STATISTICAL FITTING OF ADSORPTION ISOTHERMS

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Experiment

- The aim of the experiment — to study the influence of dietary fiber on polyphenol bioaccessibility
- Bioaccessibility — the amount of polyphenols that are actually accessible for absorption in the digestive tract
- Dietary fibers are resistant to digestion and absorption in the human small intestine.
- They have the potential to interact with polyphenols in the digestive tract, to „trap" and „carry" them unchanged to the lower parts of the digestive tract and affect their bioaccessibility.
- The influence of dietary fibers on polyphenol bioaccessibility can be studied by studying the adsorption process between fibers and polyphenols.
- Adsorption proces in a model: **polyphenol** - β-**glucan** (a dietary fiber found in cereals — barley and oats).

Adsorption isotherms

- Particles (an initial concentration) are introduced into a medium (liquid or gaseous at a particular temperature) with an adsorbent present.
- After sufficient time to allow an equilibrium of adsorption to be reached, concentration not adsorbed is observed.
- From the initial concentration and the concentration not adsorbed, the amount adsorbed is calculated.
- A key aim is to know how the amount adsorbed is related to the concentration not adsorbed in the medium for a specific temperature.

Notations

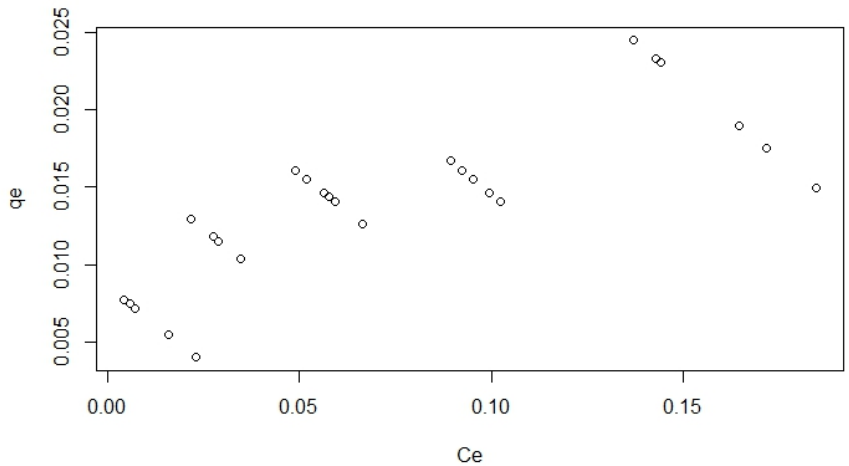
- An initial concentration M (mg/l) is set to one of various specified experimental values.
- After equilibrium is reached the remaining concentration C_e in mg/l is measured. It depends on M.
- From C_e, the amount adsorbed q_e (in mg per g of adsorbent) is determined using the principle of conservation of mass by the material balance equation

$$q_e = (M - C_e)/\gamma,$$

  where γ is the amount of adsorbent in g/l.
- $q_e \longleftrightarrow C_e$???

Data

- Observed $(C_{e,i}, q_{e,i})$, $i = 1, \ldots, n$ (n — number of trials)
- Plot reveals the experimental structure — groups of collinear points (one group for each initial condition M) with slope $-1/\gamma$



Equilibrium equations

Equilibrium equations have been most frequently employed to interpret adsorption data.

$$q_e - \text{amount adsorbed}$$

$$C_e - \text{concentration not adsorbed}$$

- Freundlich model:

$$q_e = K(C_e)^a$$

- Langmuir model:

$$q_e = Q\frac{C_e}{K_L + C_e}$$

- Dubinin-Radushkevich model:

$$q_e = Q_s e^{-a(\log \frac{C_s}{C_e})^2}$$

(K, a), (K_L,Q) and (Q_s,C_s) — constants for a given adsorbate and adsorbent at a particular temperature.

Estimation - standard procedure

- Data $(C_{e,i}, q_{e,i})$, $i = 1, \ldots, n$
- Model: $q_e = h(C_e, \boldsymbol{a})$, $\boldsymbol{a}$ unknown vector parameter

Nonlinear least squares — parameter value $\hat{\boldsymbol{a}}$ minimizes the (weighted) sum of squares of error

$$\sum_{i=1}^{n} w_i (q_{e,i} - h(C_{e,i}, \boldsymbol{a}))^2.$$

Estimation - standard procedure - problem

- Structural relationships:

$$q_e = h(C_e, \boldsymbol{a})$$

$$q_e = (M - C_e)/\gamma$$

- Measurements:

$$C_{e,i} = C_e + \varepsilon_i$$

$$q_{e,i} = (M - C_{e,i})/\gamma = (M - C_e - \varepsilon_i)/\gamma = q_e + \nu_i$$

- From the structural form we have

$$q_{e,i} = h(C_e, \boldsymbol{a}) + \nu_i$$

$$q_{e,i} = h(C_{e,i} - \varepsilon_i, \boldsymbol{a}) + \nu_i$$

- joint variability of $C_{e,i}$ and $q_{e,i}$, $E(\nu_i C_{e,i}) \neq 0$???
- endogenity - problem with inconsistency even in the linear LS

Proper statistical fitting

- Experiments vary a precisely controlled choice of an initial mass M: $m_1, \ldots, m_n$
- C_e is related to M
- Rearrange the models to express $q_e = f(M, \boldsymbol{a})$ as a function of the original input M by solving the material balance equation

$$q_e - (M - h^{-1}(q_e))/\gamma = 0$$

- Now we have a classical nonlinear regression but with M as a predictor.

$$q_{e,i} = f(m_i, \boldsymbol{a}) + \epsilon_i$$

Proper statistical fitting - problem

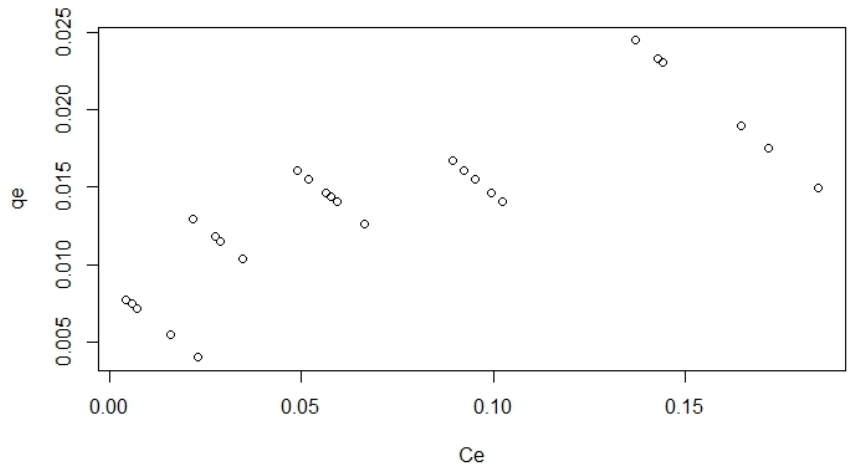
- For Langmuir model, f can be derived explicitly
- Otherwise, f is implicitly given by the equation

$$q_e - (M - h^{-1}(q_e))/\gamma = 0$$

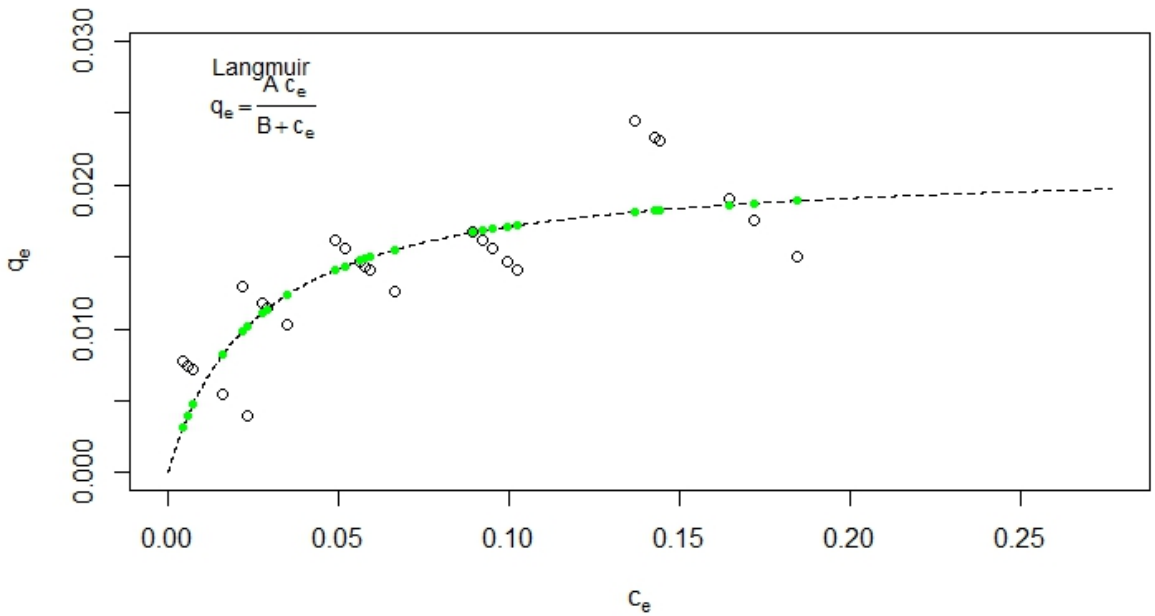
- Computation in standard statistical packages — problem if we don't have an explicit expression for f (estimations, se, CI)

Experiment and data

- Data: initial mass M at 5 levels: 25,50,75,100,150
- At each mass level, 6 experiments
- Langmuir model



Standard procedure LS



The fitted (C_e, q_e) does not correspond to the experimentally given initial mass.

Improved procedure LS

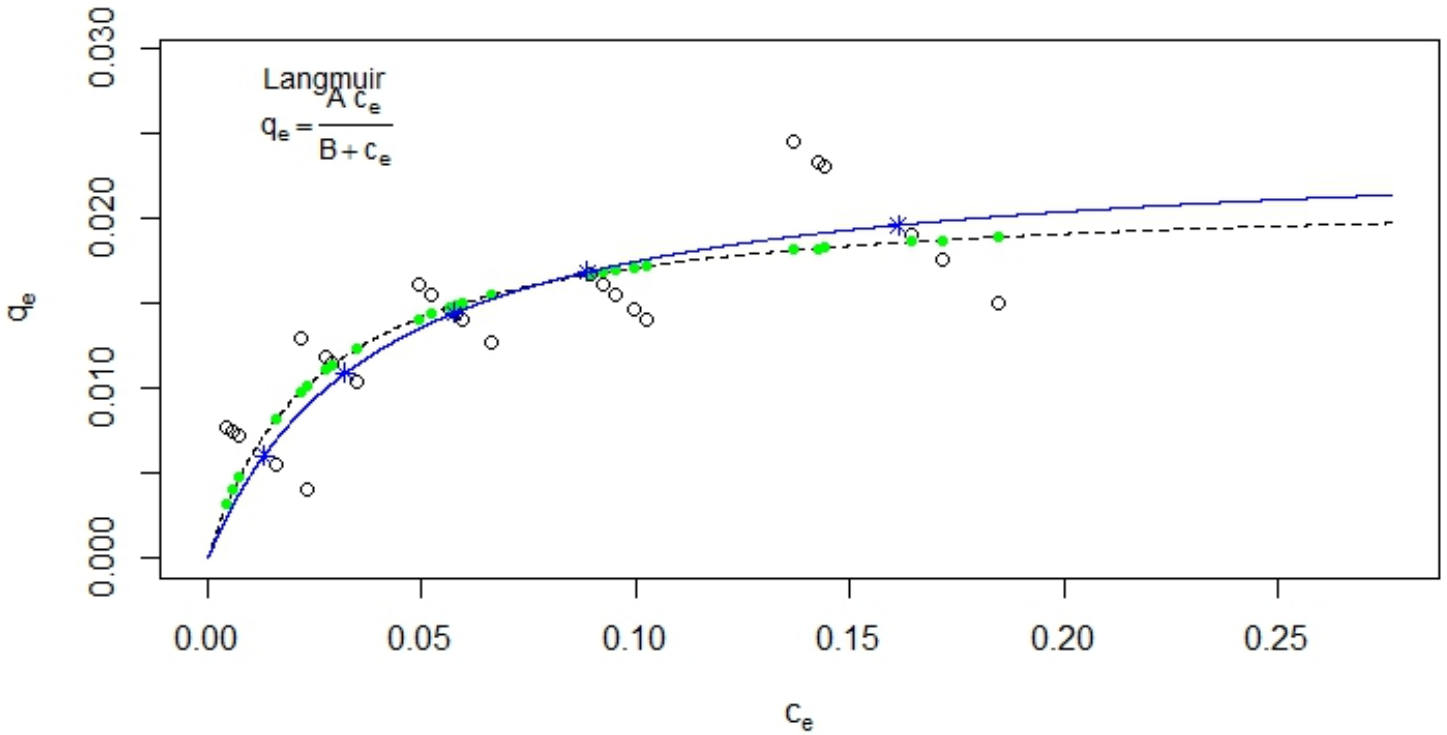
- Define $f(M, \boldsymbol{a})$ as a solution of the equation

$$q_e - (M - h^{-1}(q_e, \boldsymbol{a}))/\gamma = 0$$

- Minimize

$$S(\boldsymbol{a}) = \sum_{i=1}^{n} w_i (q_{e,i} - f(m_i, \boldsymbol{a}))^2.$$

Improved procedure LS



Improved procedure LS

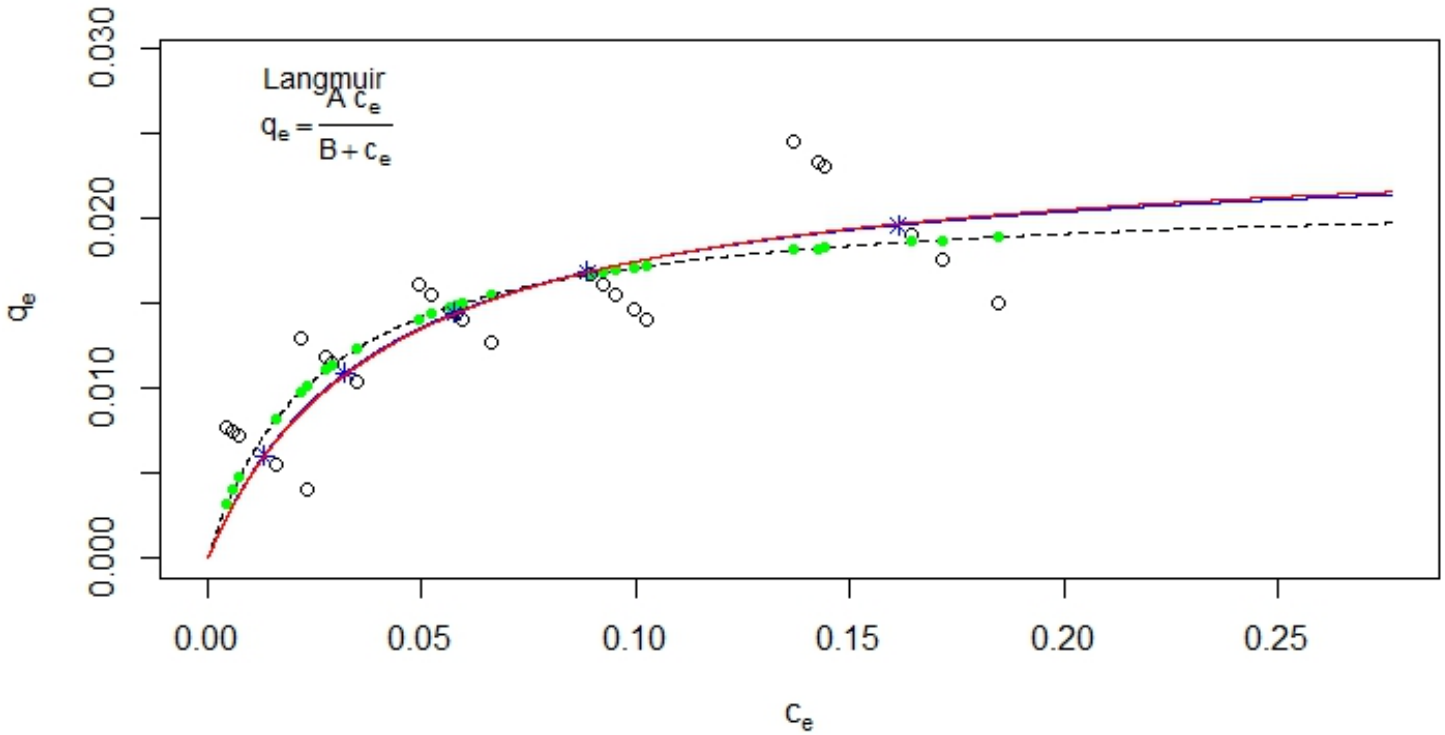
- The estimator is asymptotically normal.
- We computed the asymptotic variance and bias.
- Variance:

$$\left[\sum_{i=1}^{n} w_i \nabla f(M_i, \boldsymbol{a}) \nabla f(M_i, \boldsymbol{a})^\tau\right]^{-1} =$$

$$= \left[\sum_{i=1}^{n} w_i \frac{1}{(1 + \frac{1}{\gamma}\frac{\partial h}{\partial Ce}(Ce_i))^2} \nabla h(Ce_i, \boldsymbol{a}) \nabla h(Ce_i, \boldsymbol{a})^\tau\right]^{-1}$$

- Bias correction — Huge expression with (mostly) small impact.

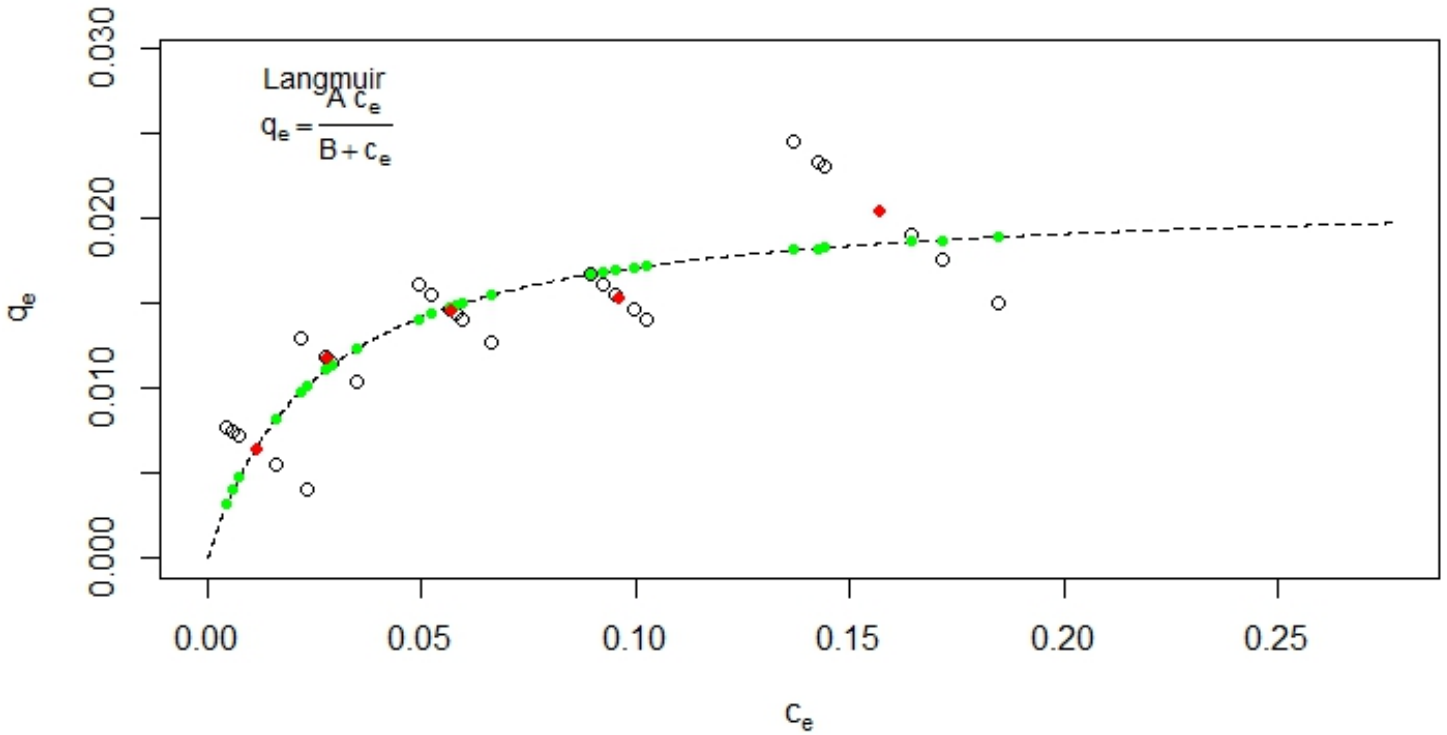
Bias corrected improved procedure LS



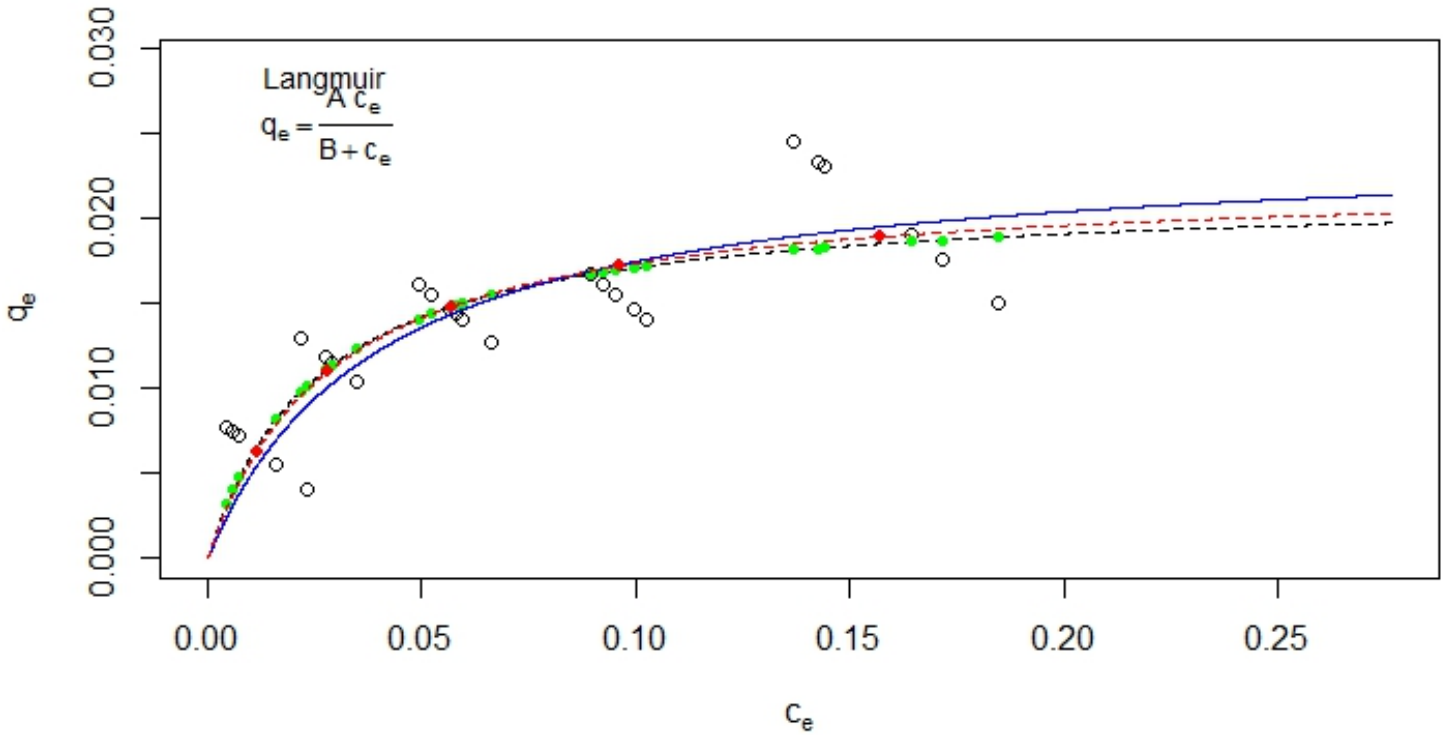
Fit from means

- Repeated experiments for the chosen levels of initial mass M.
- Use average values for C_e and q_e at each level and standard LS procedure.
- Slightly improves the naive fit.
- Asymptotically OK.

Fit from means



Fit from means



Results for polyphenol - β-glucan data

estimator	Standard	From Means	Improved
sd residuals	0.00295	0.00224	0.00211

estimator	Standard	From Means	Improved	Im. Bias Corr.
A	0.0216	0.0224	0.0245	0.0248
		(0.00226)	(0.00232)	(0.00232)
B	0.0261	0.0293	0.0401	0.0423
		(0.0118)	(0.0125)	(0.0125)

Small sample simulation

Langmuir model

$$A = 0.02,\ B = 0.03$$

$$M = (25, 50, 75, 100, 150)$$

mass equation: $580 * C_e + 2900 * q_e = M$
C_e computed from M:

$$580 * C_e + 2900 * \frac{AC_e}{B + C_e} = M$$

$$C_e = (0.01294334, 0.03347204, 0.06195567, 0.09621245, 0.17338687)$$

Data — 6 data for each M level, C_e plus normal errors, $sd = 0.0081$
10000 replications

Results

$$A = 0.02$$

estimator	Standard A	From Means A	Improved A	Im. Bias Corr. A
mean	0.019369	0.020241	0.020212	0.020069
se	0.001496	0.001555	0.001384	0.001286

$$B = 0.03$$

estimator	Standard B	From Means B	Improved B	Im. Bias Corr. B
mean	0.028098	0.031941	0.031481	0.030538
se	0.008872	0.009385	0.008288	0.007537

Confidence segments for (C_e, q_e) for improved procedure

- Based on the estimator's asymptotic normality and computed standard errors.
- For fixed M, confidence intervals can be calculated for C_e (let say I_{C_e}) and q_e (I_{q_e}).
- Each pair (C_e, q_e) should satisfy the mass equation.
- Using I_{C_e} and I_{q_e}, a confidence segment at the mass equation line can be detected for each M.

Improved procedure LS with confidence bands