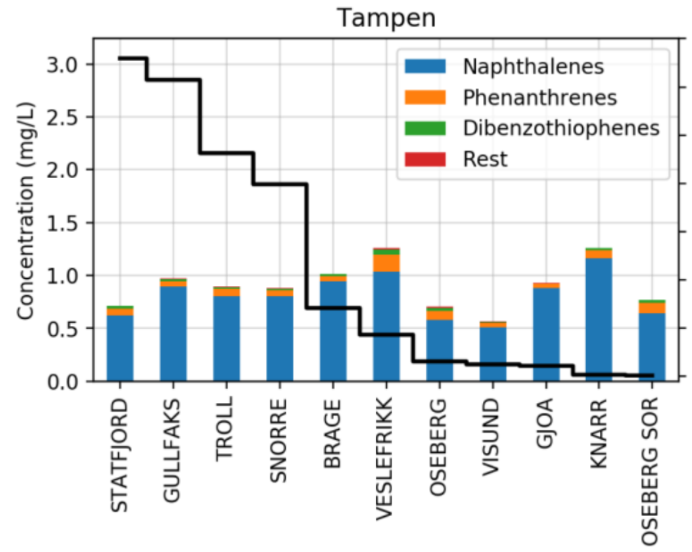
Study site

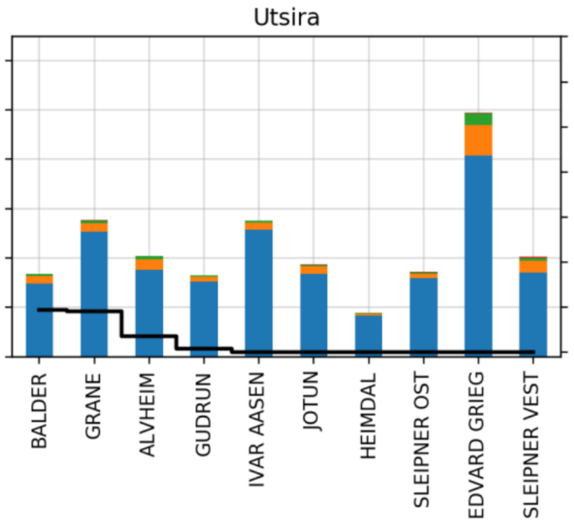
- 26 point PW sources in the North Sea
  - NPD fact pages
- 26 PAH components in PW discharge
  - Site-specific profiles (MDIR)
- Cod spawning grounds
  - Viking Bank, Linge Bank, Fisher Bank
- Ocean currents: 4 km SINMOD archive for 2009-2012

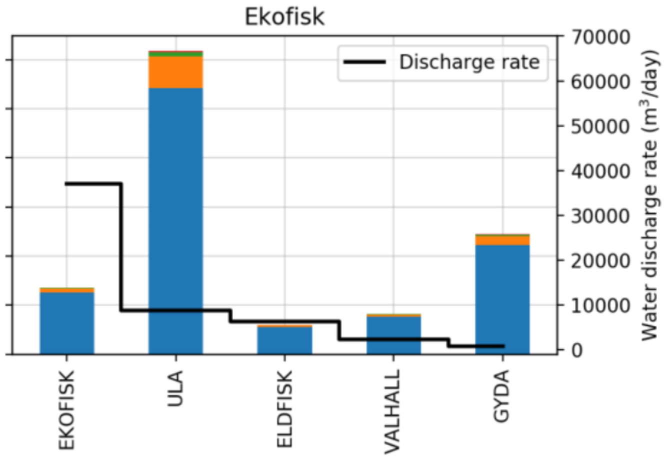


Discharges

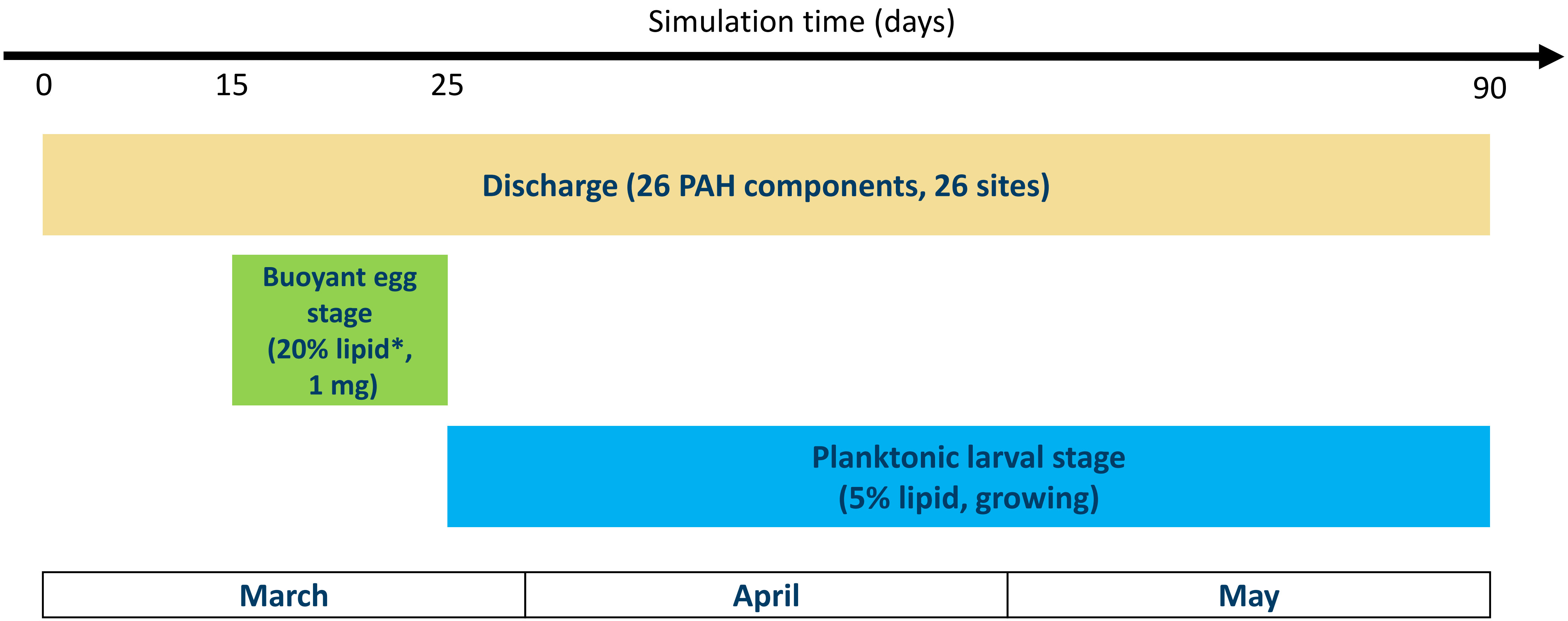
- Individual water discharge rates and PAH profiles for each point source
  - Sorted by water rate
  - Naphthalene components dominate
- Year-average values for 2017
- Large variation in rates
- Data from Miljødirektoratet







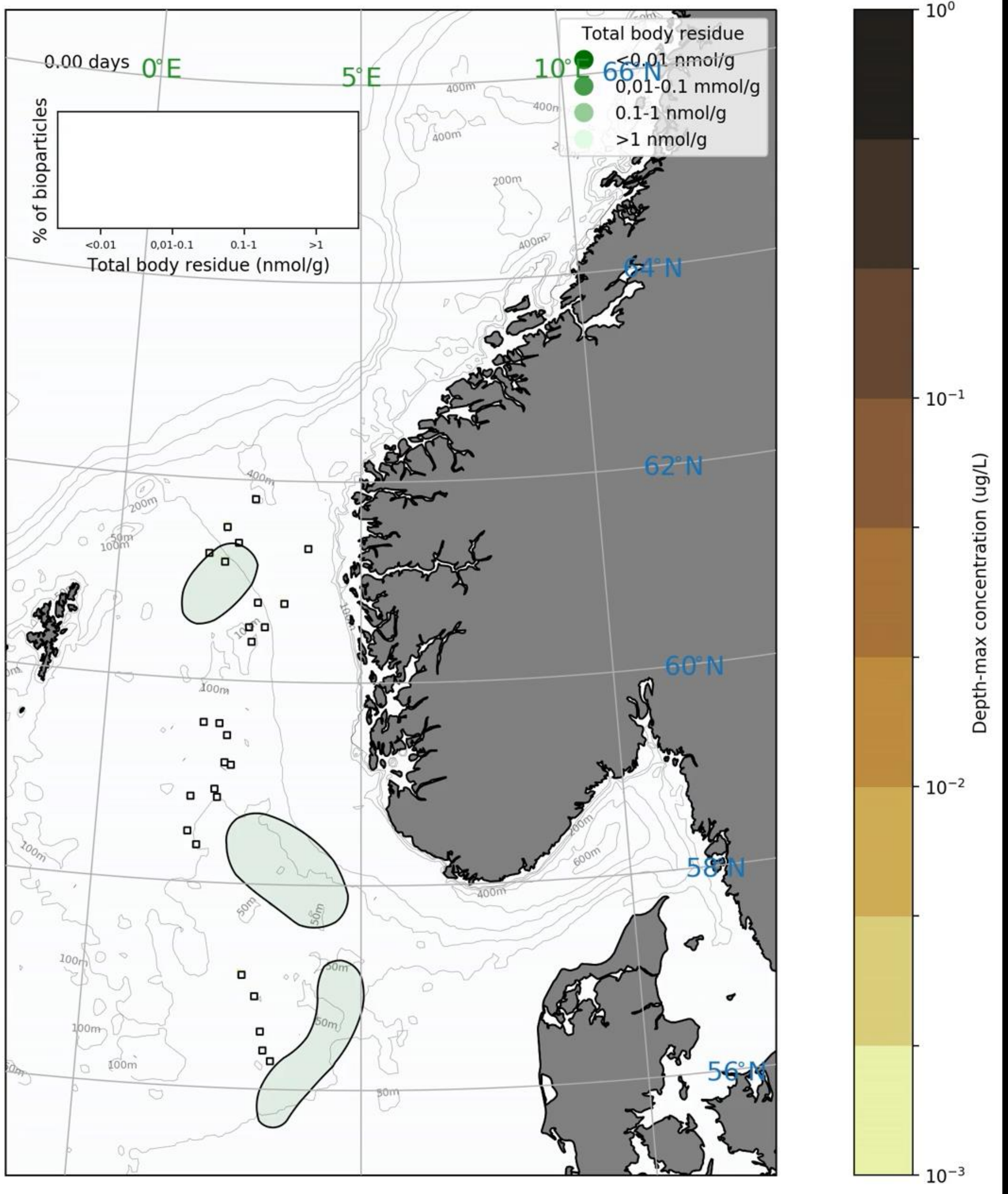
Model setup



Simulation time (days)
0
15
25
90
Discharge (26 PAH components, 26 sites)
Buoyant egg stage (20% lipid*, 1 mg)
Planktonic larval stage (5% lipid, growing)
March
April
May

Simulation result animation

- 2009 simulation
- Spawning grounds (green polygons)
- Discharge points (small squares)
- Depth-maximum total PAH concentration levels shown in brown (> 1 ng/L)
- Super-individuals shown in green (circles), shading by total internal concentration

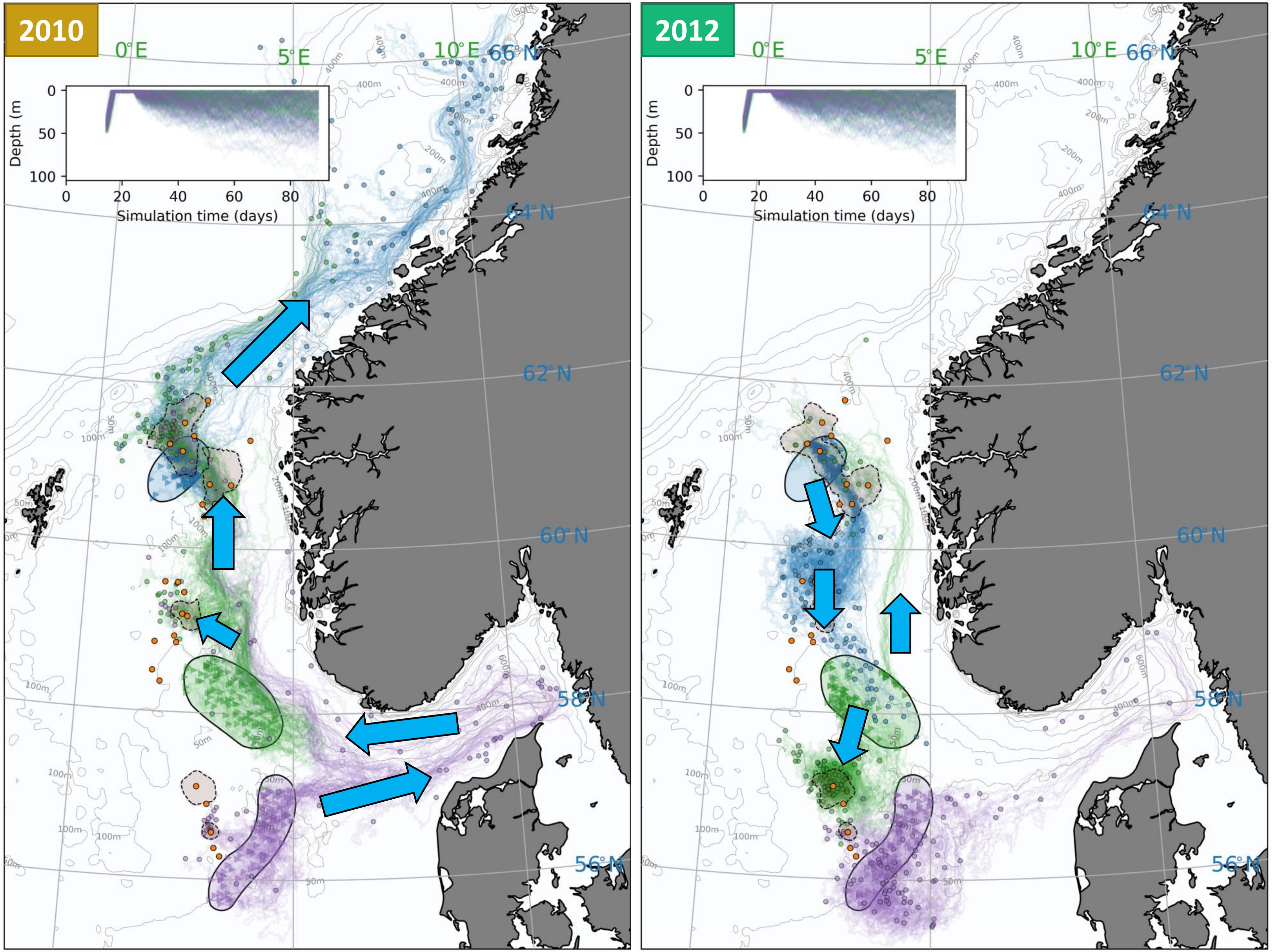


Four different years were simulation (2009-2012)

Trajectories of 100 super-individuals from each spawning ground

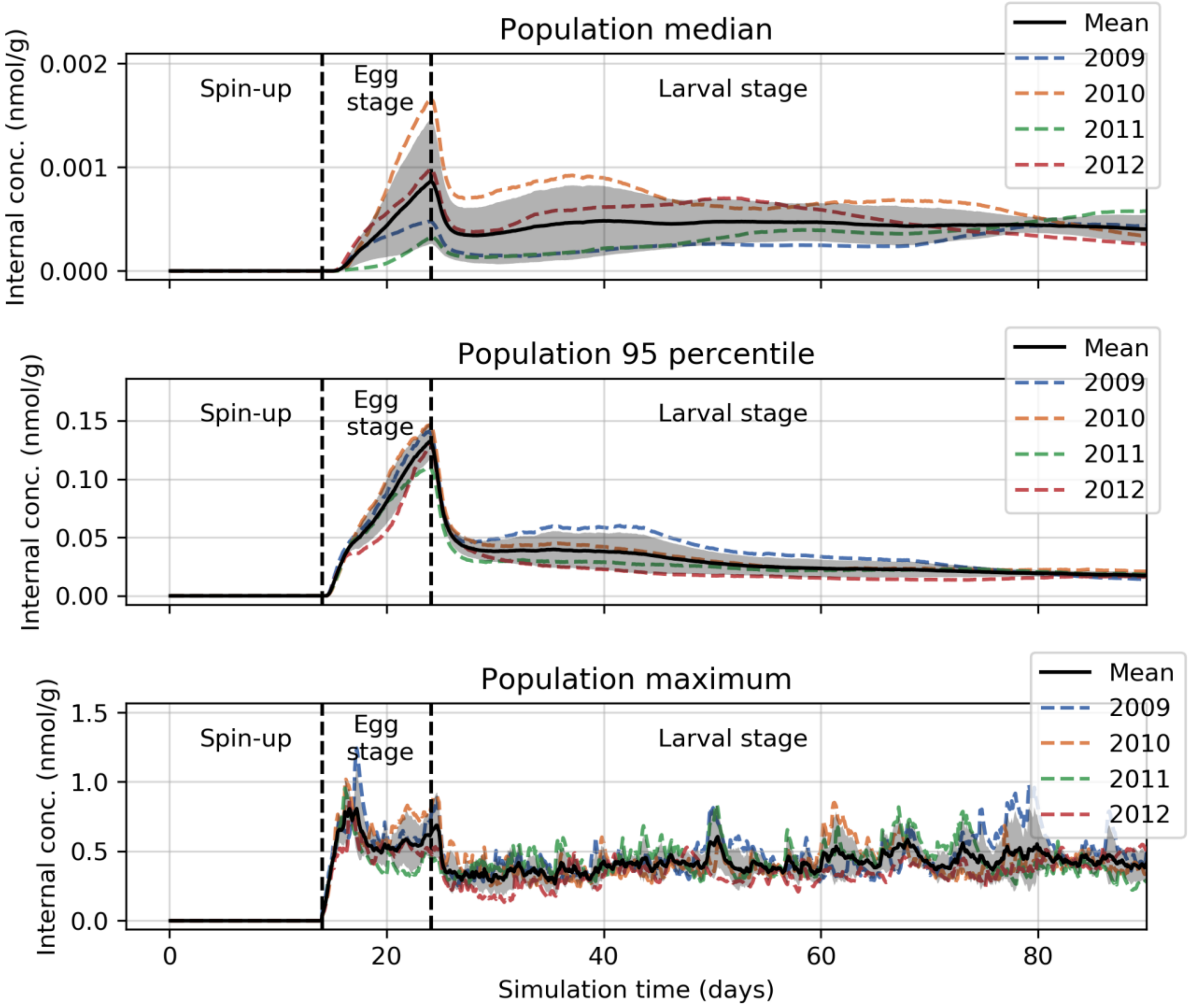
Those with highest total internal concentrations

Two different years (2010/2012)



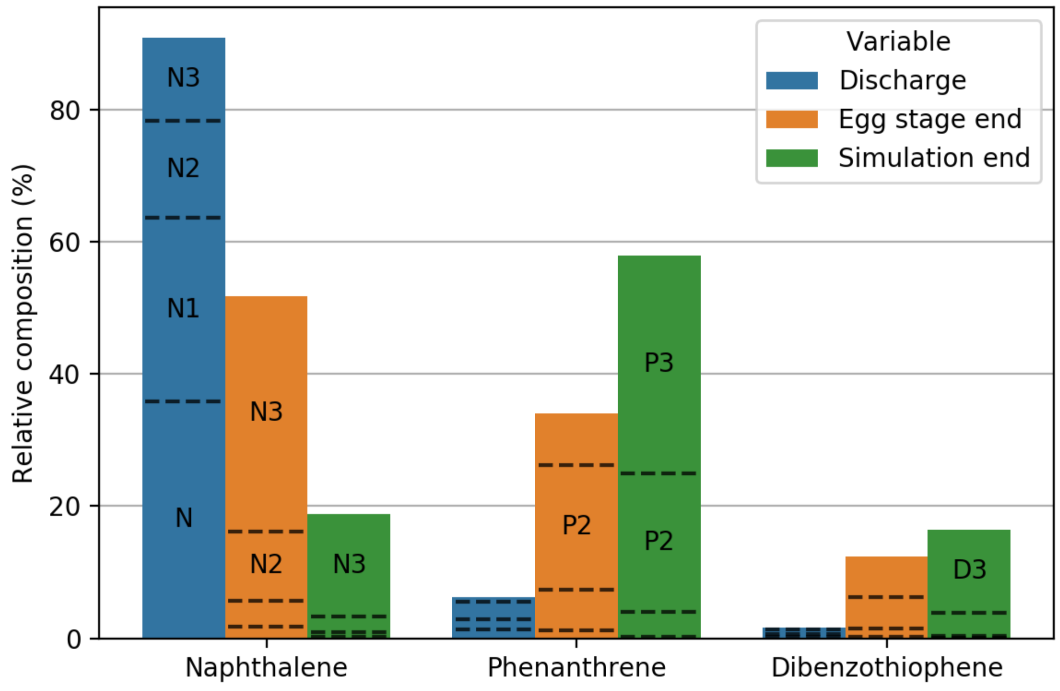
Total internal PAH concentrations

- "Population"-wide levels: max, 95-percentile and median
- Highest at end of egg stage
  - < 1.24 nmol/g (198 ng/g)
- Large variation between super-individuals
- Less variation between years, largest for population median
- Acute narcosis threshold is roughly 2 – 8 mmol/kg (Meador *et al.* 2011)
  - Sub-lethal effects (e.g. cranial deformations) can occur at lower thresholds (Sørhus *et al.* 2017)



Internal concentration compositions

- Compare relative compositions of component groups for discharge and internal concentrations (egg stage end, simulation end)
- Striking difference in these relative compositions
- Trending towards higher-K_{ow} components with time
- Transport + fate + toxicokinetics!



Comparison with field observations?

- Model predicts internal concentrations, which can also be measured
  - The present simulations give a maximum value of 198 ng/g TPAH(26)*
- Some previous field studies
  - Copepods sampled at Tampen (mean TPAH IC): ca. 231 ng/g (w.w.) (Hansen et al., 2020).
    - NB: Different species -> different exposure and toxicokinetics
  - Caged mussels at Tampen up to 205 ng/g TPAH (Durell *et al.* 2006
- Opportunity – Ekofisk Water Column Monitoring 2021
  - Caged mussels
  - Calanus sampling – (288 – 468 ng/g TPAH(46), B. H. Hansen presentation)
- No field data for internal concentrations in fish ELS (yet)

Caveats

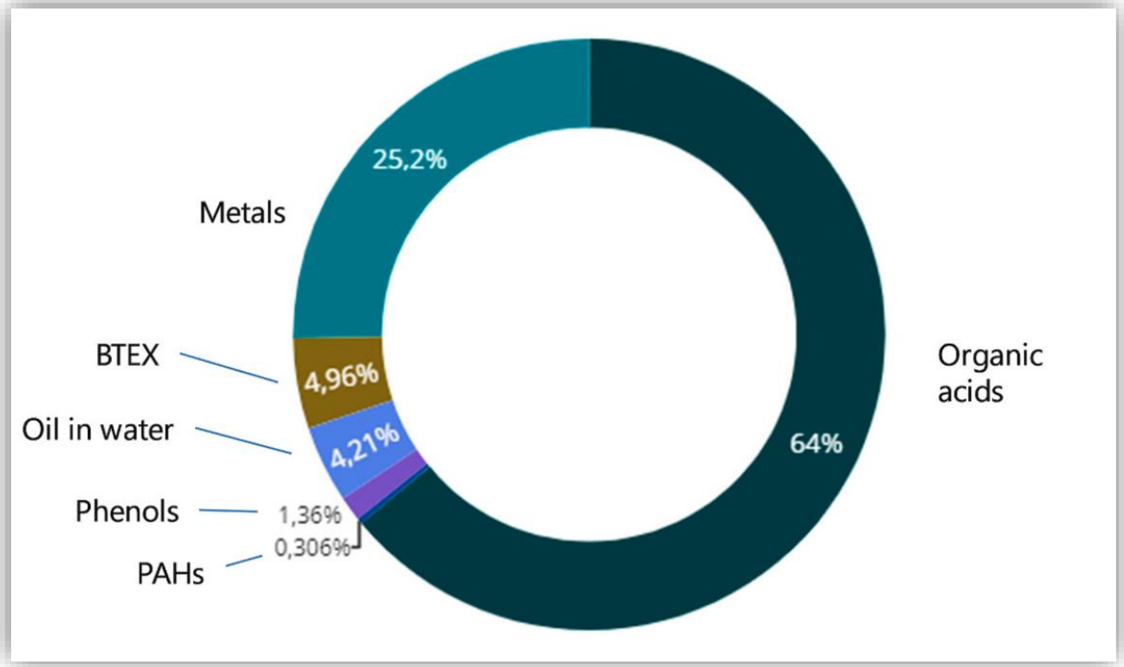
- Only a PAH subset of components in the PW discharges have been studied
  - Other components would also contribute towards the total internal concentration levels, important when comparing against other reported TPAH
  - For overall effects, must thus be considered
- Intermediate microbial biodegradation products of the primary components have not been included, and these may also contribute to internal concentrations and toxicity (Hansen *et al.*, 2018)
- Metabolic transformation products of PAHs have not been considered (Sørensen *et al.,* 2017).
  - Alters internal concentrations over time

Conclusions

- Through the DREAM-MER project we have coupled a newly developed toxicokinetic/super-individual model to an existing transport-fate mode for produced water discharges.
- We have investigated exposure and uptake of PAHs in Atlantic cod ELS.
- The highest levels of total internal PAH concentration we find are 198 ng/g, with 95-percentiles generally below 27 ng/g.
- Inter-annual variations are found in the transport patterns of the eggs and larvae, but the population-level internal concentrations remain similar between the years.
- A large variation in relative composition of internal concentrations compared to discharges are found.

Technology for a better society

Produced water

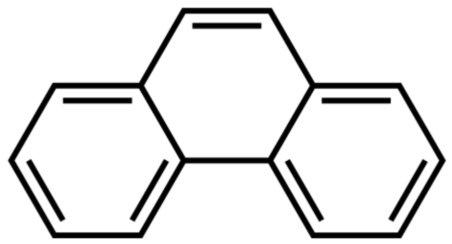


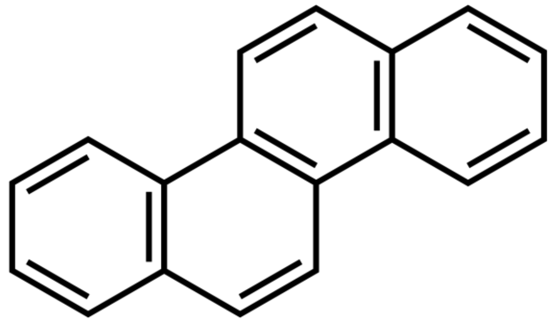
Naturally occuring substances.
Figure from Beyer, Goksøyr, *et al.* (2020). *Mar. Env. Res*, 162, 105155.

- Byproduct of offshore oil extraction
- Reinjected or discharged to sea after cleaning
- Complex dilute mixture of residual oil substances and production chemicals
- May pose a risk to the marine environment
  - Relative amount of PAHs is small, but still a key risk component (Beyer *et al.* 2020)
- Annual discharge in Norway (2017) 134 000 000 Sm^3

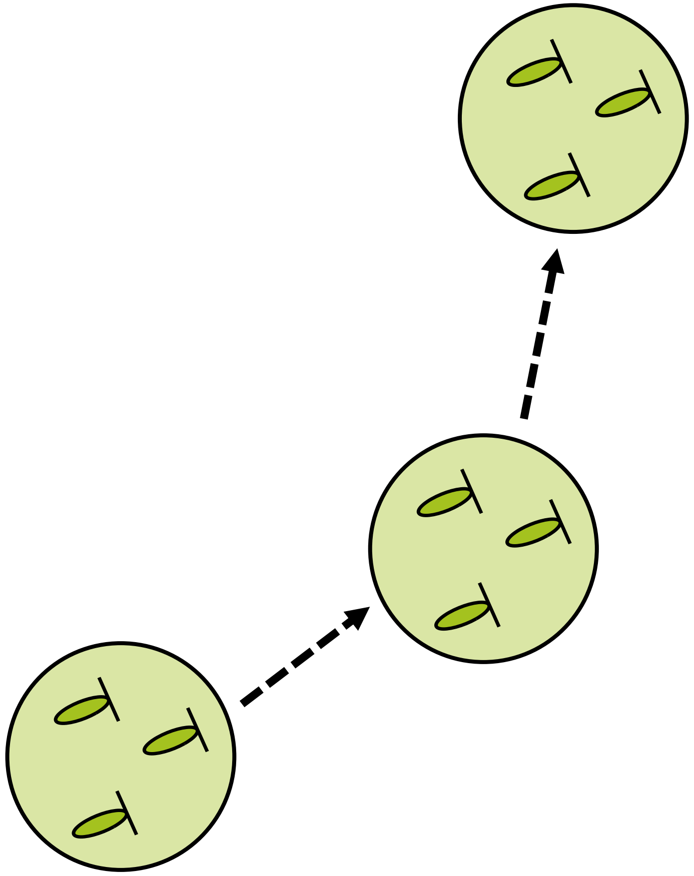
Polycyclic aromatic hydrocarbons

- Residual from extracted oil (in PW)
- Range of molecular weights, solubilities and K_{ow} (lipophilicity)
- Short to long lifetime in the marine environment
- Can be taken up and accumulate in marine organisms
  - Bioconcentration potential tend to increase with molecular weight





Transport scheme



- Euler scheme for advection
  - Fast, but less accuracte than higher order schemes (e.g. RK4)
- Milstein scheme for turbulent diffusion:
  - Consistent scheme for spatially varying diffusivity
  - Works well for strong pycnoclines
  - Fairly efficient
- Forcing by offline currents (netcdf archive)
  - Can also use wind and diffusivity fields

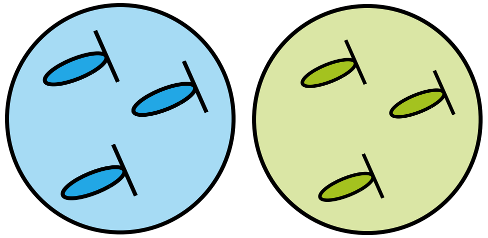
$$x_{n+1} = x_n + \Delta t \left(u(x_n, t) + K'(x_n)\right) + \Delta W \sqrt{2K(x_n)} + \frac{1}{2} K'(x_n) \left(\Delta W^2 - \Delta t\right)$$

Model setup

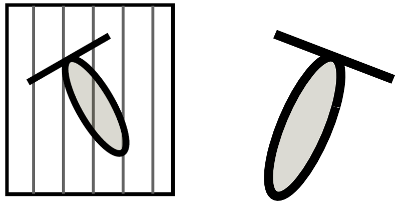
- Diffusive mixing
  - Vertical: 10^{-4} m^2/s (low mixing)
  - Horizontal: 50 m^2/s
- 70 000 dissolved particles
  - 10 per site per time step
- 30 000 super-individuals
- Simulation time: 90 days
- Model time step: 15 min, output: 2 hours
- Time-slice of spawning products (15th March)

DREAM-MER IBM-TKTD module overview

Multiple species



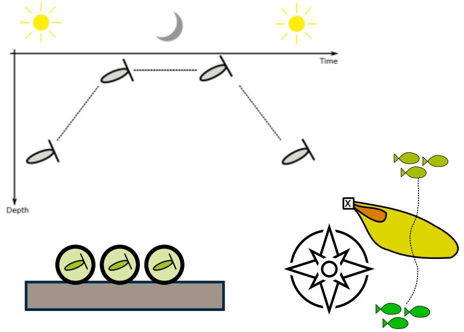
Bioparticles/cages (super-individuals)



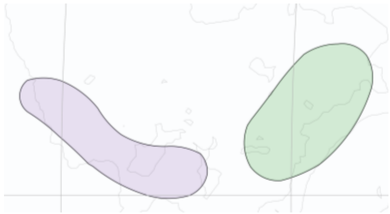
Growth and stages

$$\frac{dl}{dt} = K(L_\infty - l) \qquad w = a \cdot l^n$$

Individual behavior

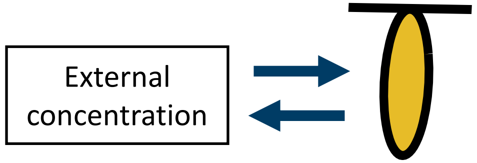


Multiple spawning options

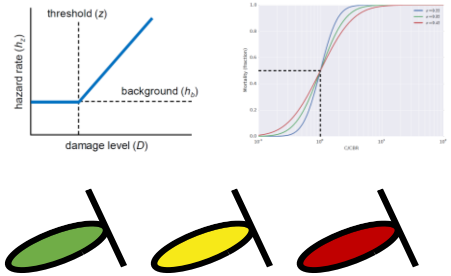


Toxicokinetics

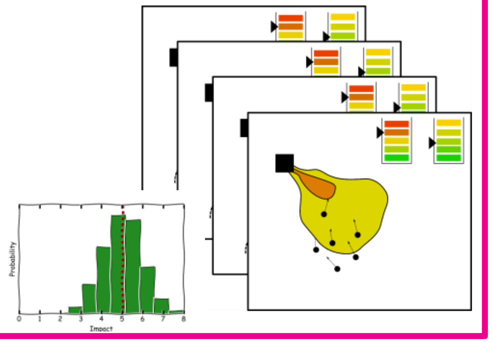
$$\frac{dC}{dt} = k_1 C_a - k_2 C - \left(\frac{1}{w}\frac{dw}{dt}\right) C$$



Effects



Ensemble simulations

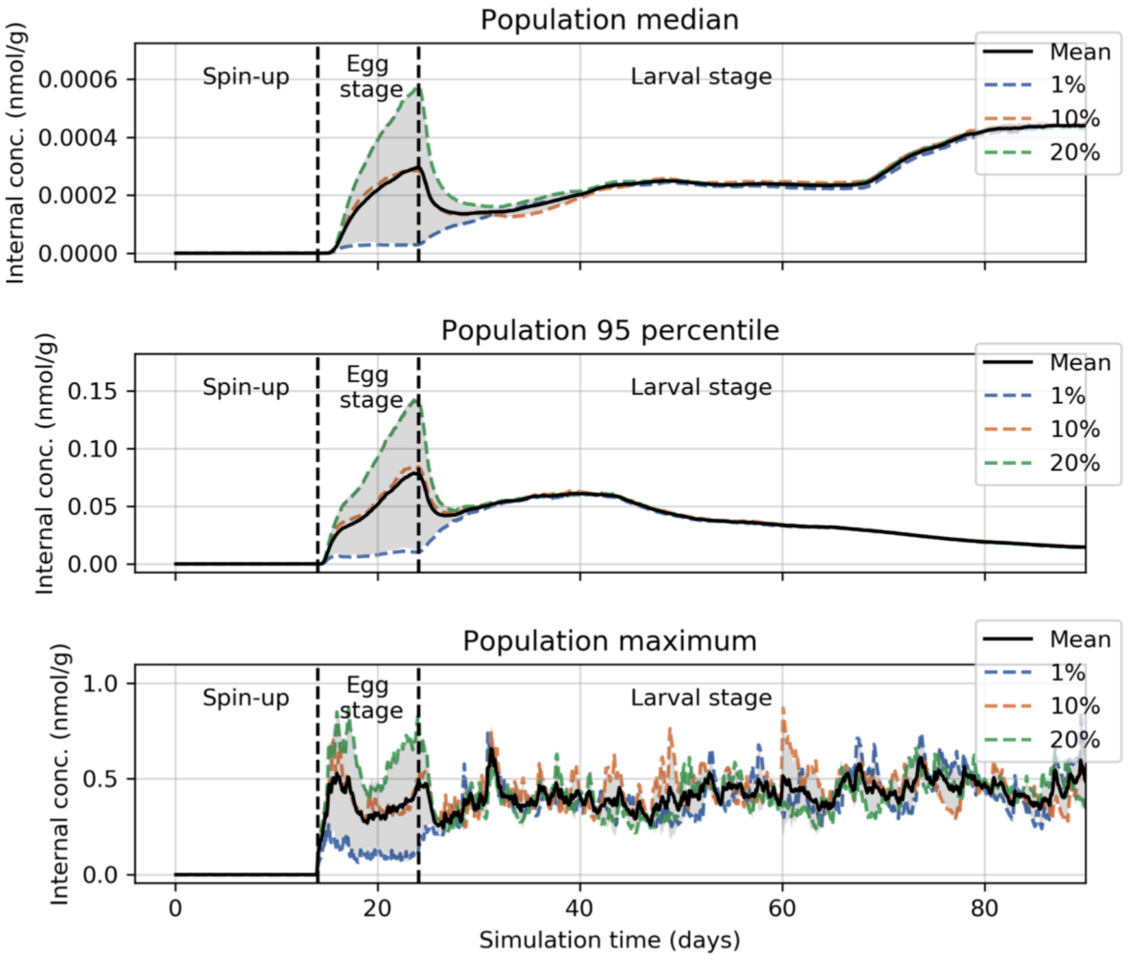


PAH component properties

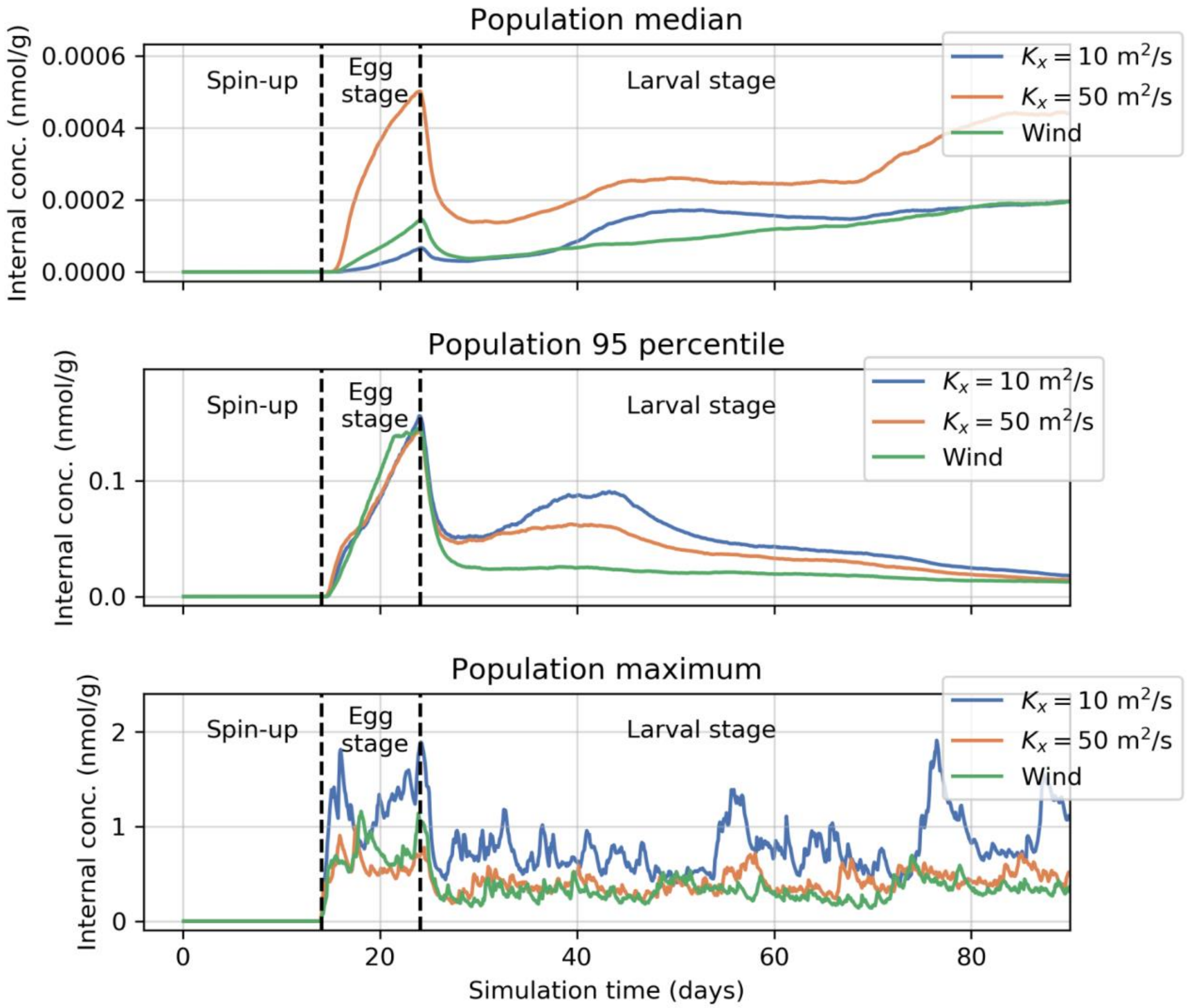
Component	LogKow	Density (kg/m^3)	Mol. weight (g/mol)	Primary biodeg. rate (1/d)
Naphthalene	3.30	0.960	128.1	0.184383
C1-Naphthalene	3.86	1.000	142.2	0.184383
Acenaphthene	3.92	1.060	154.2	0.060300
Acenaphthylene	3.94	0.899	152.2	0.031200
Fluorene	4.18	1.200	166.2	0.147123
Dibenzothiophene	4.29	1.300	184.3	0.087403
C2-Naphthalene	4.31	1.000	156.2	0.132672
Anthracene	4.35	1.250	178.2	0.060080
Phenanthrene	4.46	1.060	178.2	0.080265
C3-Naphthalene	4.81	1.000	170.3	0.044400
C1-Dibenzothiophene	4.84	1.200	192.3	0.038500
Pyrene	4.88	1.270	202.3	0.000911
C1-Phenanthrene	5.08	1.100	192.3	0.043300
Fluoranthene	5.16	1.200	202.3	0.000911
C2-Dibenzothiophene	5.39	1.200	212.3	0.030500
C2-Phenanthrene	5.44	1.100	206.3	0.035400
Benz(a)anthracene	5.52	1.274	228.3	0.000914
Benzo(b)fluoranthene	5.78	1.300	252.3	0.000914
Chrysene	5.81	1.274	228.3	0.000914
C3-Dibenzothiophene	5.93	1.200	226.3	0.024400
Benzo(a)pyrene	5.99	1.300	252.1	0.000914
C3-Phenanthrene	5.99	1.100	220.3	0.021800
Benzo(k)fluoranthene	6.67	1.200	292.1	0.000914
Benzo(g-h-i)perylene	6.70	1.400	276.3	0.000914
Dibenzo(a-h)anthracene	6.75	1.200	278.3	0.000914
Indeno(1-2-3-cd)pyrene	6.76	1.400	276.3	0.000914

Model sensitivity

- Checked sensitivity to lipid fraction in egg stage
- 20% gives highest internal concentration levels
- Differences diminish and eventually dissappear in the larval stage

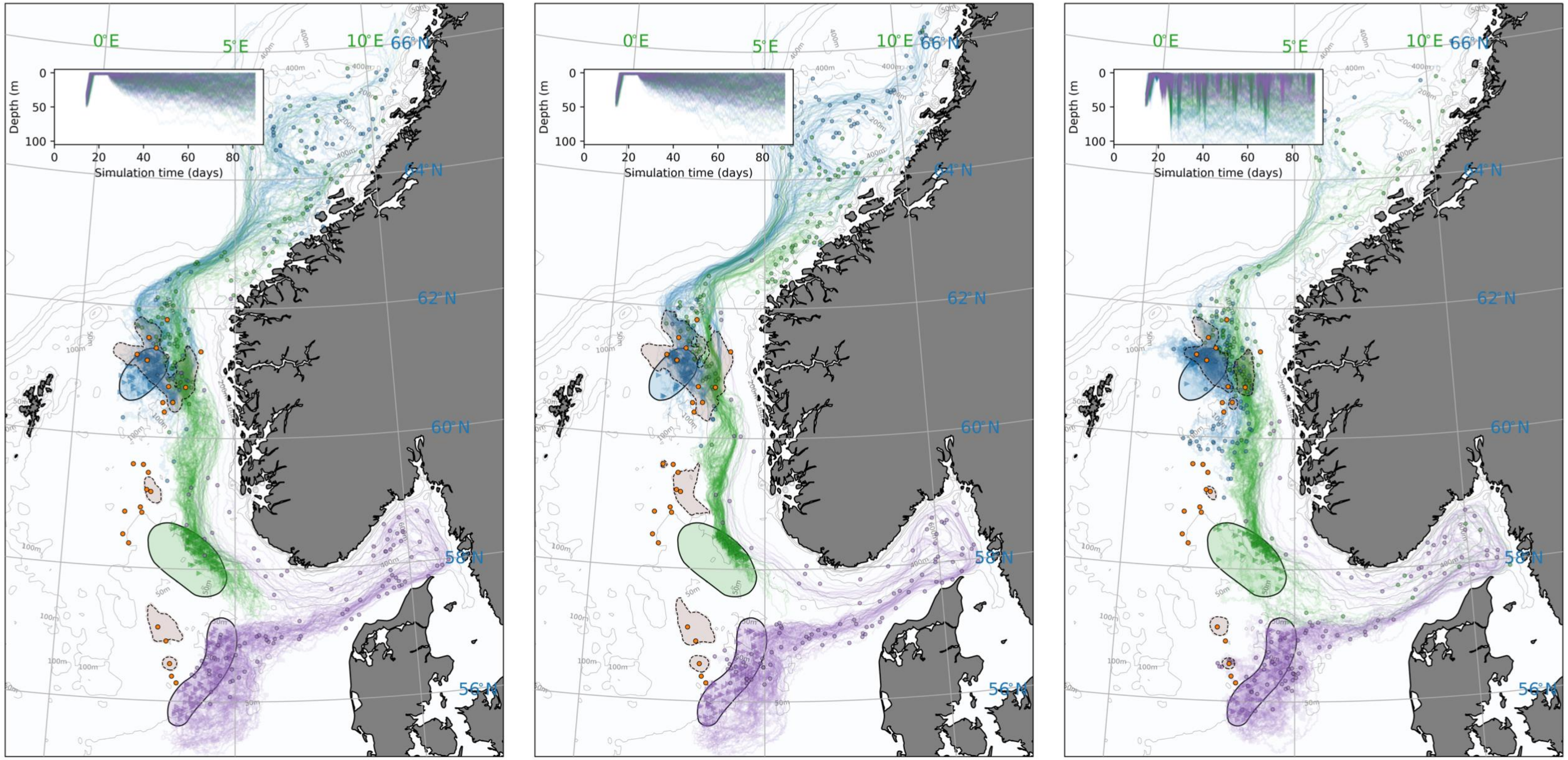


Mixing parameter sensitivity



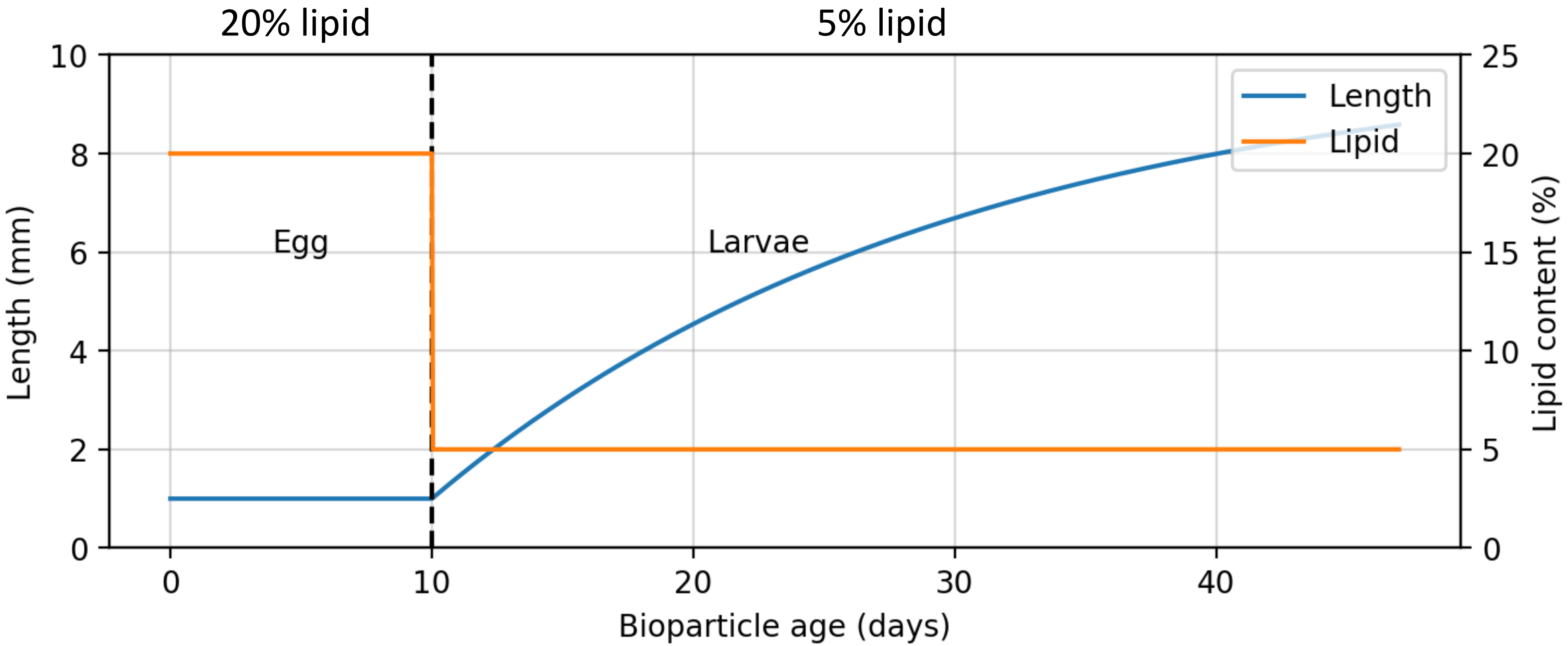
SINTEF

Mixing parameter sensitivity

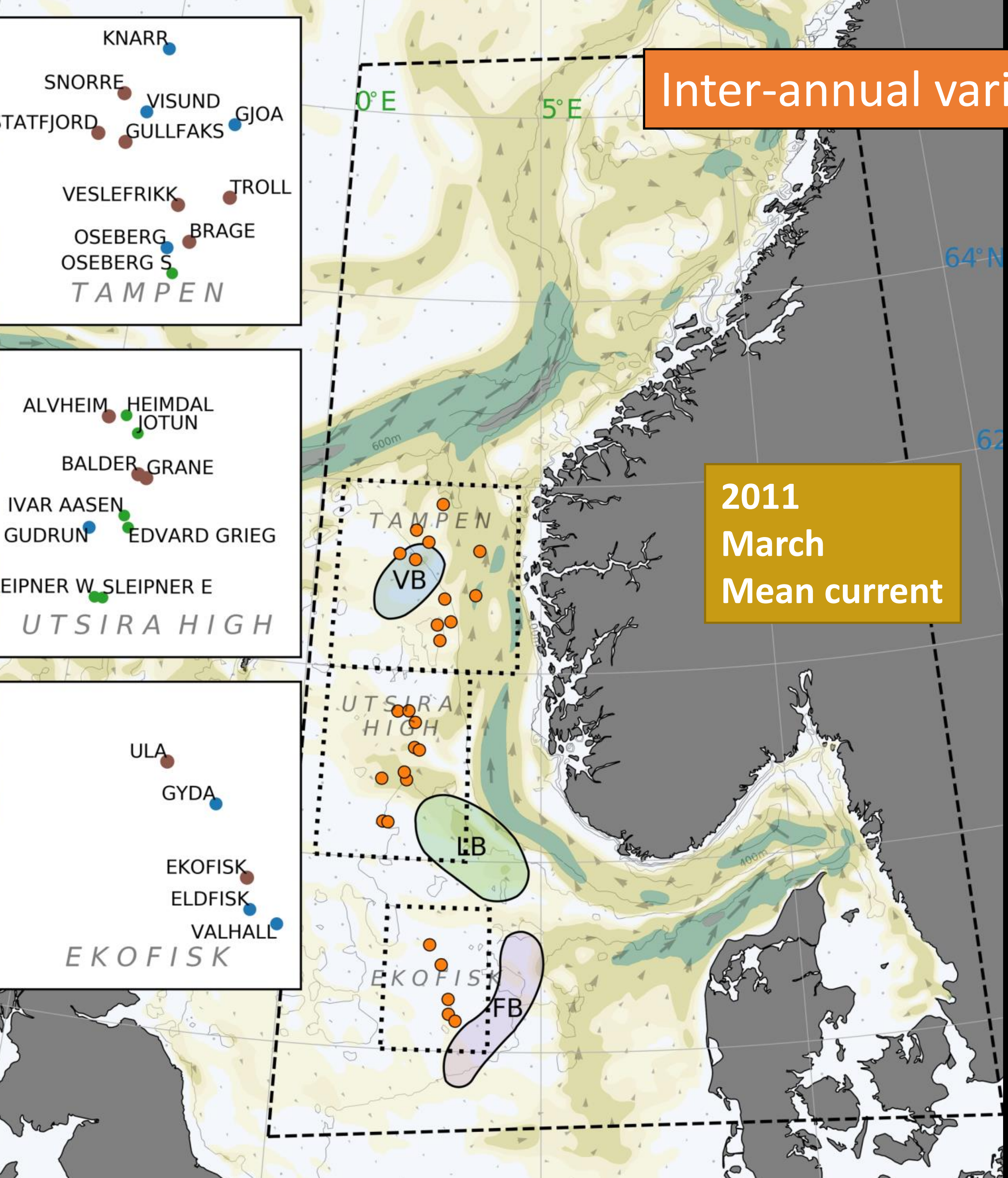


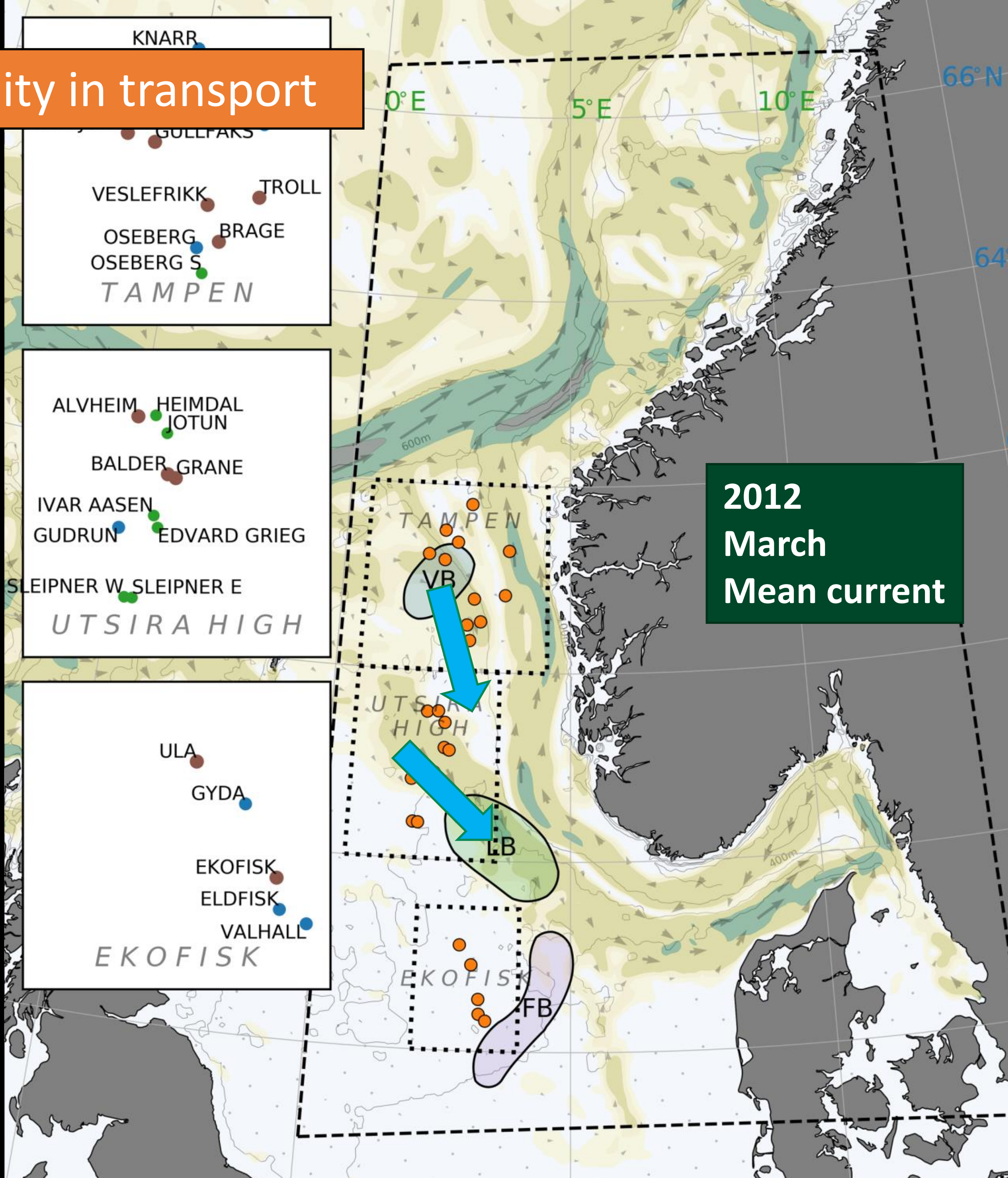
Bioparticle stages, length, lipid

- 30 000 bioparticles
- 3 spawning areas
- Spawning occurs 15th March
- Spawning depth: 30 – 50 m



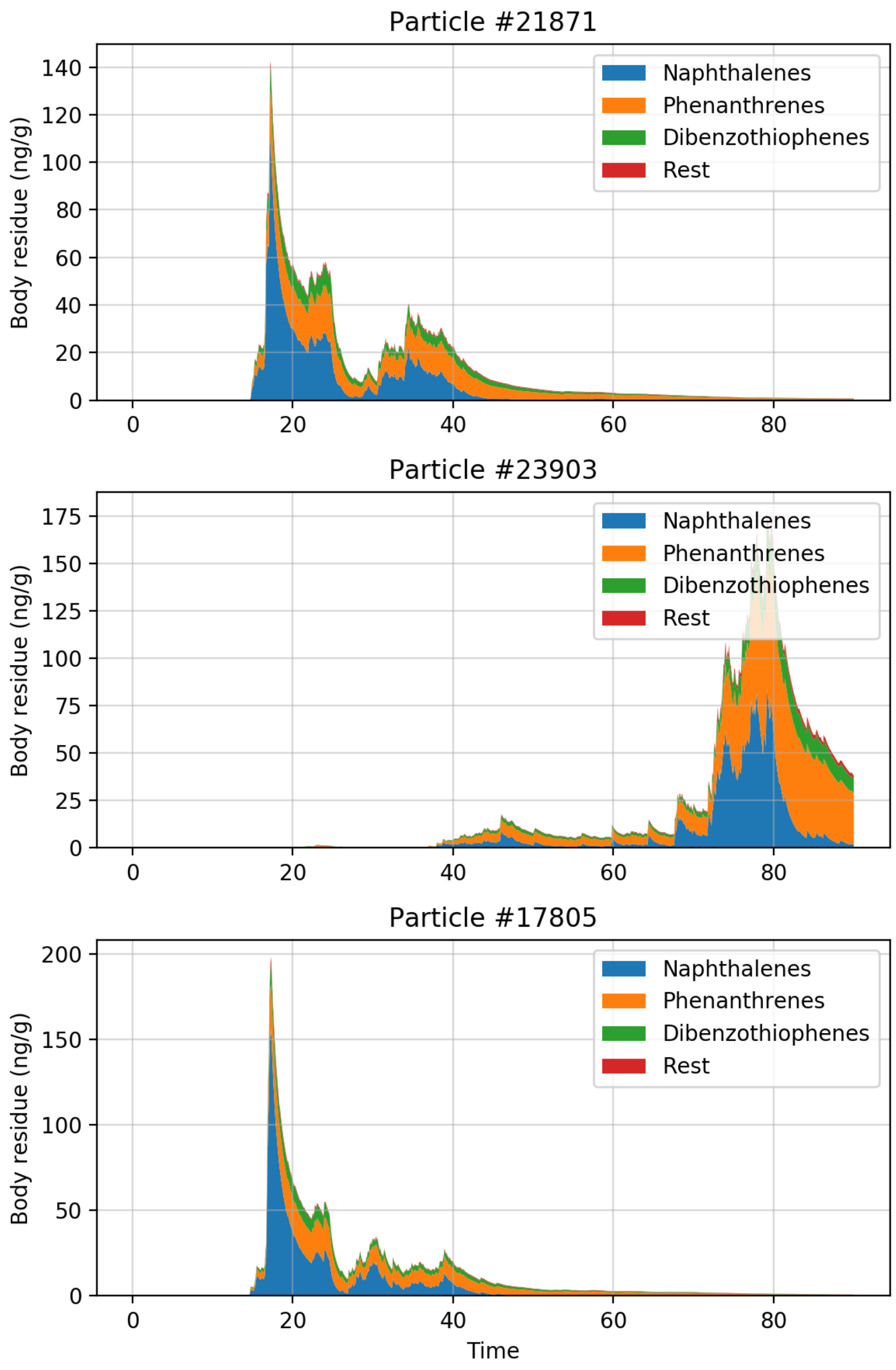
Inter-annual variability in transport





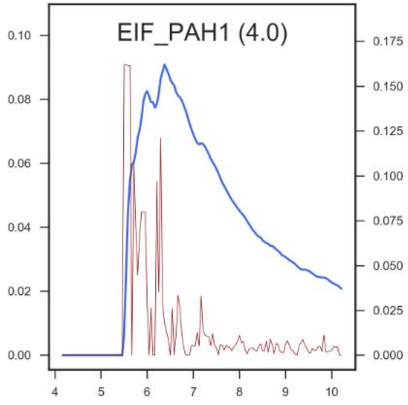
Example body residues

- Single-bioparticle body residues
- The top 3 bioparticles (TBB)
- Levels below 200 ng/g TBB
- Naphthalenes and Phenanthrenes dominate
- Napthalenes are eliminated fastest, Ps and Ds become relatively more dominant with time after exposure

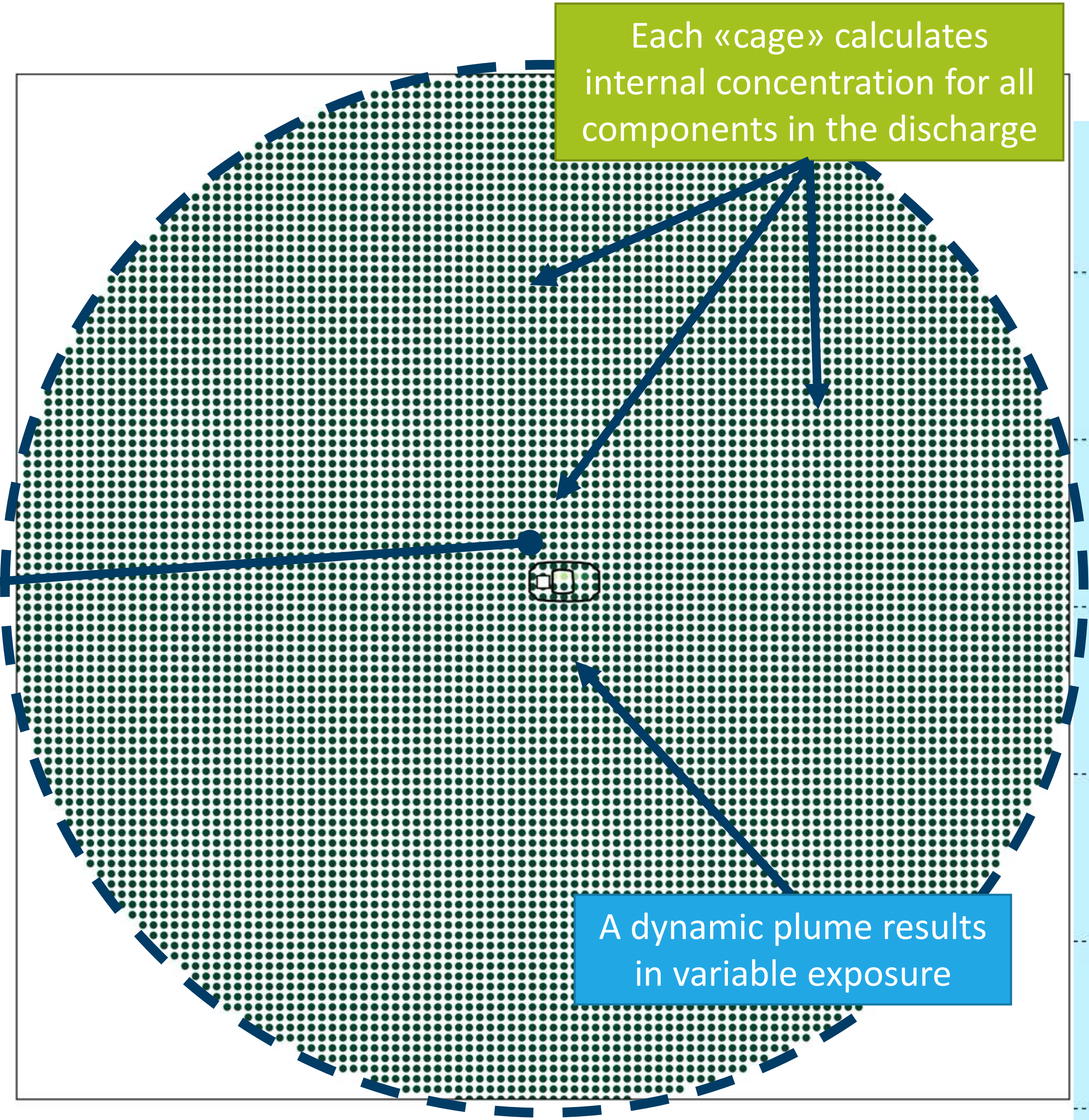


Stationary biocages

Stationary model organism



Toxicokinetics and effects



Planning field monitoring

Toxicokinetic model – dilution by growth


TYPES OF SCIENTIFIC PAPER
WE PUT A CAMERA SOMEWHERE NEW
HEY, I FOUND A TROVE OF OLD RECORDS! THEY DON'T TURN OUT TO BE PARTICULARLY USEFUL, BUT STILL, COOL!
MY COLLEAGUE IS WRONG AND I CAN FINALLY PROVE IT
THE IMMUNE SYSTEM IS AT IT AGAIN
WE FIGURED OUT HOW TO MAKE THIS EXOTIC MATERIAL, SO EMAIL US IF YOU NEED SOME
WHAT ARE FISH EVEN DOING DOWN THERE
THIS TASK I HAD TO DO ANYWAY TURNED OUT TO BE HARD ENOUGH FOR ITS OWN PAPER
HEY, AT LEAST WE SHOWED THAT THIS METHOD CAN PRODUCE RESULTS! THAT'S NOT NOTHING, RIGHT?
CHECK OUT THIS WEIRD THING ONE OF US SAW WHILE OUT FOR A WALK
WE ARE 500 SCIENTISTS AND HERE'S WHAT WE'VE BEEN UP TO FOR THE LAST 10 YEARS
SOME THOUGHTS ON HOW EVERYONE ELSE IS BAD AT RESEARCH
WE SCANNED SOME UNDERGRADUATES