Inverse problem in chemical engineering

Consider the reversible chemical reactions

$$A \rightleftarrows B,$$

with reaction rates k_1 and k_2, respectively.

Concentrations C_A and C_B satisfy

$$\begin{aligned} \frac{dC_A}{dt} &= -k_1 C_A + k_2 C_B \\ \frac{dC_B}{dt} &= k_1 C_A - k_2 C_B, \end{aligned}$$

with initial data

$$C_A(0) = C_{A,0}, \quad C_B(0) = C_{b,0}.$$

Inverse problem

Assume that we know the initial concentrations.

Data: For $0 < t_1 < t_2 \cdots < t_n$, measure $C_A(t_j)$, $1 \leq j \leq n$.

Estimate k_1 and k_2.

Noisy observations:

$$b_j = C_A(t_j) + e_j, \quad e_j \sim \mathcal{N}(0, \sigma^2).$$

Define

$$\mathbf{x}(t) = \begin{bmatrix} C_A(t) \\ C_B(t) \end{bmatrix}, \quad M = \begin{bmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{bmatrix}.$$

Dynamic system

$$\frac{d\mathbf{x}}{dt} = M\mathbf{x}, \quad \mathbf{x}(0) = \mathbf{x}_0.$$

Solution can be written as

$$\mathbf{x} = e^{Mt}\mathbf{x}_0.$$

Eigenvalue decomposition:

$$\det\big(M - \lambda I\big) = \begin{vmatrix} -k_1 - \lambda & k_2 \\ k_1 & -k_2 - \lambda \end{vmatrix} = 0,$$

or

$$\lambda^2 + (k_1 + k_2)\lambda = 0.$$

Eigenvalues are

$$\lambda_1 = 0, \quad \lambda_2 = -(k_1 + k_2) = -\frac{1}{\tau}.$$

Corresponding eigenvectors:

$$M\mathbf{v} = 0 \Leftrightarrow \begin{cases} -k_1 v_1 + k_2 v_2 = 0 \\ \quad k_1 v_1 - k_2 v_2 = 0 \end{cases} \Leftrightarrow v_2 = \frac{k_1}{k_2} v_1.$$

Similarly,

$$M\mathbf{v} = -\frac{1}{\tau}\mathbf{v} \Leftrightarrow \begin{cases} -k_1 v_1 + k_2 v_2 = -(k_1 + k_2) v_1 \\ \quad k_1 v_1 - k_2 v_2 = -(k_1 + k_2) v_2 \end{cases} \Leftrightarrow v_2 = -v_1.$$

Solution: denoting $\delta = k_1/k_2$,

$$\mathbf{x}(t) = \alpha \begin{bmatrix} 1 \\ \delta \end{bmatrix} + \beta \begin{bmatrix} 1 \\ -1 \end{bmatrix} e^{-t/\tau}.$$

Initial values:

$$\begin{cases} \alpha + \beta = C_{A,0} \\ \delta\alpha - \beta = C_{B,0} \end{cases},$$

leading to

$$\alpha = \frac{1}{1+\delta}(C_{A,0} + C_{B,0}), \quad \beta = \frac{\delta}{1+\delta}(C_{A,0} + C_{B,0}) - C_{B,0}.$$

$$b_j = \frac{1}{1+\delta}(C_{A,0} + C_{B,0}) + \left(\frac{\delta}{1+\delta}(C_{A,0} + C_{B,0}) - C_{B,0}\right) e^{-t_j/\tau} + e_j.$$

Does it matter when we measure?

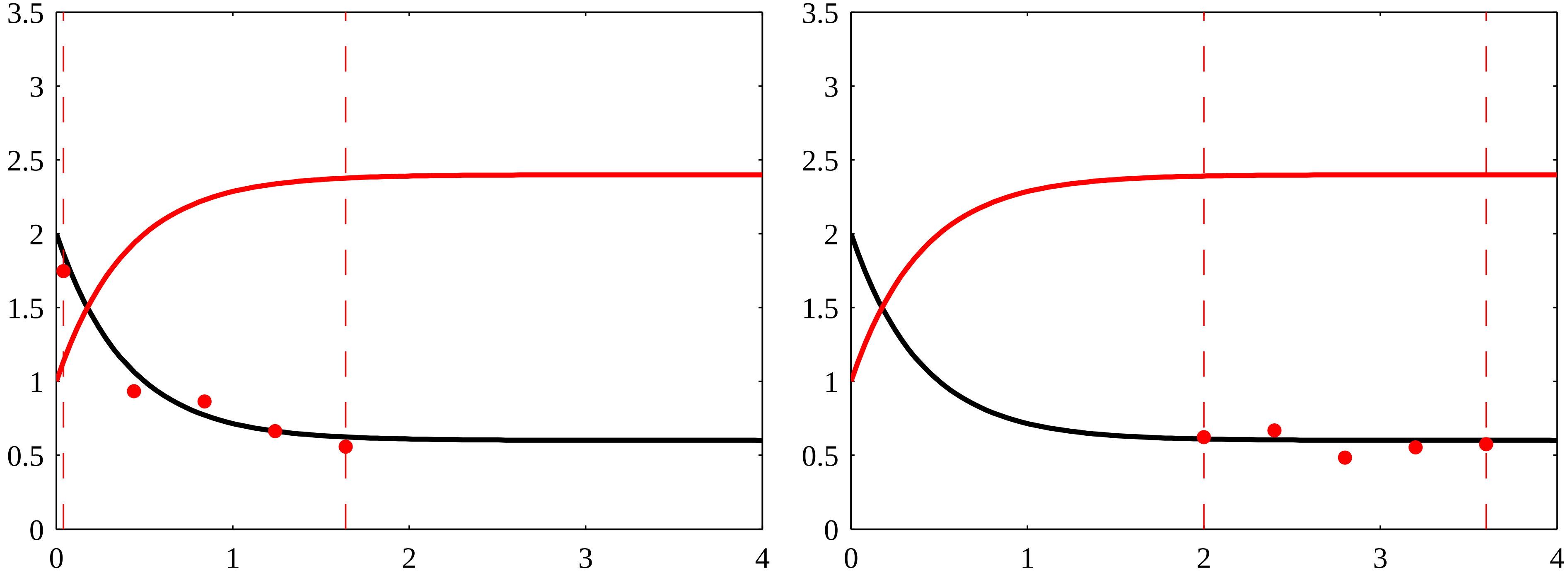
Yes: observe that as $t \to \infty$,

$$C_A(t) \to \frac{1}{1+\delta}(C_{A,0} + C_{B,0}),$$

i.e., at large times, *the data depends only on the ratio*

$$\delta = \frac{k_1}{k_2}.$$

Transient data and steady state data



$$C_{A,0} = 2, \quad C_{B,0} = 1, \quad k_1 = 2, \quad k_2 = 0.5, \quad \sigma = 0.2$$

$$\tau = 0.4 \Rightarrow e^{-t/\tau} < 0.01, \text{ as } t > 1.8.$$

Likelihood density

$$b_j = A(t_j, \mathbf{k}) + e_j,$$

where

$$A(t_j, \mathbf{k}) = \frac{1}{1+\delta}(C_{A,0} + C_{B,0}) + \left(\frac{\delta}{1+\delta}(C_{A,0} + C_{B,0}) - C_{B,0}\right) e^{-t_j/\tau},$$

and

$$\tau = \frac{1}{k_1 + k_2} \quad \delta = \frac{k_1}{k_2}.$$

Likelihood density is

$$\pi(\mathbf{b} \mid \mathbf{k}) \propto \exp\left(-\frac{1}{2\sigma^2}\sum_{j=1}^{n}(b_j - A(t_j, \mathbf{k}))^2\right).$$

Posterior density

Flat prior over an interval: assume that we believe that

$$0 < k_1 \le K_1, \quad 0 < k_2 \le K_2,$$

with some reasonable upper bounds. Write

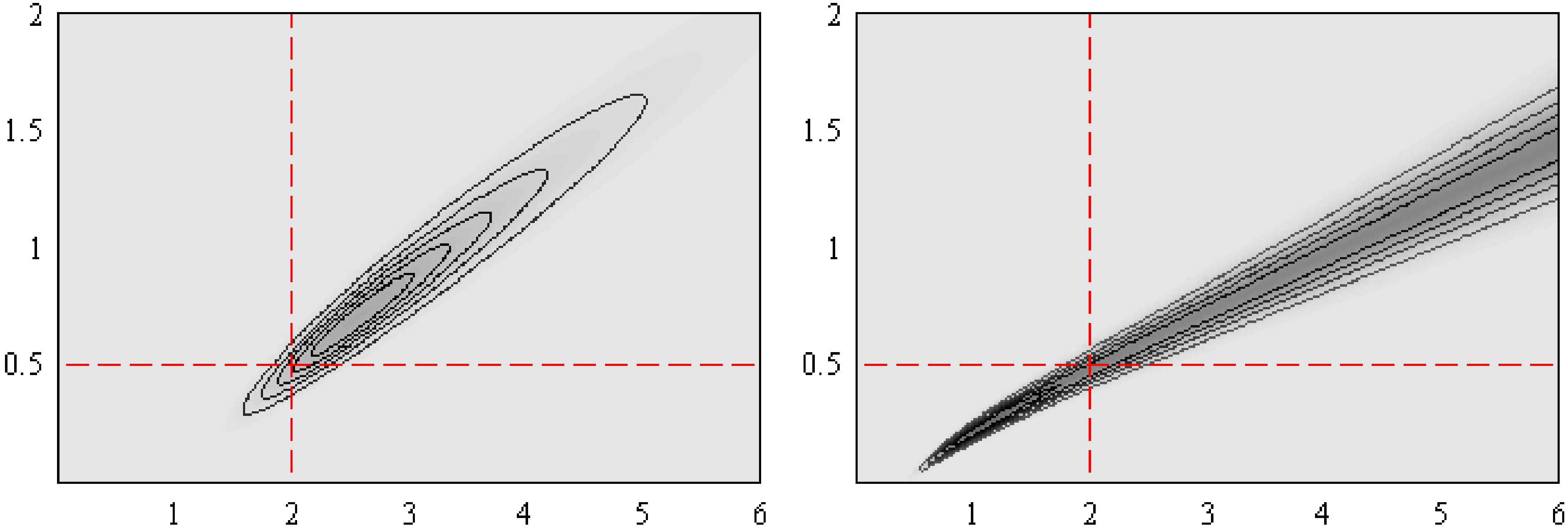
$$\pi_{\rm prior}(\mathbf{k}) \propto \chi_{[0,K_1]}(k_1)\chi_{[0,K_2]}(k_2).$$

Posterior density by Bayes' formula,

$$\pi(\mathbf{k} \mid \mathbf{b}) \propto \pi_{\rm prior}(\mathbf{k})\pi(\mathbf{b} \mid \mathbf{k}).$$

Contour plots of the posterior density?

Posterior densities



Different measurement intervals: $K_1 = 6$, $K_2 = 2$,

$$0.1\tau \leq t \leq 4.1\tau \text{ (left)} , \quad 5\tau \leq t \leq 9\tau \text{ (right)}$$

Random walk Metropolis-Hastings

Start with the transient measurements.

White noise proposal,

$$k_{\text{prop}} = k + \delta w, \quad w \sim \mathcal{N}(0, I).$$

Choose first $\delta = 0.1$, different initial points

$$k_0 = (1, 2) \text{ or } k_0 = (5, 0.1).$$

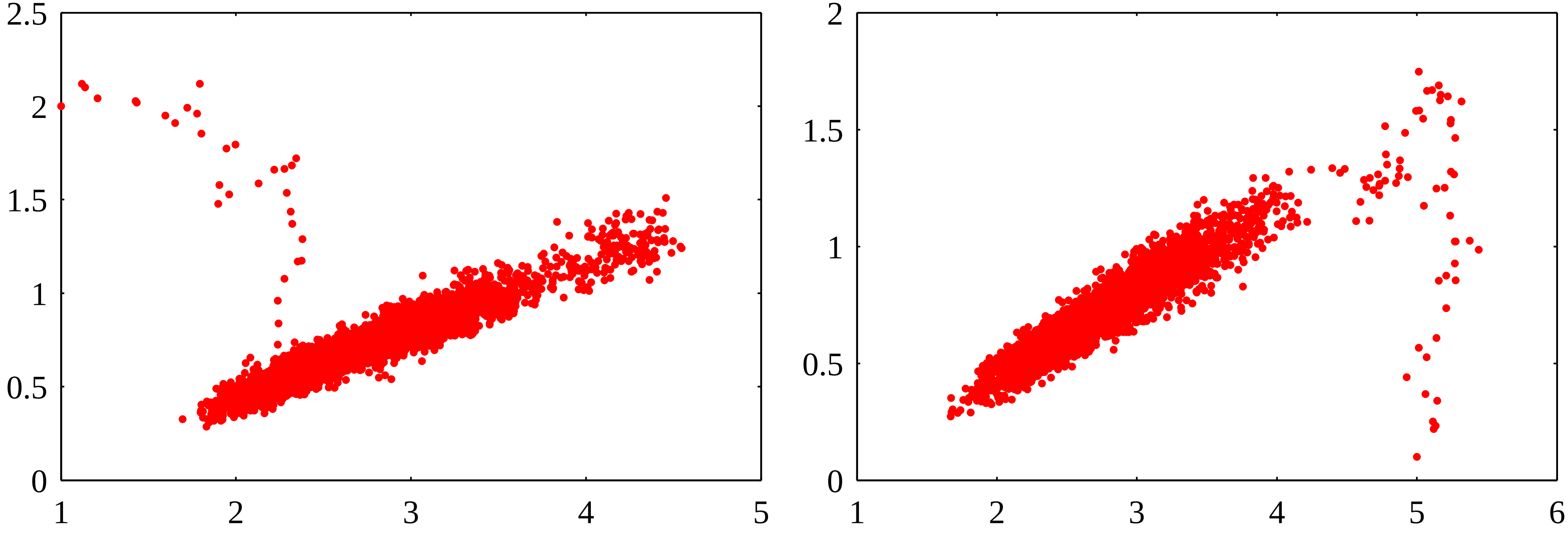
Relative acceptance rates are of the order 45%.

```
nsample = 10000;
k = [1;2];      % Initial point
nacc = 0;
step = 0.1;     % Step size of the random walk
Sample = zeros(2,nsample); Sample(:,1) = k; logpdf =
logpdf_func(k,A0,B0,Aj,tj,sigma); nacc = 0; for j = 2:nsample
    k_prop = k + step*randn(2,1);
    logpdf_prop = logpdf_func(k_prop,A0,B0,Aj,tj,sigma);
    if logpdf_prop - logpdf > log(rand);
        % Accept the proposal
        k = k_prop;
        logpdf = logpdf_prop;
        nacc = nacc + 1;
    end
    Sample(:,j) = k;
end
```

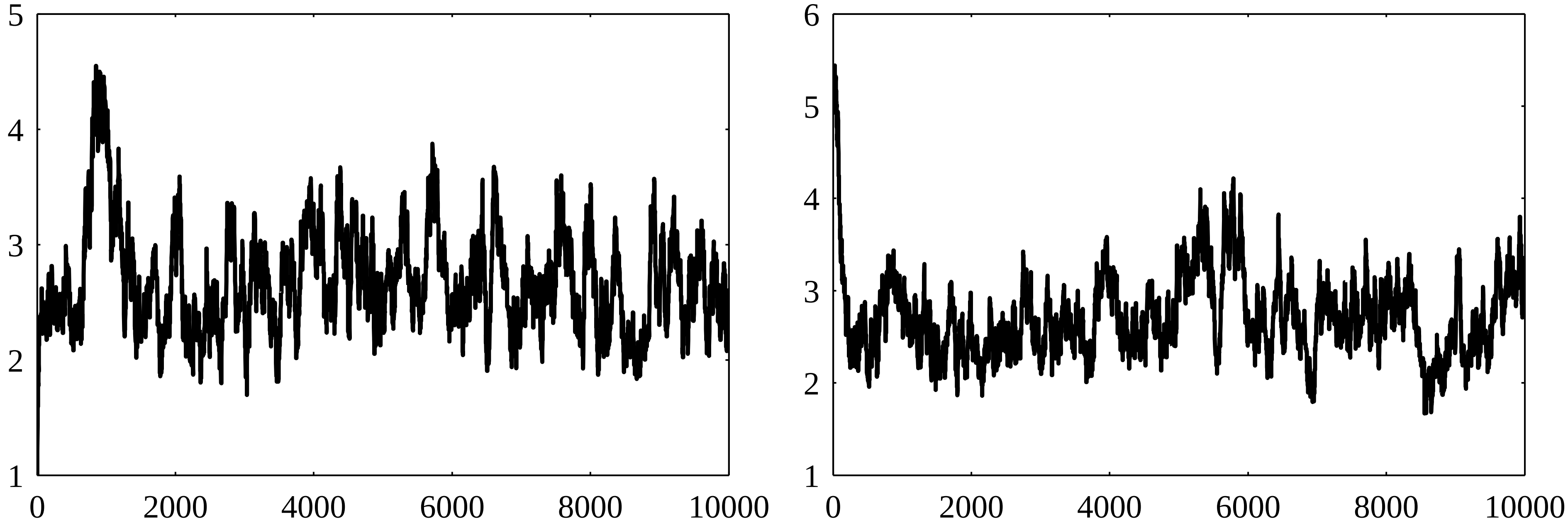
```
function logpdf = logpdf_func(k,A0,B0,Aj,t,sigma);

 tau = 1/(k(1) + k(2));
 delta = k(1)/k(2);
 alpha = (A0 + B0)/(1 + delta);
 beta = delta*alpha - B0;
 A = alpha + beta*exp(-1/tau*t);
 logpdf = -1/(2*sigma^2)*norm(A - Aj);
```

Scatter plots

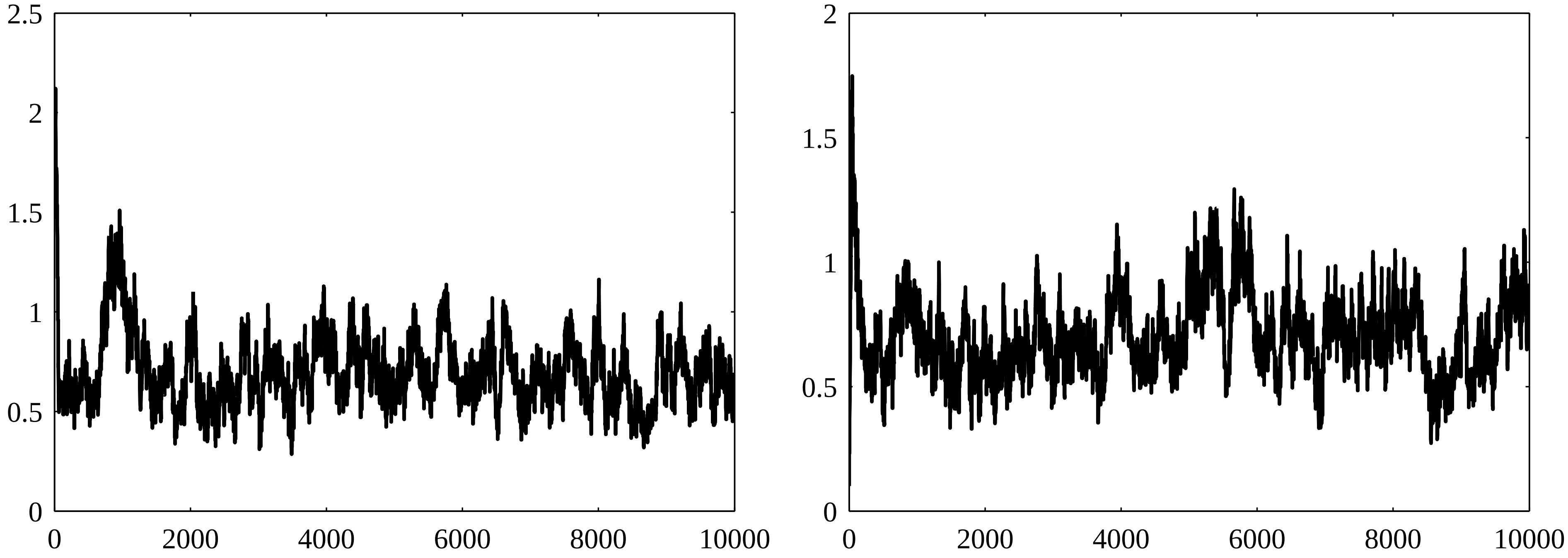


First component



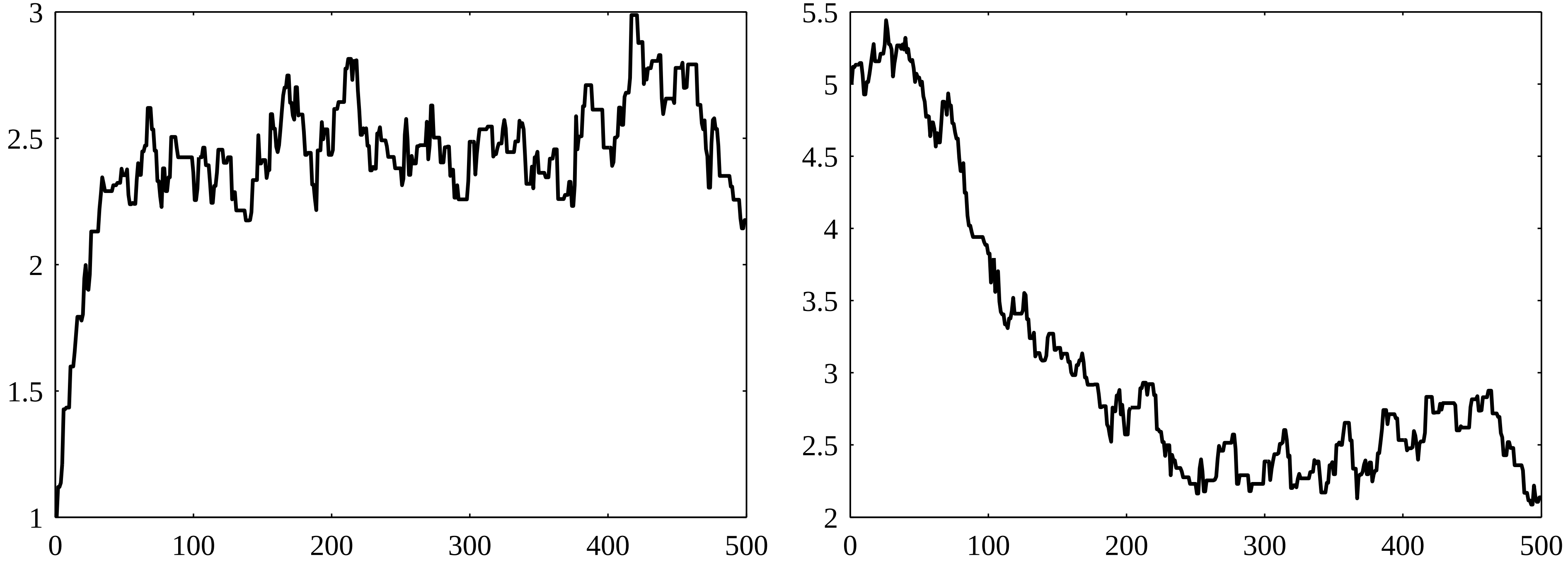
Initial value $k_1 = 1$ (left) and $k_1 = 5$ (right).

Second component



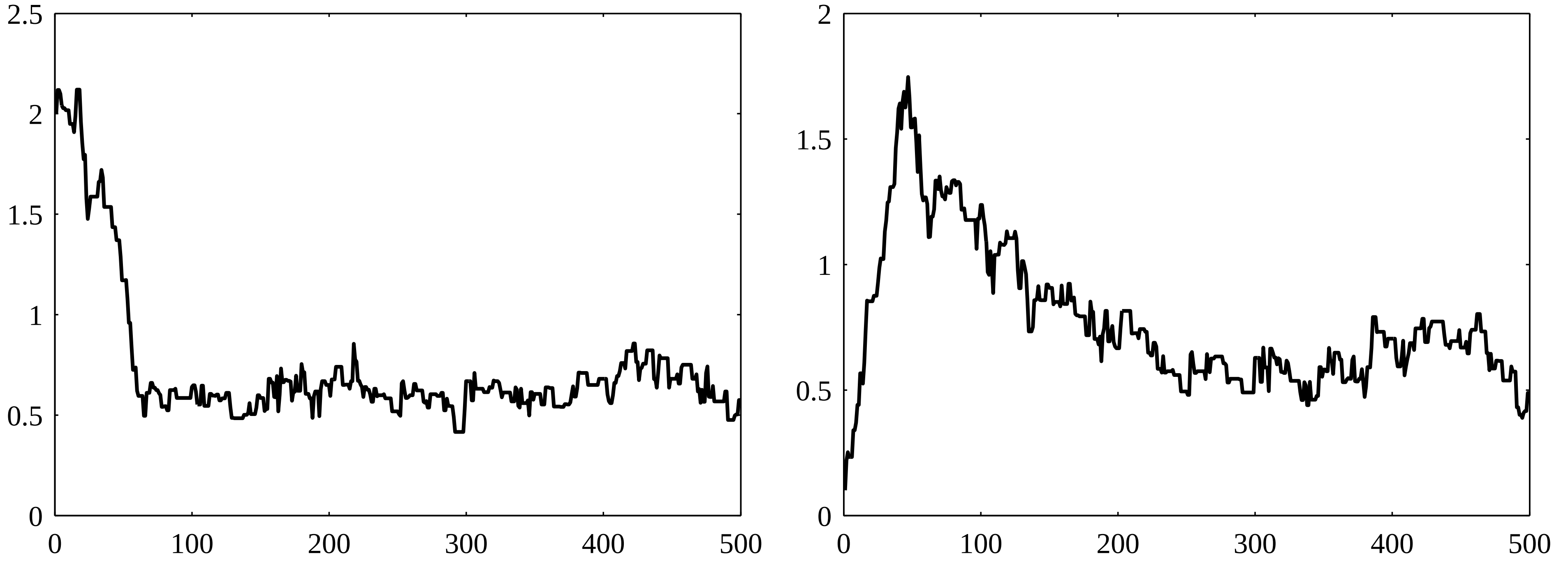
Initial value $k_2 = 2$ (left) and $k_2 = 0.2$ (right).

Burn-in: first component



Initial value $k_1 = 1$ (left) and $k_1 = 5$ (right).

Burn-in: Second component



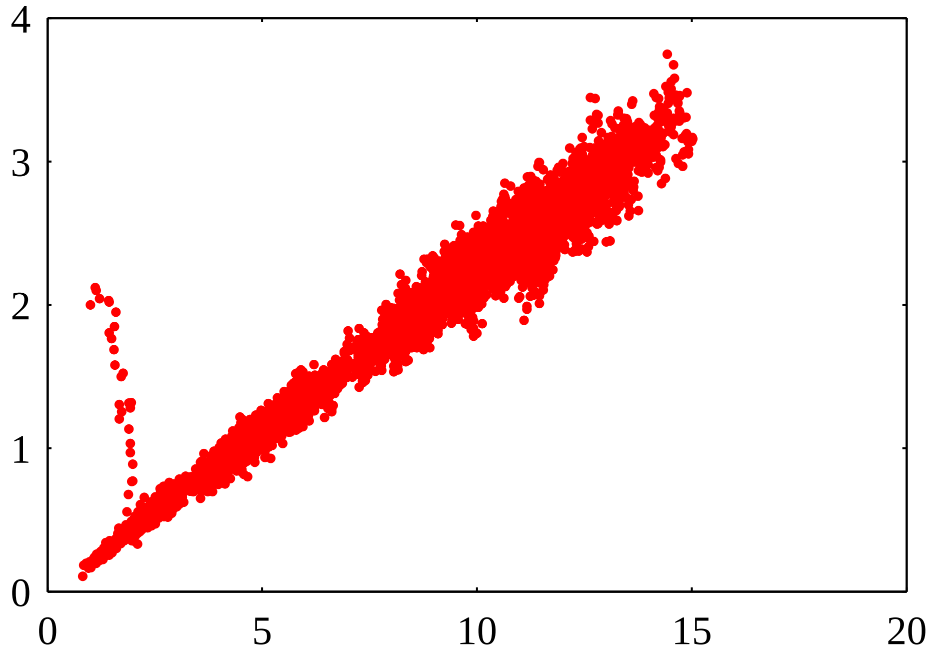
Initial value $k_2 = 2$ (left) and $k_2 = 0.2$ (right).

Steady state measurement

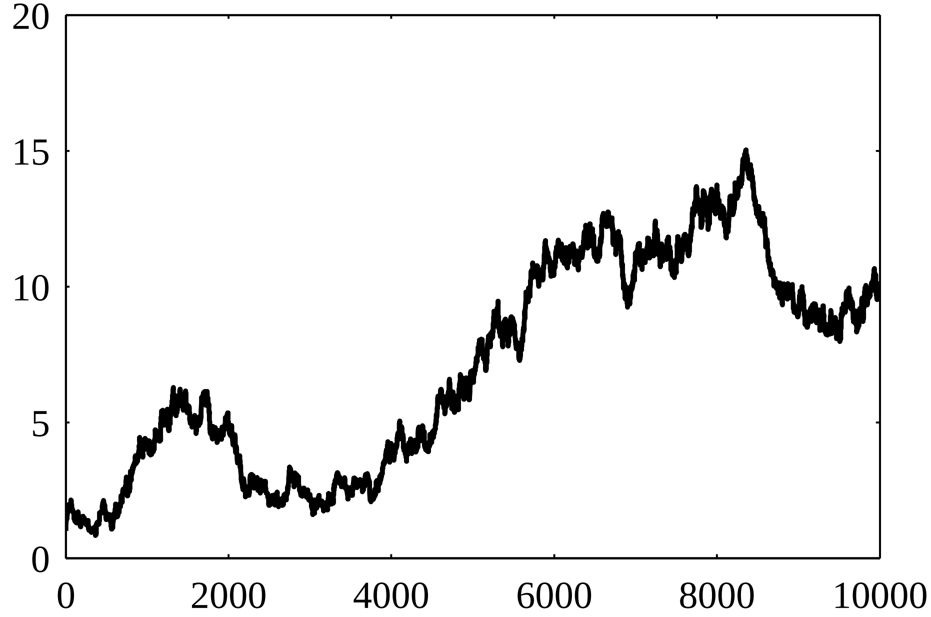
Use the same step size.

Initial point $(k_1, k_2) = (1, 2)$.

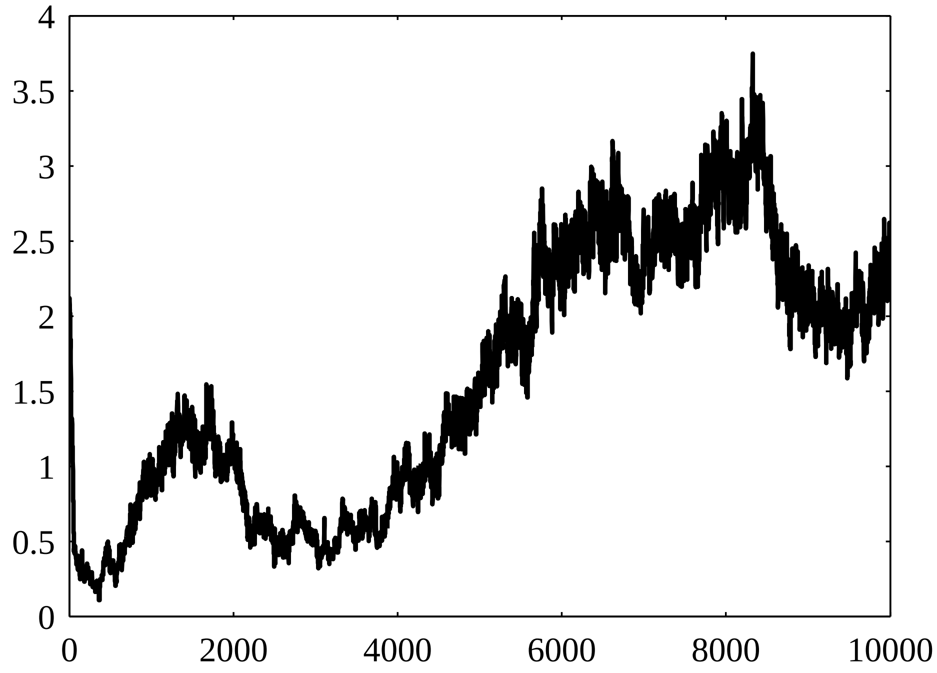
Scatter plots



Fuzzy worms



0
5
10
15
20
0
2000
4000
6000
8000
10000



0
0.5
1
1.5
2
2.5
3
3.5
4
0
2000
4000
6000
8000
10000

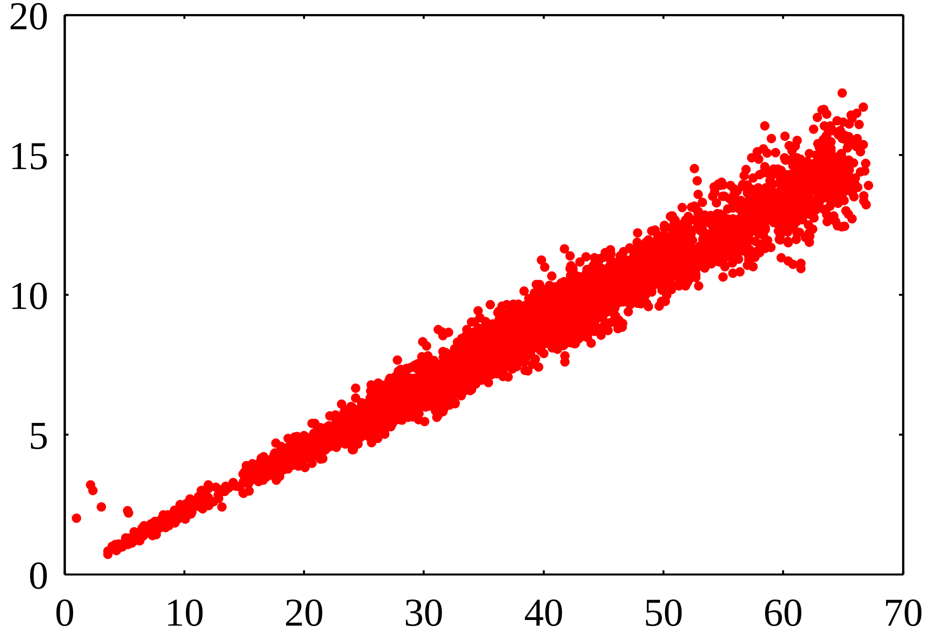
Steady state measurement, again

Increase the step size $0.1 \to 1$.

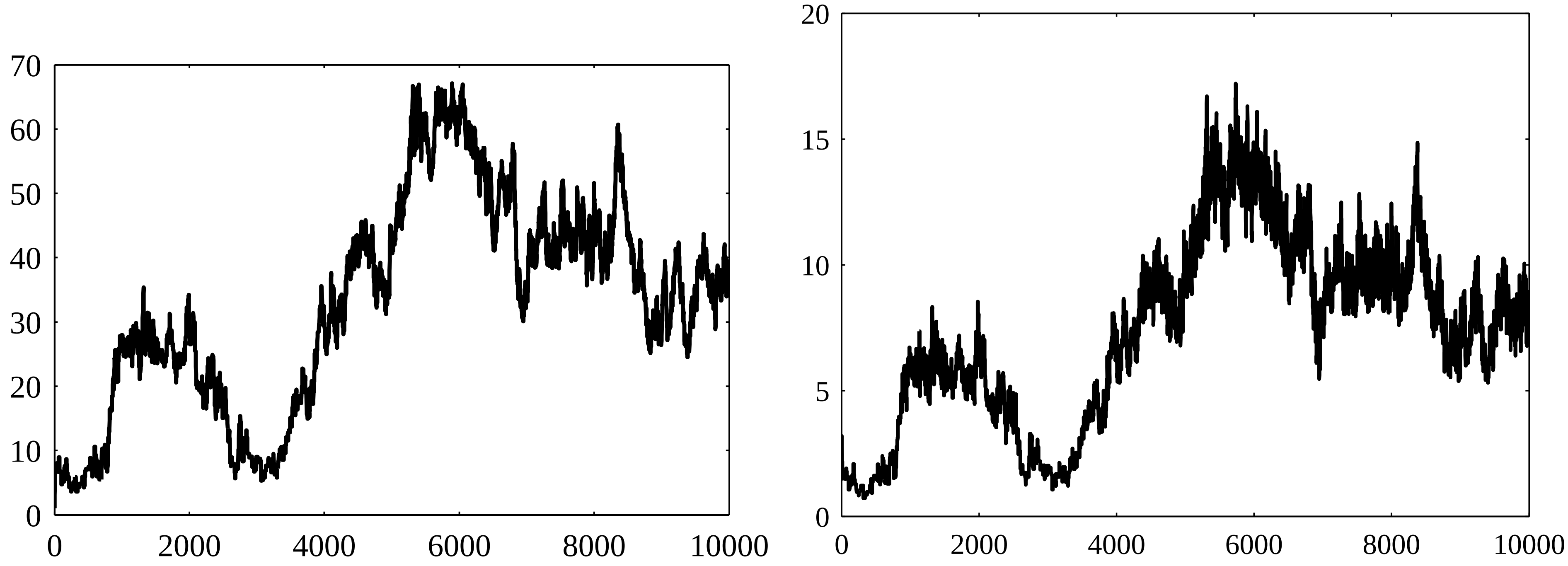
Initial point $(k_1, k_2) = (1, 2)$.

Acceptance remains high, about 55%

Scatter plots



Fuzzy worms



70
60
50
40
30
20
10
0
0
2000
4000
6000
8000
10000
20
15
10
5
0
0
2000
4000
6000
8000
10000

What did we learn?

- Statistical approach helps in experiment design
- To identify the burn-in, try multiple starts
- If the sample histories are "walking", try longer steps: maybe you are just explring too slowly the distribution
- If the samples continue to walk, maybe you are exploring an improper density. You need more information: better prior, new observations, different measurement setting?