Modeling radiocarbon in Earth system reservoirs

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Outline

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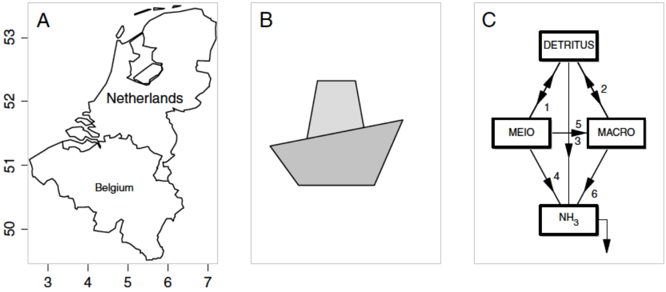
What is a model?



Three examples of models. They have in common that they focus only on the object of interest, ignoring the irrelevant details. What is irrelevant depends on the aim of the model.

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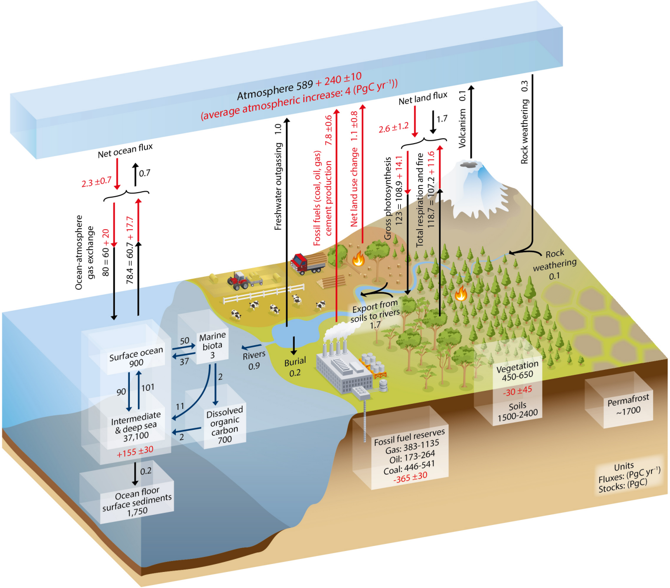
The global carbon cycle as a conceptual model



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Why we use models?

- Synthesis and integration
- Prediction and forecasting
- Guidance in observation and experimentation

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Why do we model radiocarbon?

- To keep track of radiocarbon concentrations in heterogeneous open systems
- To understand rates of carbon exchange
- To learn about time scales of carbon cycling

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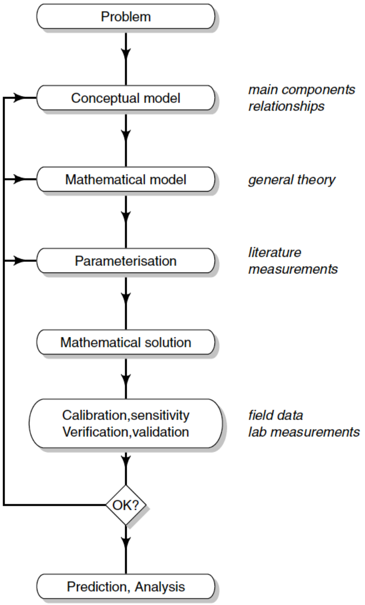
Modeling steps and ingredients



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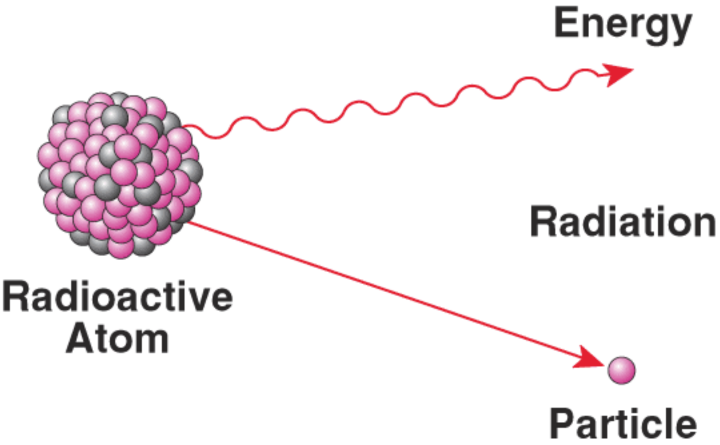
Simple example: radioactive decay



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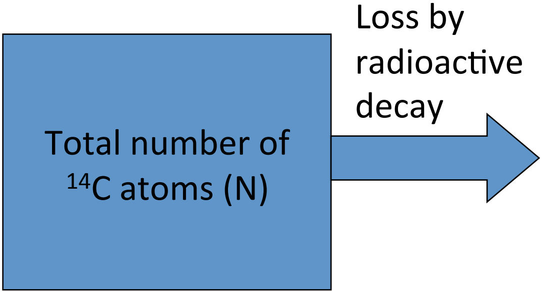
Conceptual model: radioactive decay



Question: *How many atoms remain after x units of time?*

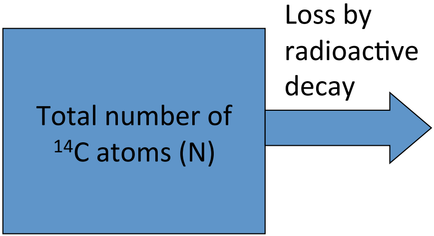
Mathematical model

$$\frac{dx}{dt} = Inputs - Outputs$$

or

$$\frac{dx}{dt} = Sources - Sinks$$

Conceptual model: radioactive decay



$$\frac{dN}{dt} = -\lambda \cdot N$$

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Mathematical solution

Initial value problem

$$\frac{dN}{dt} = -\lambda \cdot N, \quad N(t=0) = N_0$$

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Mathematical solution

Initial value problem

$$\frac{dN}{dt} = -\lambda \cdot N, \quad N(t=0) = N_0$$

Solution:

$$N(t) = N_0 \exp(-\lambda \cdot t)$$

Parameterization

Libby half-life for radiocarbon is 5568 years!

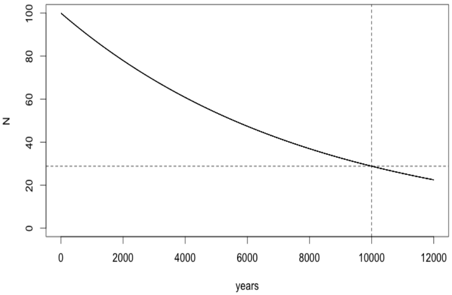
$$t_{1/2} = 5568 = \frac{\ln 2}{\lambda},$$

Then,

$$\lambda = 0.0001244876 \quad \text{years}^{-1}$$

Prediction

How much radiocarbon would be available after 10,000 years of radioactive decay if the initial amount of ^{14}C atoms $N_0 = 100$?



$$N(t = 10000) = 100 \exp(\lambda \cdot 10000)$$
$$= 28.8$$

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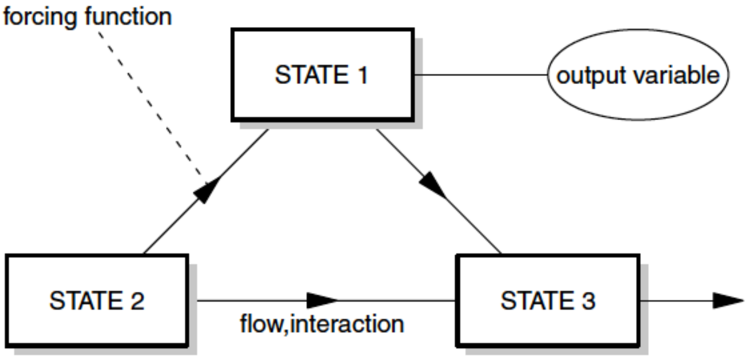
Model formulation

General recommendations:

- Start with a conceptual diagram
- Define compartment or state variables with similar characteristics
- Define boundaries, external inputs and outputs
- Define flows and interactions
- Define spatial and temporal scale
- Define model currency

Conceptual model example



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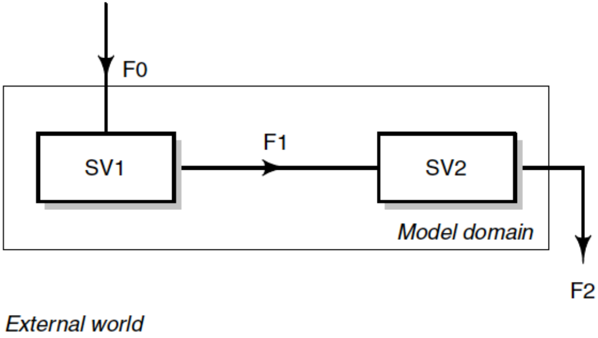
Concept to math: balance equations



$$\frac{d\mathrm{SV}_1}{dt} = F0 - F1$$
$$\frac{d\mathrm{SV}_2}{dt} = F1 - F2$$

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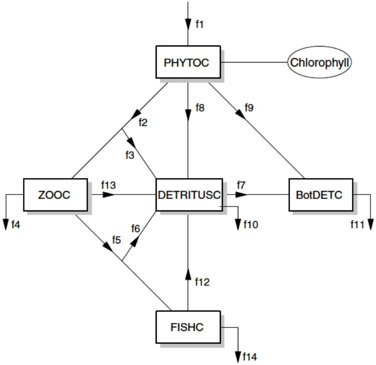
Example: a lake ecosystem

C cycle



$$\frac{d\text{PHYTOC}}{dt} = \text{f1} - \text{f2} - \text{f8} - \text{f9}$$
$$\frac{d\text{ZOOC}}{dt} = \text{f2} - \text{f3} - \text{f4} - \text{f5} - \text{f13}$$
$$\frac{d\text{DETRITUSC}}{dt} = \text{f3} + \text{f8} + \text{f6} + \text{f12} + \text{f13} - \text{f7} - \text{f10}$$
$$\frac{d\text{FISHC}}{dt} = \text{f5} - \text{f6} - \text{f12} - \text{f14}$$
$$\frac{d\text{BOTTOMDETRITUSC}}{dt} = \text{f7} + \text{f9} - \text{f11}$$

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The compartmental matrix

$$\mathbf{F} = \begin{pmatrix} f_{1,1} & f_{1,2} & \cdots & f_{1,n} \\ f_{2,1} & f_{2,2} & \cdots & f_{2,n} \\ \vdots & \vdots & \ddots & \vdots \\ f_{n,1} & f_{n,2} & \cdots & f_{n,n} \end{pmatrix}$$

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Mathematical formulations

The law of mass action:

$$\text{Reaction Rate} = k \cdot [A]^{\alpha} \cdot [B]^{\beta}$$

The rate of the reaction is proportional to a power of the concentrations of all substances taking part in the reaction

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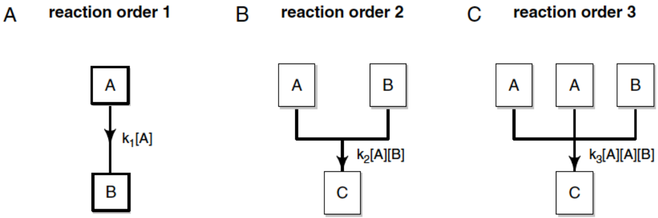
Reaction order



- Zero order: k_0
- First order: $k_1 \cdot [A]$
- Second order: $k_2 \cdot [A] \cdot [B]$
- Third order: $k_3 \cdot [A]^2 \cdot [B]$

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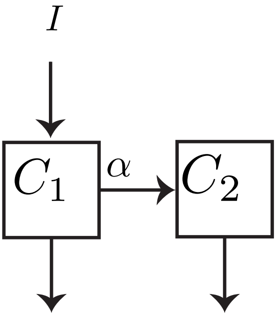
First order models apply (almost) always for tracers



$$\frac{dC_1}{dt} = I - k_1 C_1$$
$$\frac{dC_2}{dt} = \alpha k_1 C_1 - k_2 C_2$$

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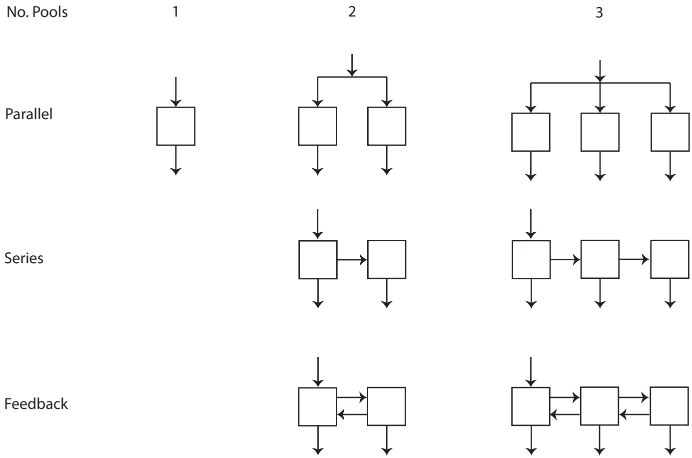

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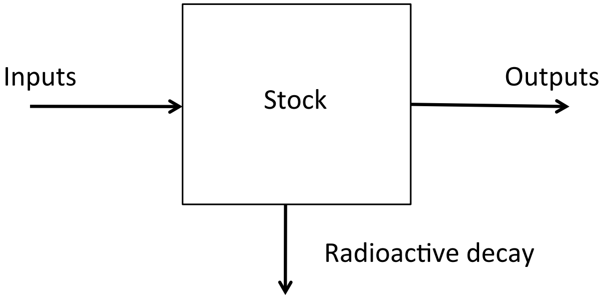
Radiocarbon models: one homogeneous pool



$$\frac{d^{14}C}{dt} = \frac{dFC}{dt} = IF_{atm} - kFC - \lambda FC$$
$$= IF_{atm} - (k+\lambda)FC$$

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Steady-state solution for one homogeneous pool

- Differential equation:
  $\frac{dFC}{dt} = IF_{atm} - (k + \lambda)FC$
- Steady-state solution:
  $IF_{atm} = (k + \lambda)FC$
- Solve for FC:
  $FC = \frac{IF_{atm}}{k+\lambda}$
- Assuming $F_{atm} = 1$ (pre-1950), and $I = kC$:
  $F = \frac{k}{k+\lambda}$

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Cycling rate from fraction modern (not recommended!)

You can also solve for k if a value of F is available:

$$k = \frac{\lambda F}{1 - F}$$

or obtain a *turnover time*:

$$\tau = \frac{1}{k} = \frac{1 - F}{\lambda F}$$

Notice that this approach relies on several assumptions: 1) single homogeneous pool, 2) constant inputs and rates 3) steady-state, 4) constant radiocarbon values in the atmosphere.

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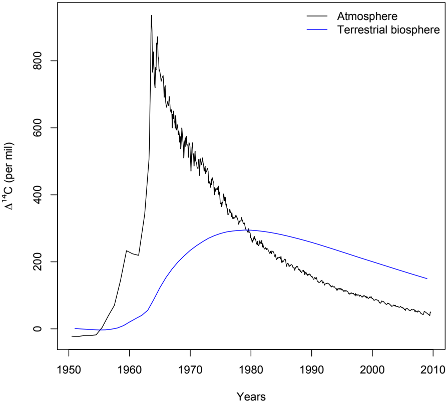
Example: the terrestrial biosphere as a one-pool

- Carbon inputs as GPP = 120 Pg C yr^{-1}
- Cycling rate as $k = 0.05$ yr^{-1} or $\tau = 20$ yr.
- Atmospheric radiocarbon as for the Northern Hemisphere
- For a value of Δ^{14}C in 2000 of 200.47 (permil) ($F = 1.2$), $\tau = 49503$ yr.



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Model implementation

- Analytical solutions
- Numerical solutions
  - Specialized commercial software
  - Open source software

Analytical solution

Any model using first-order reaction terms with constant coefficients of the form

$$\frac{dx_1}{dt} = I_1 + \sum \alpha_{1,j} k_j x_j - k_1 x_1$$
$$\frac{dx_i}{dt} = I_i + \sum \alpha_{i,j} k_j x_j - k_i x_i$$
$$\frac{dx_n}{dt} = I_n + \sum \alpha_{n,j} k_j x_j - k_n x_n$$

can be expressed as a system of the form

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{I} + \mathbf{A} \cdot \boldsymbol{x}$$

Analytical solution

The system

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{I} + \mathbf{A} \cdot \boldsymbol{x},$$

with initial conditions $\boldsymbol{x}(t = 0) = \boldsymbol{x}_0$, has solution

$$\boldsymbol{x}(t) = e^{\mathbf{A} \cdot (t - t_0)} \boldsymbol{x}_0 + \left(\int_{t_0}^{t} e^{\mathbf{A} \cdot (t - \tau)} d\tau \right) \boldsymbol{I}.$$

At steady-state:

$$\boldsymbol{x}_{ss} = -\mathbf{A}^{-1} \cdot \boldsymbol{I}$$

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Limitations analytical solution

- Only possible for models formulated as first-order reactions
- Assumes constant parameters (rate limitation and inhibition terms)
- Still difficult to compute for high dimensional systems

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Numerical solutions

Calculate the solution of the IVP taking advantage of the know values of the derivatives and the initial value. For the IVP

$$x'(t) = f(t, x(t)), \qquad x(t_0) = x_0,$$

an approximation to the solution is

$$x(t + h) \approx x(t) + hf(t, x(t)).$$

This leads to a recursion of the form

$$x_{n+1} = x_n + hf(t_n, x_n).$$

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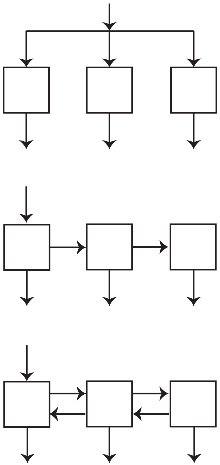
Run radiocarbon models numerically



- Parallel: no exchange of matter among pools
- Series: Progressive transfer of matter among pools
- Feedback: Multiple exchange of matter among pools.

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Mathematical form

- Parallel:

$$\frac{d\mathbf{C}(t)}{dt} = I \begin{pmatrix} \gamma_1 \\ \gamma_2 \\ 1 - \gamma_1 - \gamma_2 \end{pmatrix} + \begin{pmatrix} -k_1 & 0 & 0 \\ 0 & -k_2 & 0 \\ 0 & 0 & -k_3 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

- Series:

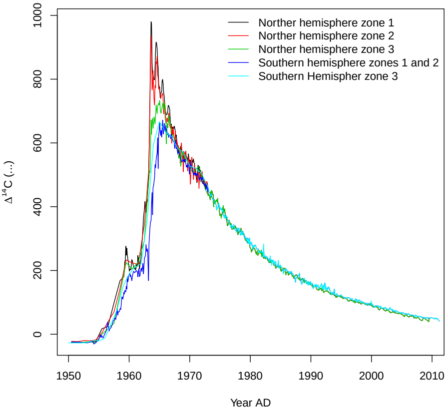
$$\frac{d\mathbf{C}(t)}{dt} = I \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} -k_1 & 0 & 0 \\ a_{21} & -k_2 & 0 \\ 0 & a_{32} & -k_3 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

- Feedback:

$$\frac{d\mathbf{C}(t)}{dt} = I \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} -k_1 & a_{12} & 0 \\ a_{21} & -k_2 & a_{23} \\ 0 & a_{32} & -k_3 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

Atmospheric radiocarbon curves

We need an atmospheric radiocarbon curve to determine inputs to the system



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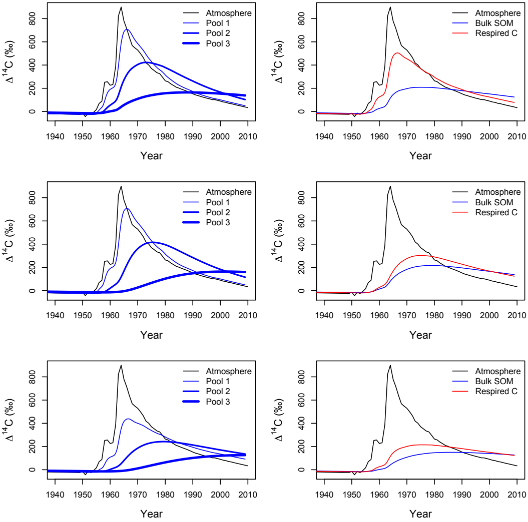
Radiocarbon trends for different model structures



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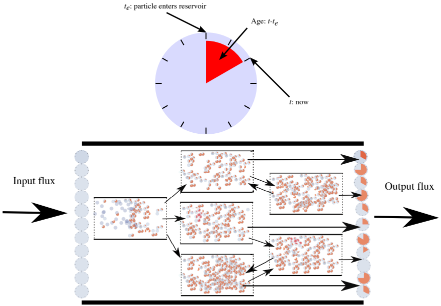
Model properties: Ages and transit times



- *System age* is a random variable that describes the age of particles or molecules within a system since the time of entry.
- *Pool age* is a random variable that describes the age of particles or molecules within a pool since the time of entry.
- *Transit time* is a random variable that describes the ages of the particles at the time they leave the boundaries of a system; i.e., the ages of the particles in the output flux.

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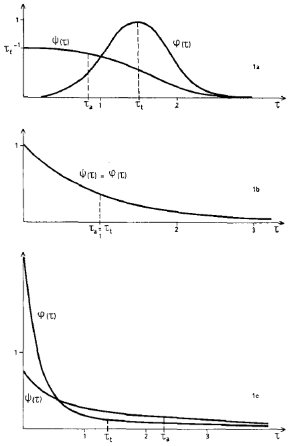
Age and transit time are not always equal



Bolin & Rodhe (1973, Tellus 25: 58)

- Mean transit time > mean age: human population
- Mean transit time = mean age: Uranium, Radiocarbon
- Mean transit time < mean age: Ocean water

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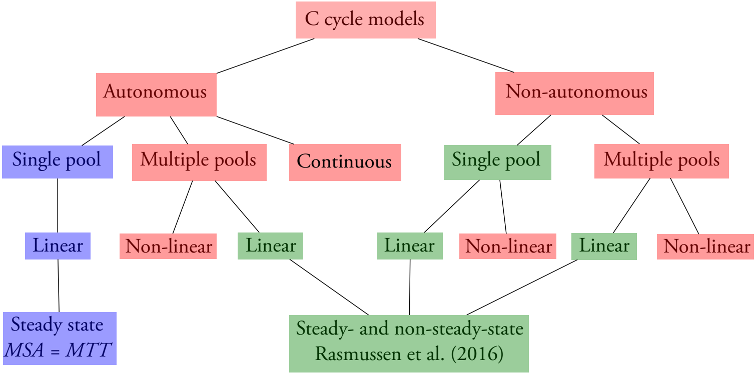
System age and transit time are not equal

System age and transit times are model dependent



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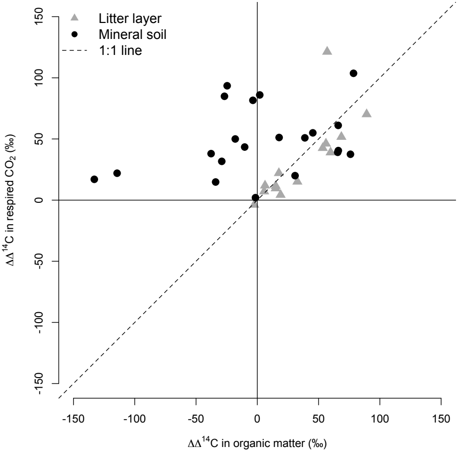
System age and transit time are not equal

Radiocarbon evidence



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New formulas for transit times and ages

Let $\mathbf{B} = \mathbf{T} \cdot \mathbf{N}$, and assume a system at steady-state, then

- *System age*
  - $f_A(y) = \boldsymbol{z}^T \, e^{y\,\mathbf{A}} \, \boldsymbol{\eta} = \boldsymbol{z}^T \, e^{y\,\mathbf{A}} \, \frac{\boldsymbol{x}^*}{\|\boldsymbol{x}^*\|}$
  - $\mathbb{E}[A] = -\mathbf{1}^T \, \mathbf{A}^{-1} \, \boldsymbol{\eta} = \frac{\|\mathbf{A}^{-1}\,\boldsymbol{x}^*\|}{\|\boldsymbol{x}^*\|}$
- *Pool age*
  - $\boldsymbol{f_a}(y) = (\mathbf{X}^*)^{-1} \, e^{y\,\mathbf{A}} \, \boldsymbol{u}$
  - $\mathbb{E}[\boldsymbol{a}] = -(\mathbf{X}^*)^{-1} \, \mathbf{A}^{-1} \, \boldsymbol{x}^*$
- *Transit time*
  - $f_T(t) = \boldsymbol{z}^T \, e^{t\,\mathbf{A}} \, \boldsymbol{\beta}$
  - $\mathbb{E}[T] = \|\mathbf{A}^{-1}\,\boldsymbol{\beta}\| = \frac{\|\boldsymbol{x}^*\|}{\|\boldsymbol{s}\|}$

Metzler & Sierra (2017, Math Geosci *in press*)

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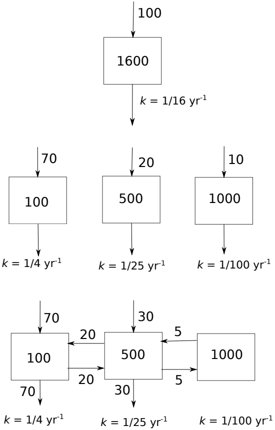
Three-pool model example



- One pool model:
  $dC/dt = 100 - (1/16)C$

- Three-pool model in parallel:

$$\frac{d\mathbf{C}(t)}{dt} = \begin{pmatrix} 70 \\ 20 \\ 10 \end{pmatrix} + \begin{pmatrix} -(1/4) & 0 & 0 \\ 0 & -(1/25) & 0 \\ 0 & 0 & -(1/100) \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

- Three-pool model in feedback:

$$\frac{d\mathbf{C}(t)}{dt} = \begin{pmatrix} 70 \\ 30 \\ 0 \end{pmatrix} + \begin{pmatrix} -(1/4) & 20/(55 \cdot 25) & 0 \\ 2/(9 \cdot 4) & -(1/25) & 1/100 \\ 0 & 5/(55 \cdot 25) & -(1/100) \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$$

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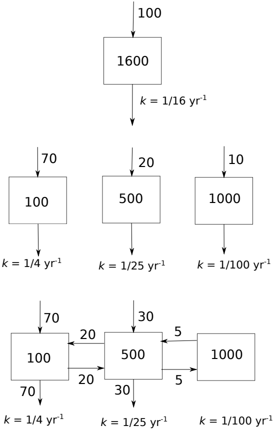
Three-pool model example



- One pool model:
  - Mean Age: 16 yrs
  - Mean transit time: 16 yrs
- Three-pool model in parallel:
  - Mean Age: 63.8 yrs
  - Mean transit time: 32.3 yrs
  - Mean pool ages: 4, 25, 100 yrs.
- Three-pool model in feedback:
  - Mean Age: 60.5 yrs
  - Mean transit time: 22.35 yrs
  - Mean pool ages: 13, 43, 143 yrs.

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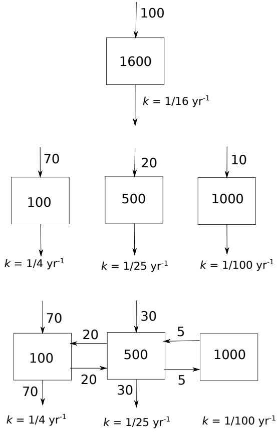
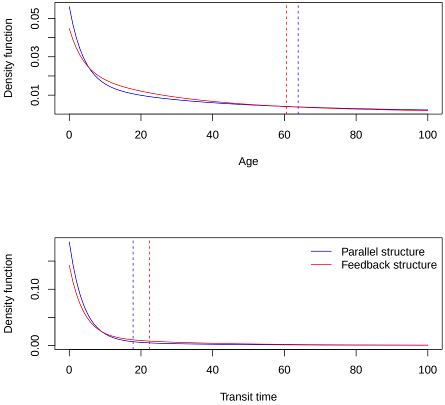
Three-pool model example





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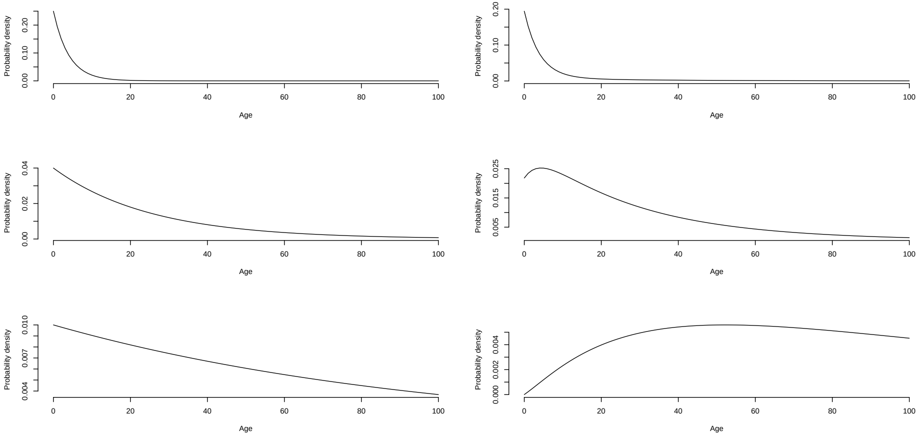
Three-pool model example

Pool age distributions: Parallel and feedback model structures



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Harvard Forest example

Biogeochemistry **51:** 33–69, 2000.

Soil carbon cycling in a temperate forest: radiocarbon-based estimates of residence times, sequestration rates and partitioning of fluxes

JULIA B. GAUDINSKI[1], SUSAN E. TRUMBORE[1], ERIC A. DAVIDSON[2] & SHUHUI ZHENG[1]
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Received 27 December 1999; accepted 4 January 2000

Key words: carbon, dynamics, isotope disequilibrium, radiocarbon, soil respiration, temperate forests

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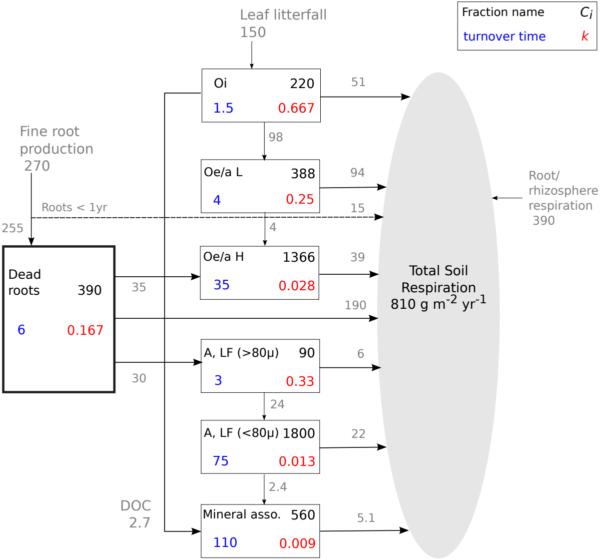
The Harvard Forest model



Sierra et al. (2012, Biogeosciences 9: 3013–3028)

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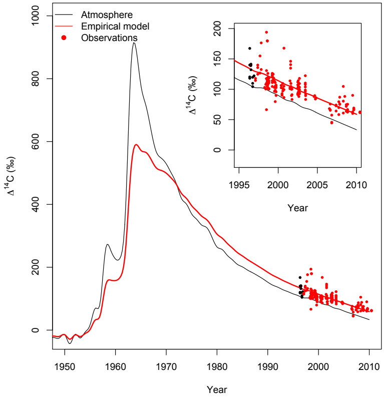
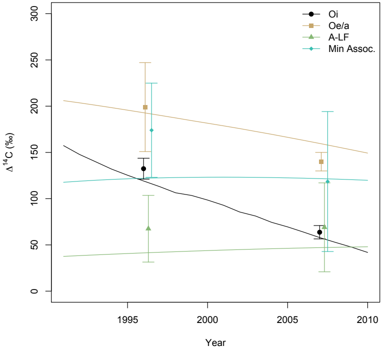
Testing the Harvard Forest model





Sierra et al. (2012, Biogeosciences 9: 3013–3028)

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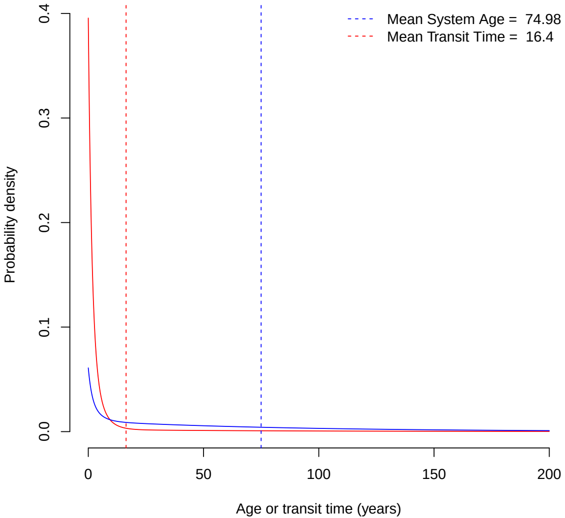
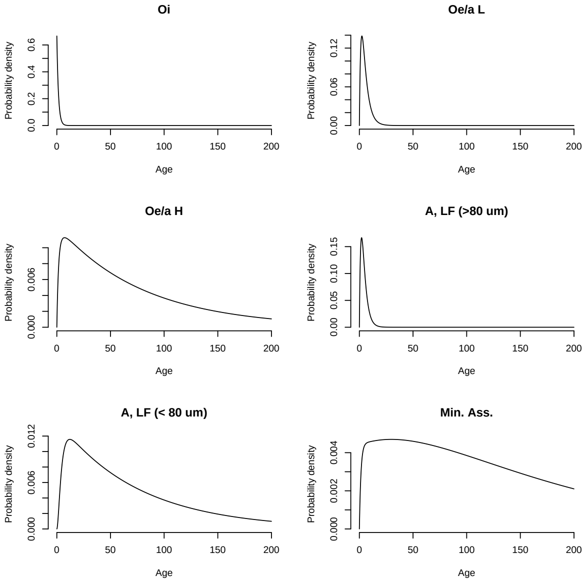
System age and transit time distributions



Pool ages



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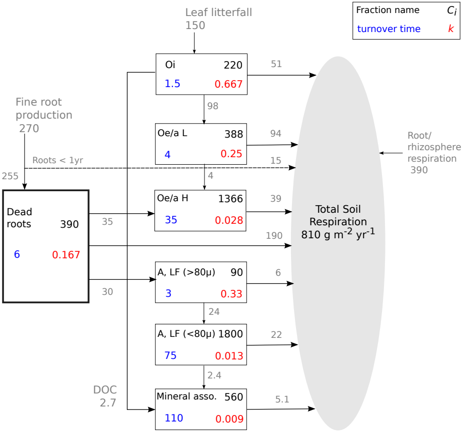
Mean pool ages vs 'turnover times'



Mean pool age (yrs)

- Oi = 1.5
- Oe/a L = 5.5
- Oe/a H = 81.9
- A, LF ($> 80\mu$) = 4.5
- A, LF ($< 80\mu$) = 79.5
- Mineral ass. = 149.96

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Parameter estimation

- You can run now a model, but what parameter values to use?
- Find reasonable parameter values in the literature
- Use data to obtain the best parameter set for a specific case

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Parameter estimation methods

- Optimization: maximization or minimization of an objective function
- Bayesian parameter estimation

Optimization

An optimization problem can be represented in the following way:

- Given: a function $f : A \to R$ from some set A to the real numbers
- Sought: an element x_0 in A such that $f(x_0) \leq f(x)$ for all x in A ("minimization") or such that $f(x_0) \geq f(x)$ for all x in A ("maximization").

Example:

$$\min_{x \in \mathbb{R}} (x^2 + 1)$$

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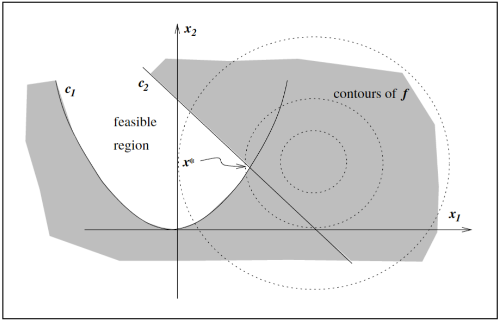
Optimization with constrains



Objective function:

$$\min\left((x_1-2)^2+(x_2-1)^2\right)$$

Subject to

$$x_1^2 - x_2 \leq 0$$
$$x_1 + x_2 \leq 2$$

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The objective function

We are interested in minimizing the difference between observations y_i and model predictions $f(x_i)$

- For univariate cases:

$$\sum_{i=1}^{n}(y_i - f(x_i))^2$$

- For multivariate cases:

$$\sum_{i=1}^{n}\frac{(y_{i,j} - f(x_{i,j}))^2}{\sigma_j}$$

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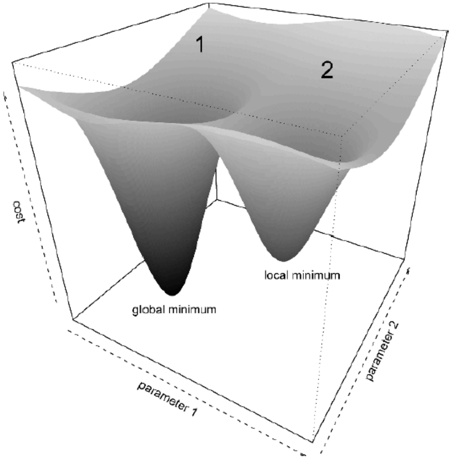
Common or popular optimization methods

- Newton or Newton-Raphson method: finding roots of a function
- Nelder-Mead method: Finds minimum of nonlinear function over an n-dimensional space
- Levenberg-Marquardt method: nonlinear least-squares
- Gradient descent method: moves solution along negative of the gradient

Global versus local minimum



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Bayesian parameter estimation

- Powerful method for parameter estimation
- Parameters are assumed to be random variables instead of fixed values
- Bayesian methods seek to estimate a posterior probability distribution given some prior knowledge and some observed data.

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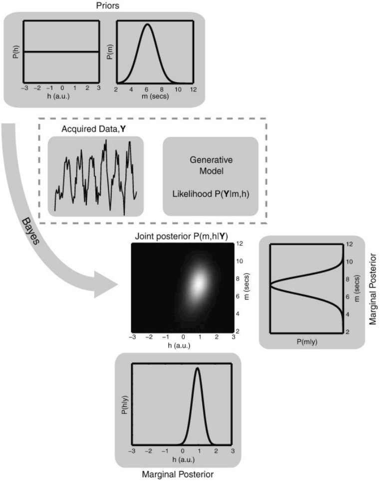
Bayesian inference



$$P(\theta|\mathbf{D}) = \mathbf{P}(\theta)\frac{\mathbf{P}(\mathbf{D}|\theta)}{\mathbf{P}(\mathbf{D})}$$

Posterior distribution provides knowledge about the mean and variance of the parameters. Can be used to estimate uncertainty of the predictions

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How to implement Bayesian techniques?

- R is a powerful environment for fitting Bayesian models
- Package FME provides functions to fit models to data using Bayesian techniques
- We will run an example in the practical session

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Recommended workflow

- Perform measurements of carbon stocks and fluxes in combination with their radiocarbon signature
- Find the best model or set of models that best represent the observed data
- Calculate age and transit time distributions from the obtained models

Summary

- Models are necessary to represent carbon and radiocarbon dynamics in open systems
- Radiocarbon is an excellent constraint to identify appropriate models
- Models can be used to estimate the age and the transit time of carbon in open systems

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