Data analysis – basic theory

- What we measure with microsensors is the result of biological and chemical activity, and transport.
- Biological and chemical activity = transformation of chemical compounds: $\alpha + \beta \rightarrow \gamma$
- Transport: in time and space
- The purpose of microsensor measurements is to collect data from which the parameters characterizing the activity and transport can be deduced.
- Thus, we need theoretical concepts that couple 'what we want' (rates of activity and transport) with 'what we have' (profiles, time-series).

Data analysis – basic theory

Let us consider a reaction $\alpha + \beta \rightarrow \gamma$. The analytes α and β are consumed and transformed into γ , which is thus produced. We want to quantify the rate of this consumption/production, which is defined as the change in the analyte concentration per unit time, $\Delta c/\Delta t$.

General kinetics: (Michaelis-Menten)

$$\frac{\Delta c}{\Delta t} = \frac{K c}{c_{1/2} + c}$$

Zero-order kinetics:

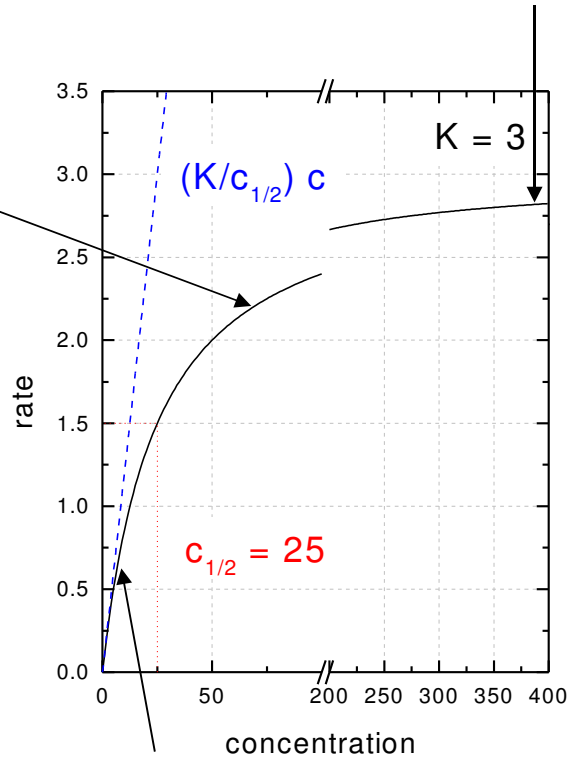
$$c \gg c_{1/2} \quad \rightarrow \quad \frac{\Delta c}{\Delta t} \approx K$$

First-order kinetics:

$$c \ll c_{1/2} \quad \rightarrow \quad \frac{\Delta c}{\Delta t} \approx \frac{K}{c_{1/2}} c$$

For reaction $\alpha + \beta \rightarrow \gamma$ with zero order kinetics:

$$\frac{\Delta c_\alpha}{\Delta t} = \frac{\Delta c_\beta}{\Delta t} = -\frac{\Delta c_\gamma}{\Delta t} = -K$$



Example: Rate of aerobic respiration or rate of gross photosynthesis: d[O2]/dt

– volume specific (mol m^{-3} s^{-1})

- areal (mol m^{-2} s^{-1})

Data analysis – basic theory

Generally, **all is in motion**.

– Motion on a **microscopic level:** Brownian motion

  – particle path is random →**diffusion**

  – The fundamental law describing the *macroscopic effects* of the Brownian motion is the Fick's law:

Fick's law:
flux = number of molecules transported per unit area per unit time

$$J_{\text{diff}} = -D\frac{\Delta c}{\Delta z} \quad [\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}]$$

– Motion on a **macroscopic level:** Flow

  – Particle path is **not** totally random →**advection**

  – Example: dissolved analyte in a flowing medium

Advective flux:

$$J_{\text{adv}} = c\,v_f$$

– Total transport: diffusion + advection

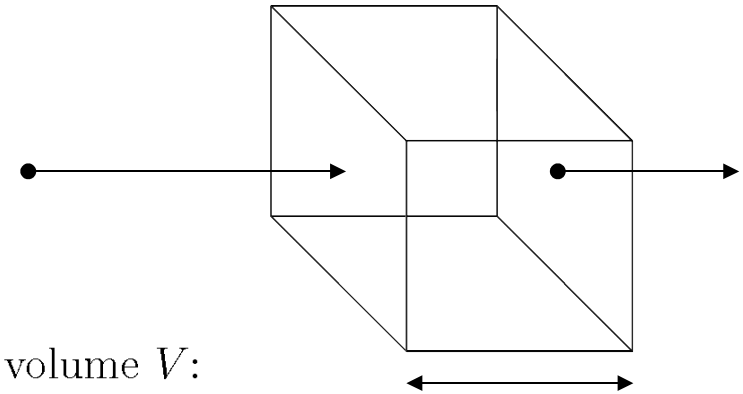
Total flux:

$$J = J_{\text{diff}} + J_{\text{adv}}$$

Data analysis – basic theory

Mass balance in volume V (assuming 1-D transport for simplicity):

What comes in, minus what comes out, plus the net amount produced as a result of biological or chemical activity, must equal to the amount accumulated in volume V.



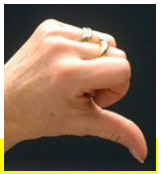
Chemical reaction (zero-order kinetics):

$$\frac{\Delta c}{\Delta t} = K \quad \rightarrow \quad \Delta c = K\Delta t$$

Total change of number of molecules (mol) of analyte in volume V:

$$\Delta N = \underbrace{J(z_1)S\Delta t - J(z_2)S\Delta t}_{\substack{\text{transport} \\ \text{(diffusion + advection)}}} + \underbrace{KV\Delta t}_{\substack{\text{(bio)chemical} \\ \text{reaction}}}$$

rule of thumb:

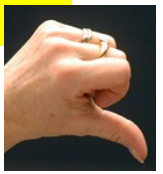


Considering $\Delta N/V \equiv c$ and $V = S\Delta z$:

$$\frac{\Delta c}{\Delta t} = -\frac{\Delta J}{\Delta z} + K$$

Diffusion-advection-reaction equation:
The rate of change in the analyte concentration in *time* equals minus the rate of change in the analyte flux in *space* plus the volume-specific rate of activity which results in the *net* analyte production.

In a steady state ($\Delta c/\Delta t$=0), the average volume-specific rate of activity in an interval Δz equals the difference in the analyte flux at the borders of the interval, divided by the interval thickness, i.e., $K = \Delta J/\Delta z$.



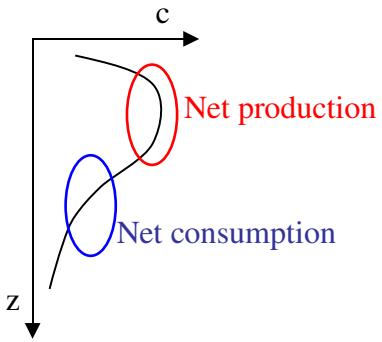
Data analysis – basic theory

Employing infinitesimal calculus (Newton), i.e., $\Delta z \to 0$, $\Delta t \to 0$, $\Delta \to \partial$, and assuming $D \neq D(z)$, $v_f \neq v_f(z)$:

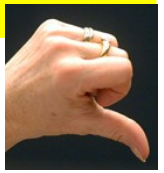
$$\left.\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - v_f\frac{\partial c}{\partial z} + K\right\}$$ 1D diffusion – advection – reaction equation, zero order kinetics

Assuming no advection ($v_f = 0$) and steady state (dc/dt=0):

$$0 = D_\gamma \frac{\mathrm{d}^2 c_\gamma}{\mathrm{d}z^2} + K$$



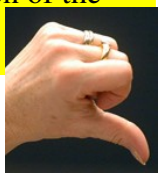
Thus, in a steady state and for diffusive transport, volume-specific rate of net analyte production (in mol m^{-3} s^{-1}) around a given point equals minus the spatial curvature (second derivative) of the analyte concentration profile in that point, multiplied by the diffusion coefficient.



Fick's law:
flux = number of molecules transported per unit area per unit time

$$J_{\mathrm{diff}} = -D\frac{\Delta c}{\Delta z} \quad [\mathrm{mol\,m^{-2}\,s^{-1}}]$$

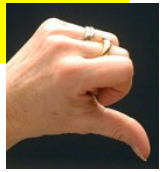
Thus, in a steady state and for diffusive transport, areal rate of net analyte transport (flux, in mol m^{-2} s^{-1}) through an (imaginary) area equals minus the spatial gradient (first derivative) of the analyte concentration profile, multiplied by the diffusion coefficient. The flux calculated this way corresponds to the flux through an area which is perpendicular to the direction of the profile, i.e., in the direction of the profile.



Data analysis – basic theory

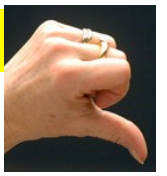
Light-dark shift method according to Joergensen & Revsbech (1983):

Volume-specific rate of *gross* photosynthesis (in mol m^{-3} s^{-1}) around a given point equals minus the rate of change in oxygen concentration during a short period of darkness, which followed a prolonged period of sample illumination with light of constant intensity.



Areal content:

Areal content of an analyte (in mol m^{-2}) in a layer between depths z_1 and z_2 is the integral of the analyte concentration from z_1 to z_2.



Summary:

To interpret the measured profiles or time-series, we need to calculate
- spatial gradients of the concentration profiles
- spatial curvatures of the concentration profiles
- rates of change in concentration with time
- integrals of concentration profiles from z_1 to z_2

Rapid calculation of these basic quantities is enabled by the *mprplotter* and *calfluxrate* programs.