On the Reactive Transport at Catchment Scales with StorAge Selection Functions
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Outline

- Travel Time Distributions and Age
- StorAge Selection Functions
- Reactivity from High-res data
- Potential pitfalls with common assumptions in SAS modelling
Why Age Matters
Two Water-Worlds Hypothesis
Modelling over the Ages
A Eulerian Catchment

- Explicitly define the heterogeneity
- Parameterize the physics
- Recover the travel-times from particle tracking
Time, Residence Time (Age), and Travel Time

Time of Entrance \( t_i \)

Time of Exit \( t_e \)

Age \( T = t - t_i \)

Travel Time \( T_r = t_i - t_e \)
Contribution of Stored Water of Various Ages to Stream Flow

A - Uniform

B - Dirac delta

C - Gamma

Water age $T$
A Simple Pesticide Transport Model

Aerobic
\[ t_{1/2} = 20 \text{ days} \]

Anaerobic
\[ t_{1/2} = 200 \text{ days} \]

Modified from Bertuzzo et al., 2013, WRR
Variability of Residence Times
Basic Equations and Common Assumptions

**Tracers**
Stream concentration = sum over all input times of input concentration ($C_{in}$) at time $t_i$ and the distribution of stream water ages ($p_Q$) at time $t$

$$C_Q(t) = \int_{-\infty}^{t} C_{in}(t_i)p_Q(t - t_i, t)dt_i$$

**Reactive Solutes**
Stream concentration = sum over all input times of resident concentration ($C_S$) at time $t_i$ and the distribution of solute flux ages ($p_F$) at time $t$

$$C_Q(t) = \int_{-\infty}^{t} C_S(t - t_i, t)p_F(t - t_i, t)dt_i$$
Learning From High-res Reactive P Response Functions

Time-invariant response functions

- $Q_{\text{IRF}}(\text{Precip})$
- $\text{RP}_{\text{IRF}}(Q)$
- $\text{RP}_{\text{IRF}}(\text{Precip})$

Graphs showing discharge and concentration over time (d) for $Q_{\text{IRF}}(\text{Precip})$, $\text{RP}_{\text{IRF}}(Q)$, and $\text{RP}_{\text{IRF}}(\text{Precip})$. The graphs illustrate the response functions over time.
Reactive P Conceptual Model

Gradual build up in concentration in mobile zone ($C_{mobile}$) when $Q$ is low
Rapid flush of $C_{mobile}$ when $Q$ increases
Rapid dilution of $C_{mobile}$ during high flows to rate limited mass exchange
Cross Wavelet Spectra
RP and Precipitation
Q: Are these catchments really all that different?

\[ P[c>\text{C}] \sim C^{-2.6} \]
A: Differently organized sources and flux distributions
Damköhler Number $Da = k_r T_r$

- $k_r \sim 0.1 \ T_r^{-0.76}$
- $Da \sim 0.1 \ T_r^{0.24}$

$\phi_Q(t) = \int_{-\infty}^{t} \phi_{In}(t_i) \frac{Q(t)}{S(t)} \ e^{-\int_{t_i}^{t} \frac{Q(x)}{S(x)} \ dx} \left(1 - \int_{t_i}^{t} \frac{\alpha \ ET(x)}{S(x)} \ dx - k(t-t_i) \right) \ dt_i$

Steady Conditions

$\frac{\phi_Q}{\phi_{in}} = e^{-Da}$

$T_r = \frac{S}{Q}$

Residence Time Distribution

Dynamic Damköhler

Mixing

Storage
Water fluxes
Solute fluxes

$ET \quad I \quad \phi_I \quad T_r \quad S, M \quad \phi_Q \quad \phi_{ET}$
### A Possible Resolution

Use Tracers to Establish the rSAS function and $p_Q$ then weigh $p_F$ by $p_Q$

#### Tracers

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$$C_Q(t) = \int_{-\infty}^{t} C_{in}(t_i)p_Q(t - t_i, t)dt_i$$

#### Reactive Solutes

Stream concentration = sum over all input times of resident concentration ($C_S$) at time $t_i$ and the distribution of solute flux ages ($p_F$) at time $t$

$$C_Q(t) = \int_{-\infty}^{t} C_S(t - t_i, t)p_F(t - t_i, t)p_Q(t - t_i, t)dt_i$$
Summary

- The SAS approach
  - current flavour-of-the-month for catchment-scale solute transport modelling
  - intuitive interpretation of hydrological processes contributing to solute export

- Reactive solutes remain a challenge

- Combining multiple highres solutes can possibly help untangle
  - Sources
  - Pathways; and
  - Mitigation timescales

- Need good input data!