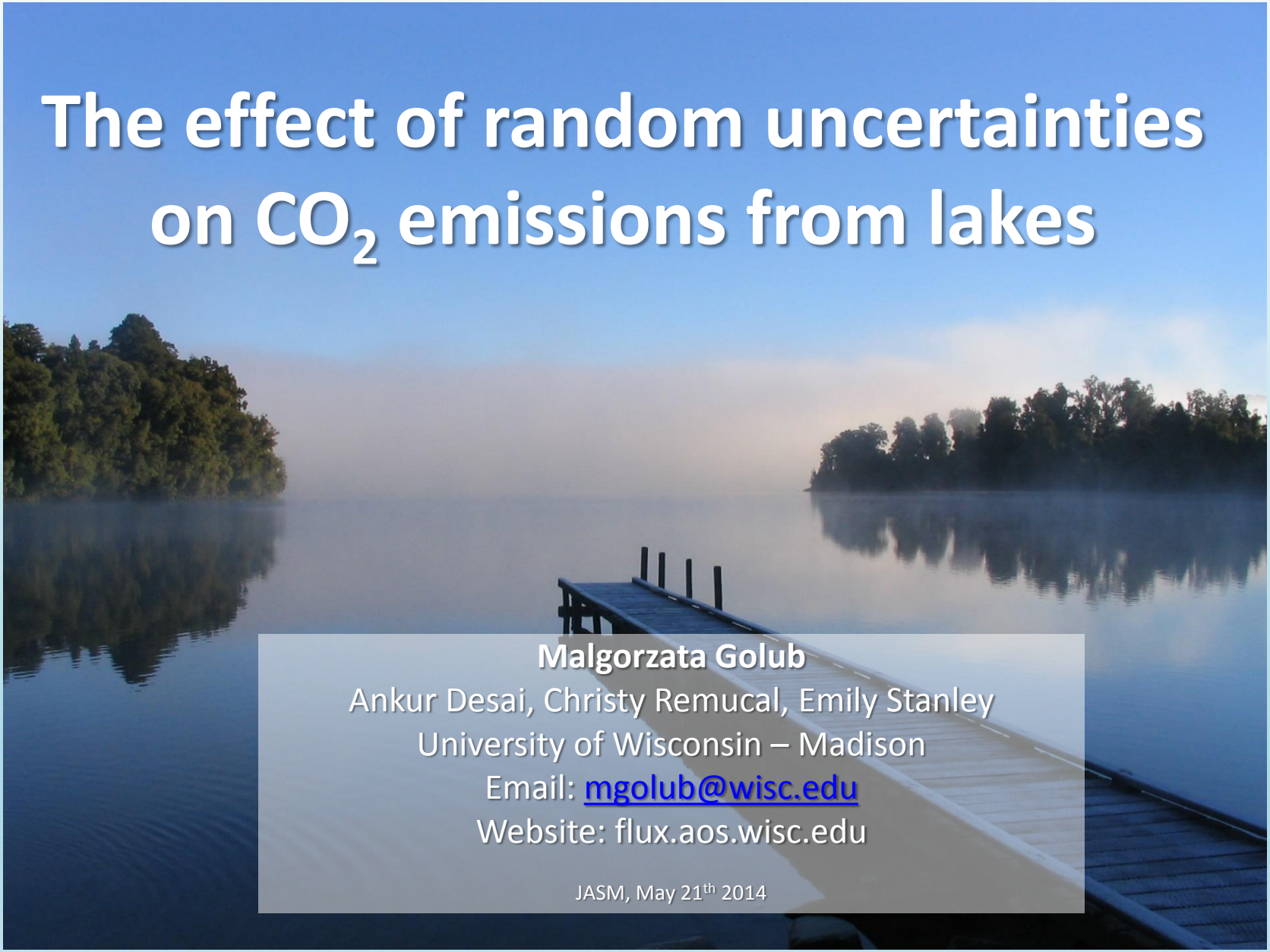
The effect of random uncertainties on CO_2 emissions from lakes



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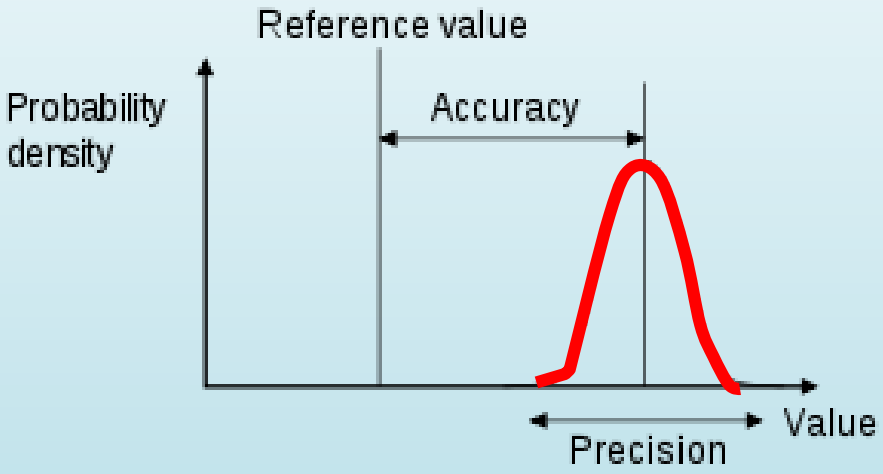
JASM, May 21th 2014

Accuracy vs. Precision



Systematic error affects **accuracy**

- Instrumental errors
- Methodological limitations
- Personal errors

Random error affects **precision**

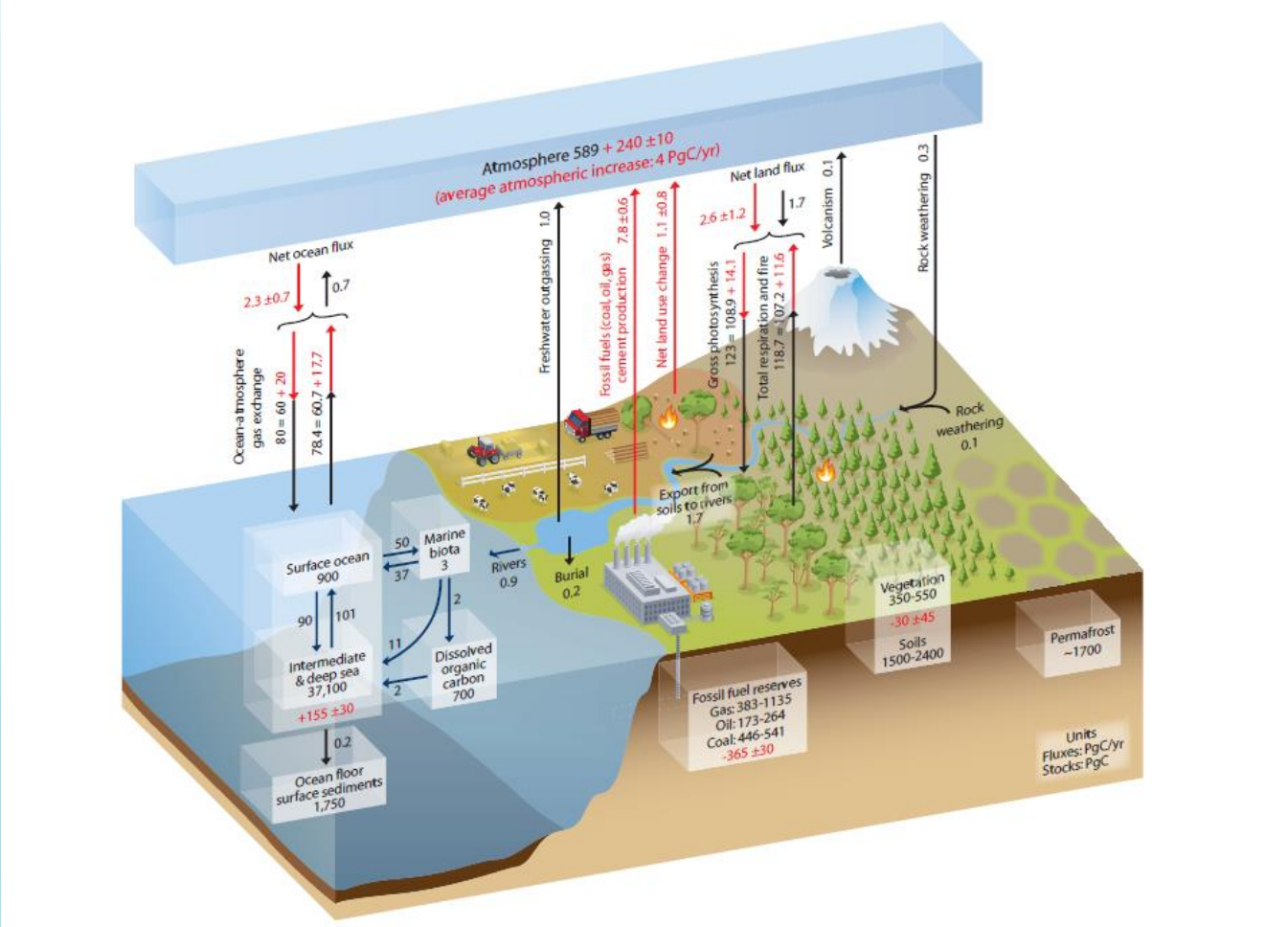
- Caused by many hard to control variables

Image source: Wiki

Why random error matters?

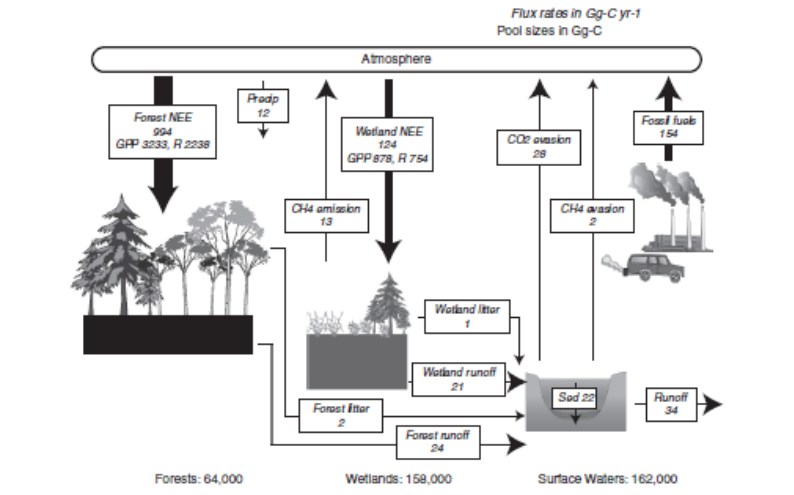
- Unlike systematic errors we cannot remove random error effect (Bevington & Robinson 2003)
- Might be the largest source of uncertainty (Skoog et al., 2013)
- Needs to be taken into consideration during data analysis and interpretation (Hollinger and Richardson, 2005)
- Little attention paid but might have serious implications for comparisons across time and across site

Freshwater outgassing offsets 40% of net land flux

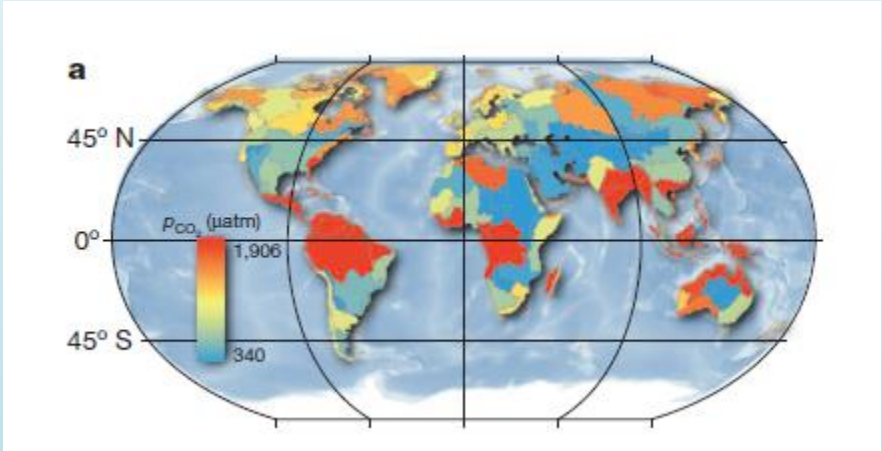


IPCC 2013

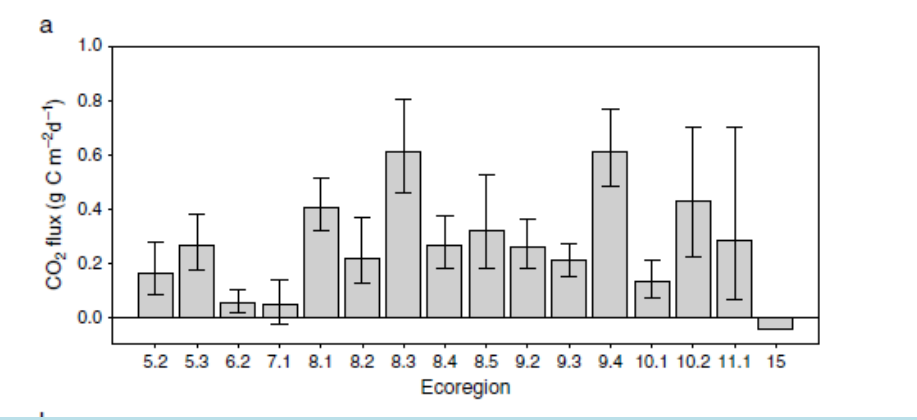
Limited # of direct CO_2 measurements



Buffam et al., 2010



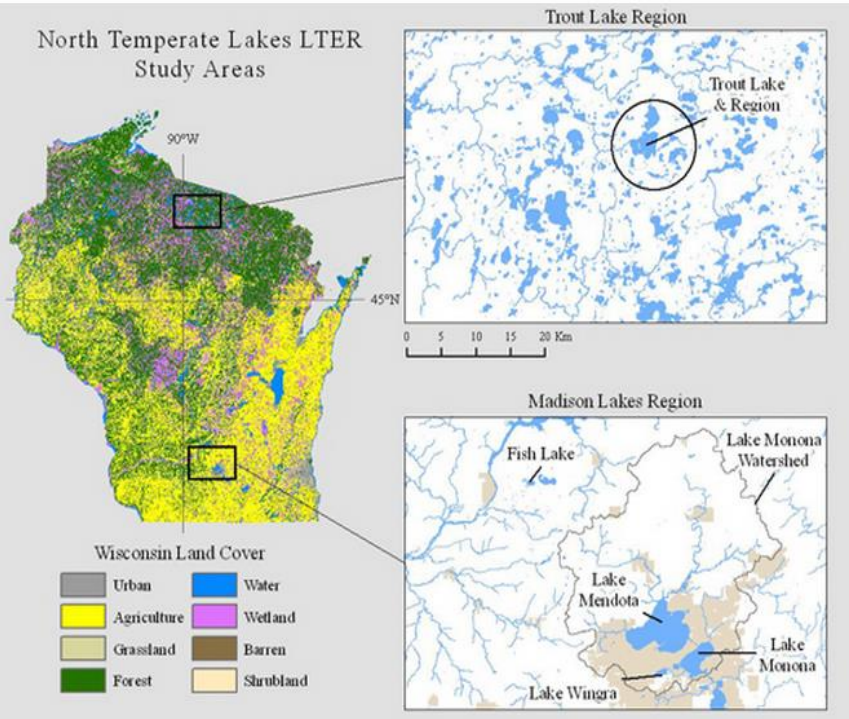
Raymond et al., 2013



McDonald et al., 2013

- CO_2 emissions often estimated from CO_2-related parameters

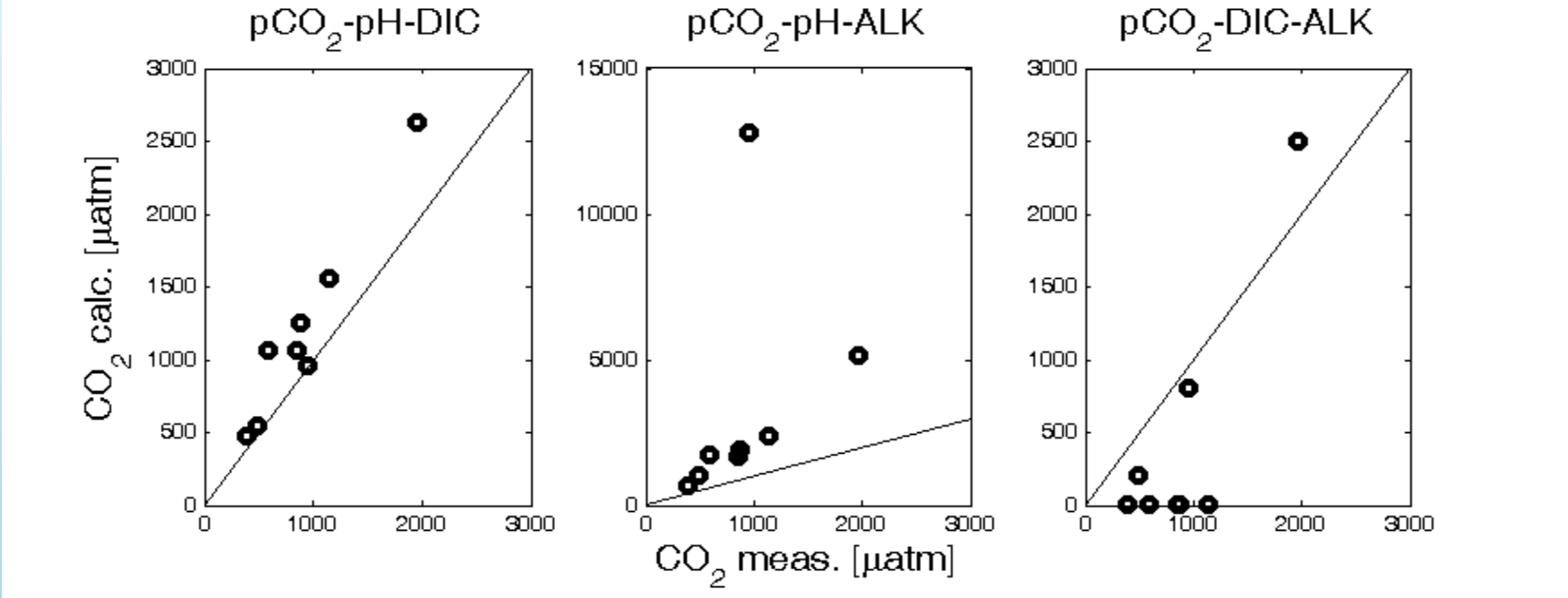
North Temperate Lakes LTER site



- Limited direct CO_2 measurements
- CO_2-related parameters data
  - **pH**
  - Alkalinity (**ALK**)
  - Dissolved Inorganic Carbon (**DIC**)
- Available:
  - Since 1986
  - Since 1996

How reliably can we estimate CO_2 in lakes from CO_2-related parameters?

Direct vs. Indirect CO_2 Mismatch



RMSE = **364** µatm

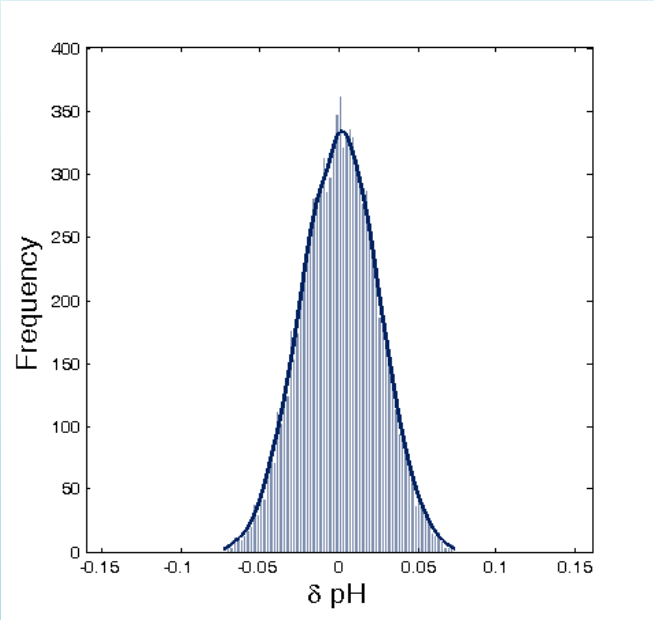
RMSE = **4410** µatm

RMSE = **675** µatm

How does observational error propagates into uncertainties of CO_2 estimates in lakes?

Random error calculated from paired samples

Low ALK



$\mu = 0$

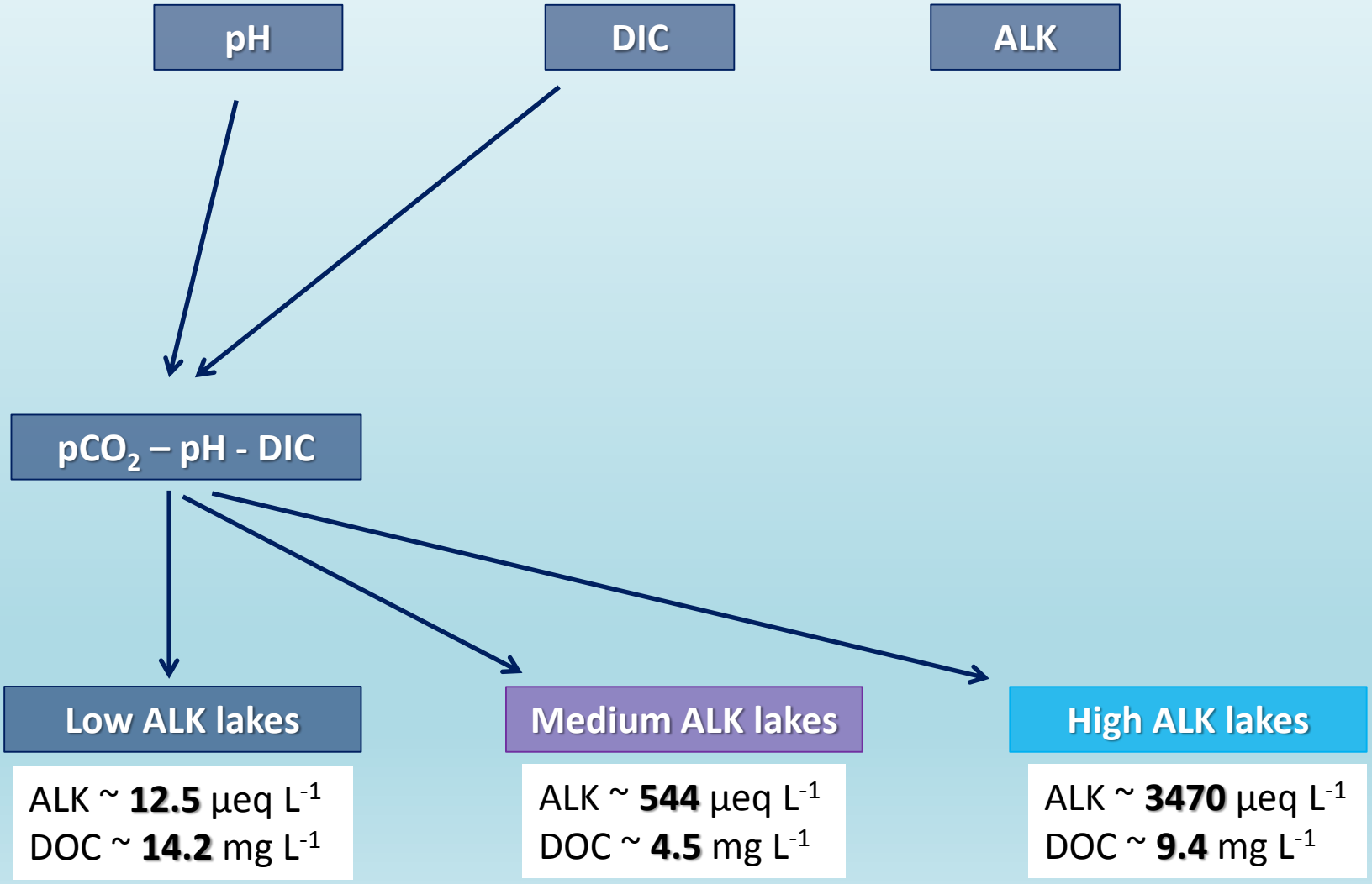
$\sigma\ (\boldsymbol{\delta}) = 0.024$

$$\sigma(\delta) = \frac{1}{\sqrt{2}}\sigma(X_1 - X_2)$$

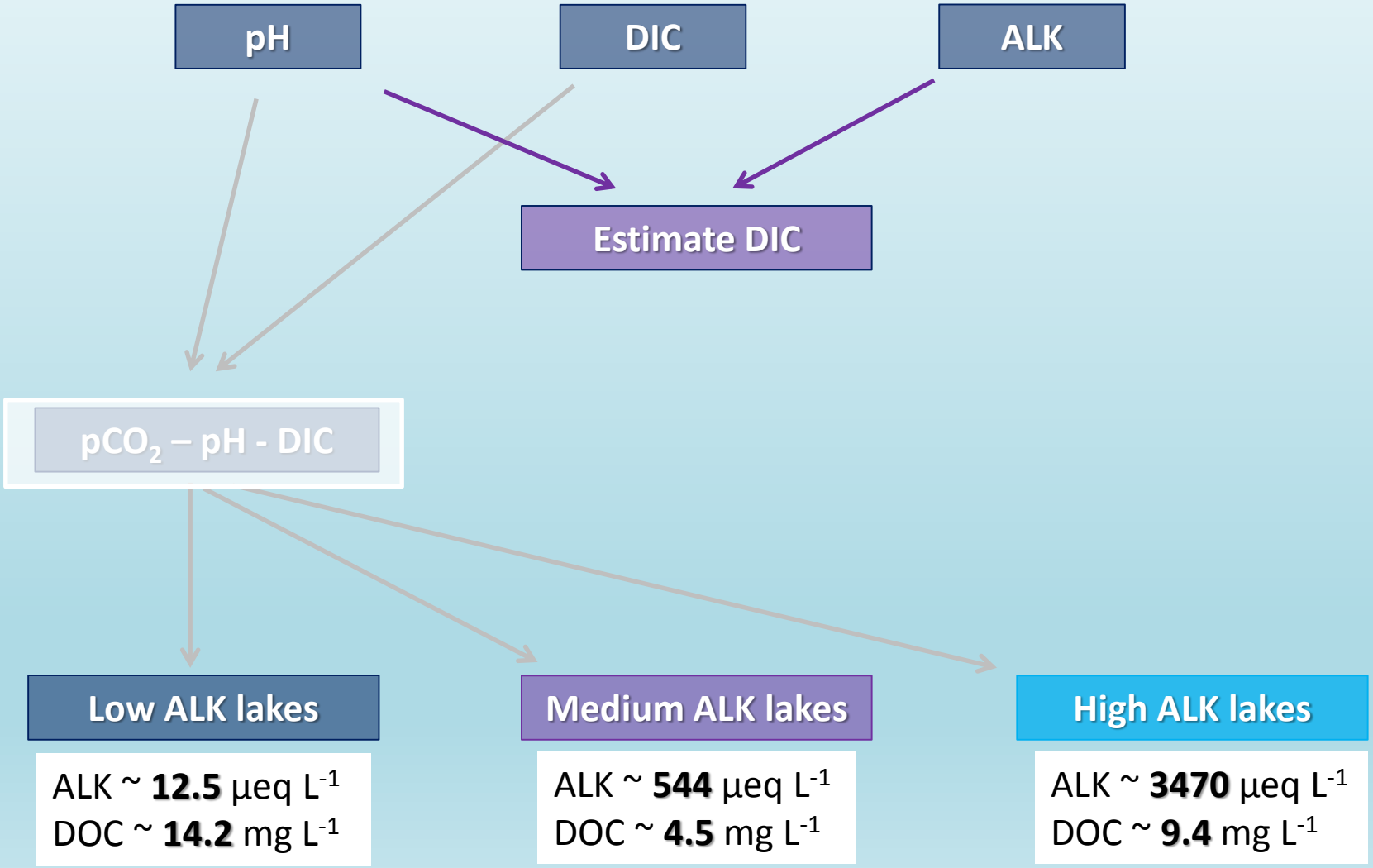
- Probability distribution functions (PFDs) fitted to the error distribution
- The mean and standard deviation of the population estimated

Bevington & Robinson 2003

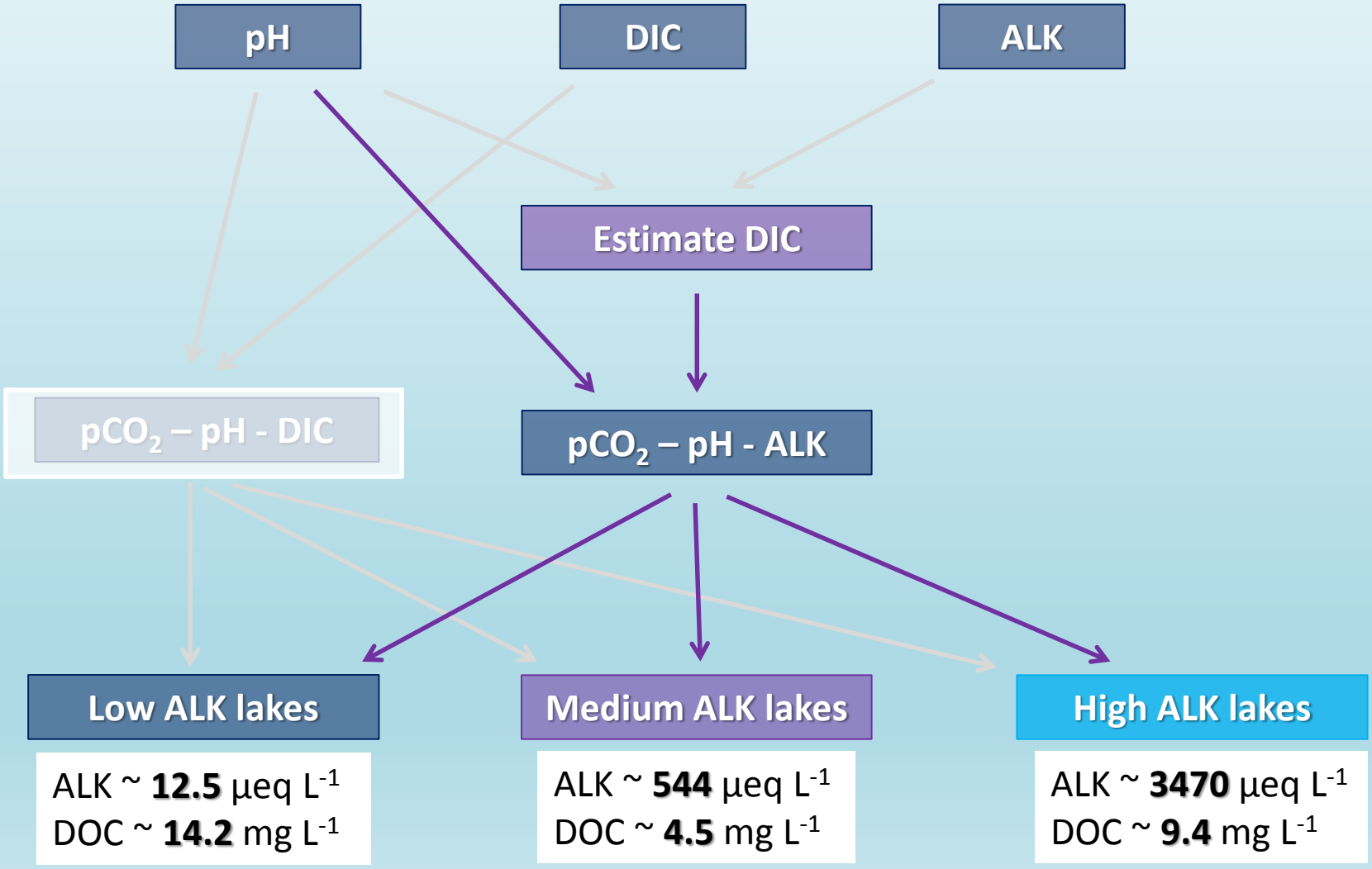
Error Propagated Through Three Carbonate Equilibrium Constants Models



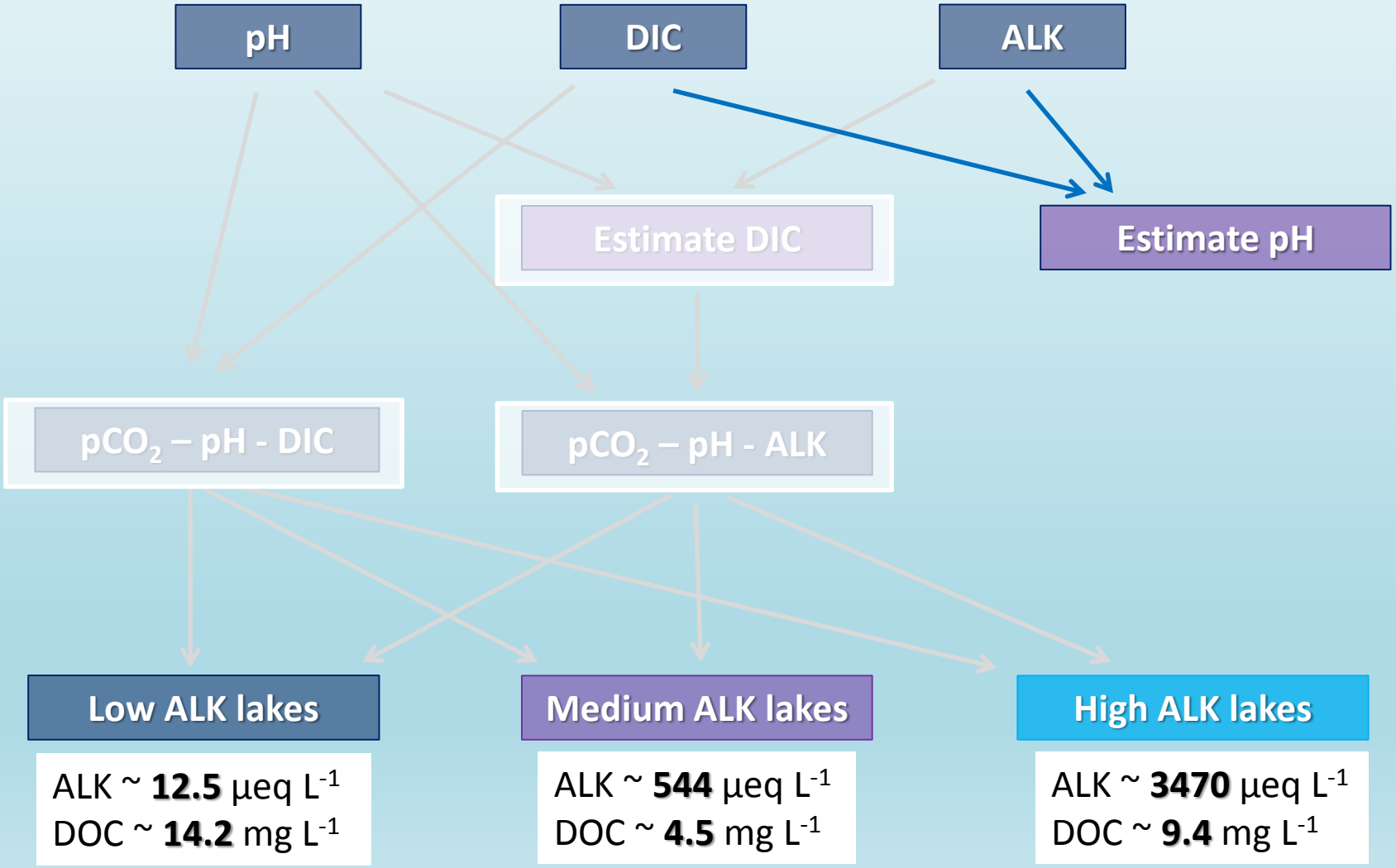
Error Propagated Through Three Carbonate Equilibrium Constants Models



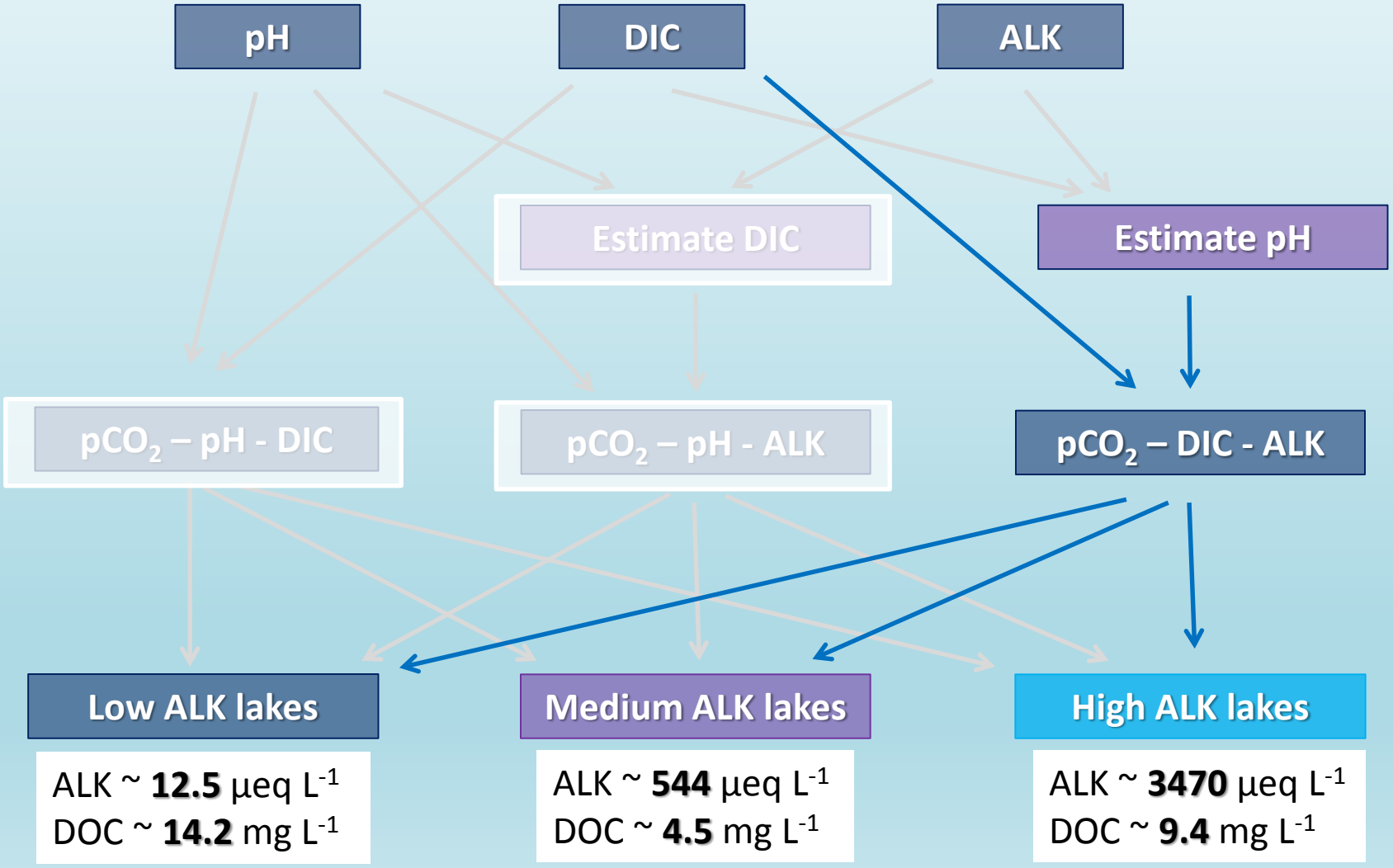
Error Propagated Through Three Carbonate Equilibrium Constants Models



Error Propagated Through Three Carbonate Equilibrium Constants Models



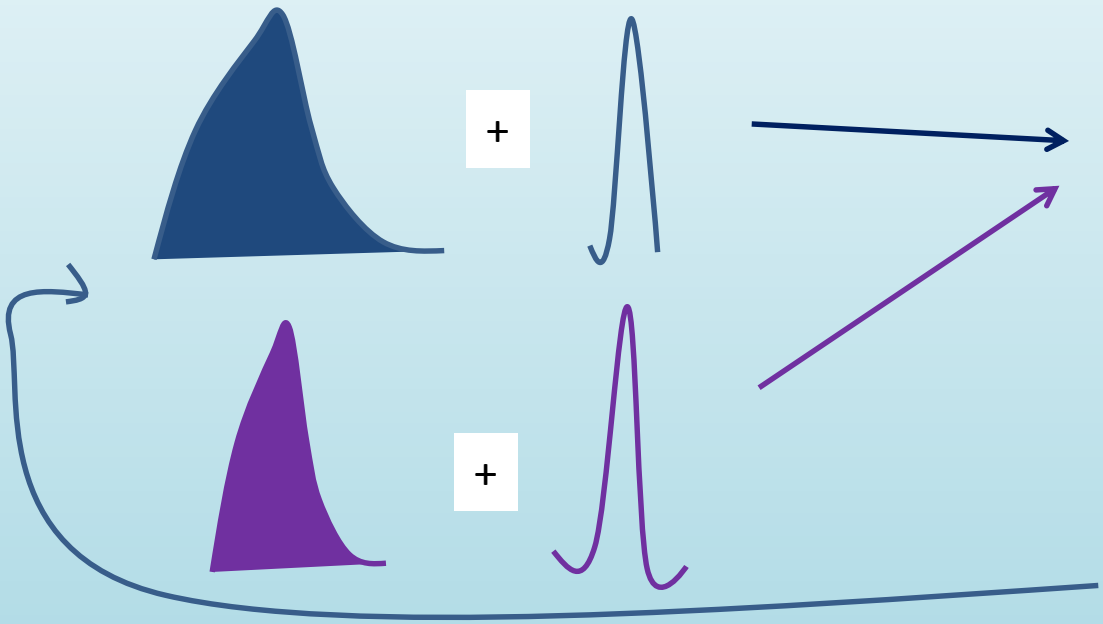
Error Propagated Through Three Carbonate Equilibrium Constants Models



Monte Carlo Technique

Parameters' Probability Density Functions

Random Error with $\mu = 0$ & $\sigma = X$



CO_2 Estimated using Three Carbonate Equilibrium Constants Models

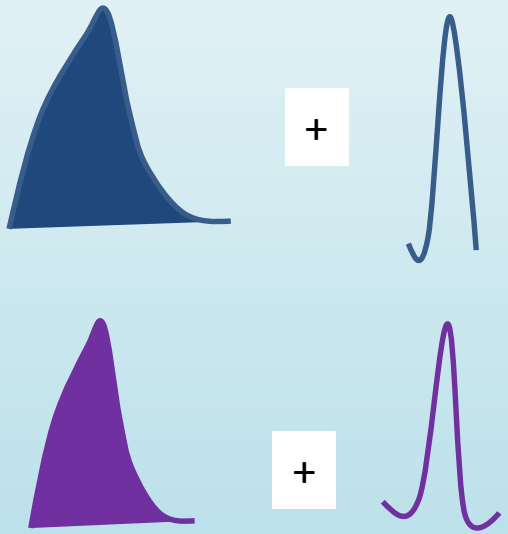
Estimated Median, 95% Credible Intervals at Each Iteration

10,000 iterations

Monte Carlo Technique

Parameters' Probability Density Functions

Random Error with $\mu = 0$ & $\sigma = X$

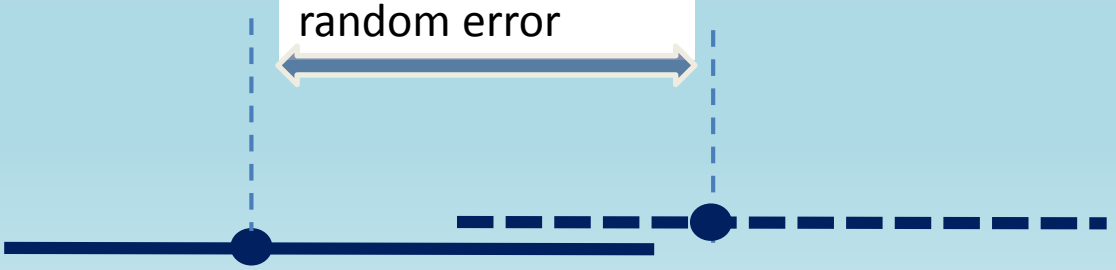


CO_2 Estimated using Three Carbonate Equilibrium Constants Models

Estimated Median, 95% Credible Intervals at Each Iteration

10,000 iterations

pCO_2 bias due to random error



Median without error

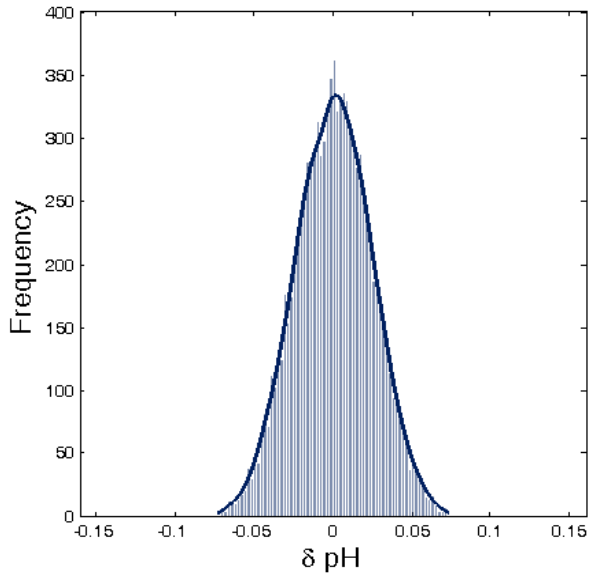
Median with error

Estimates of errors in model parameters

Random parameter errors show normal or near-normal distribution

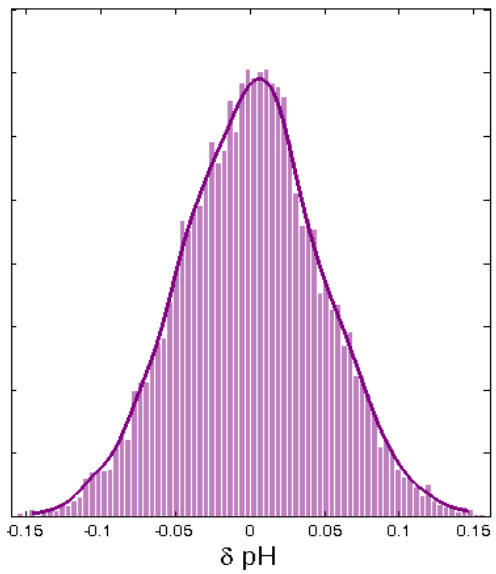
$$\sigma(\delta) = \frac{1}{\sqrt{2}}\sigma(X_1 - X_2)$$

Low ALK



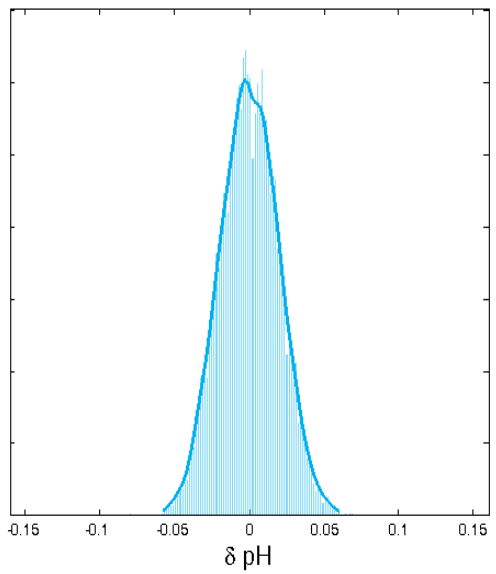
$\mu = 0$
$\sigma = 0.024$

Medium ALK



$\mu = 0$
$\sigma = 0.048$

High ALK



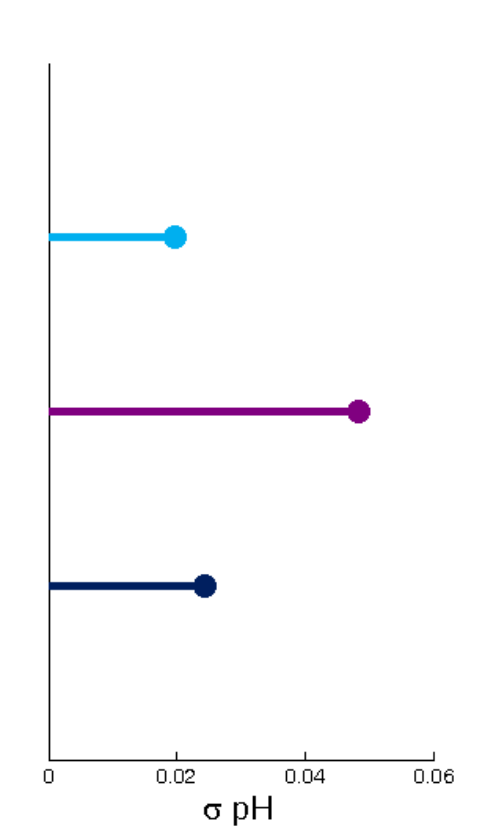
$\mu = 0$
$\sigma = 0.019$

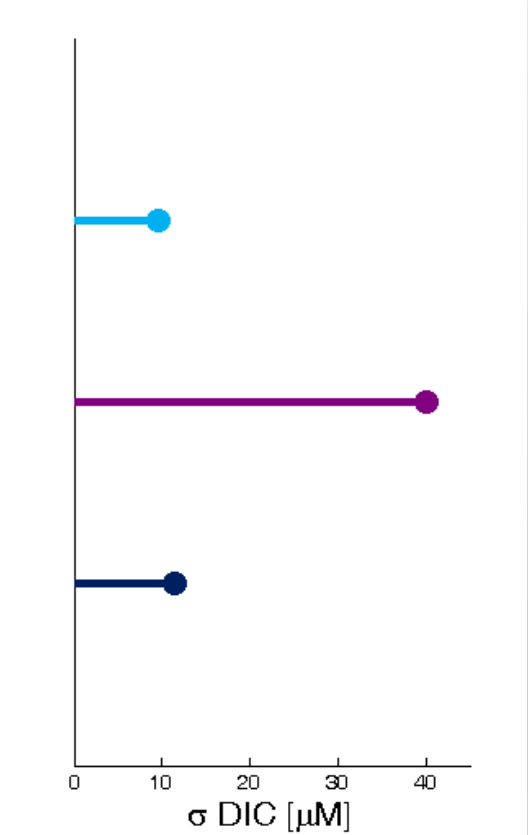
Largest random error in model parameters in medium ALK lakes

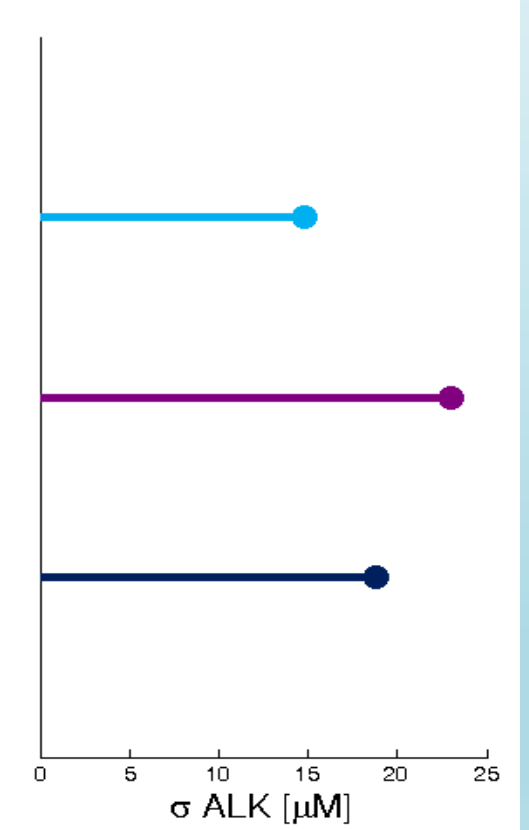
High ALK
ALK ~**3470** µeq L^{-1}
DOC ~ **9.4** mg L^{-1}

Med ALK
ALK ~ **544** µeq L^{-1}
DOC ~ **4.5** mg L^{-1}

Low ALK
ALK ~ **12.5** µeq L^{-1}
DOC ~ **14.2** mg L^{-1}







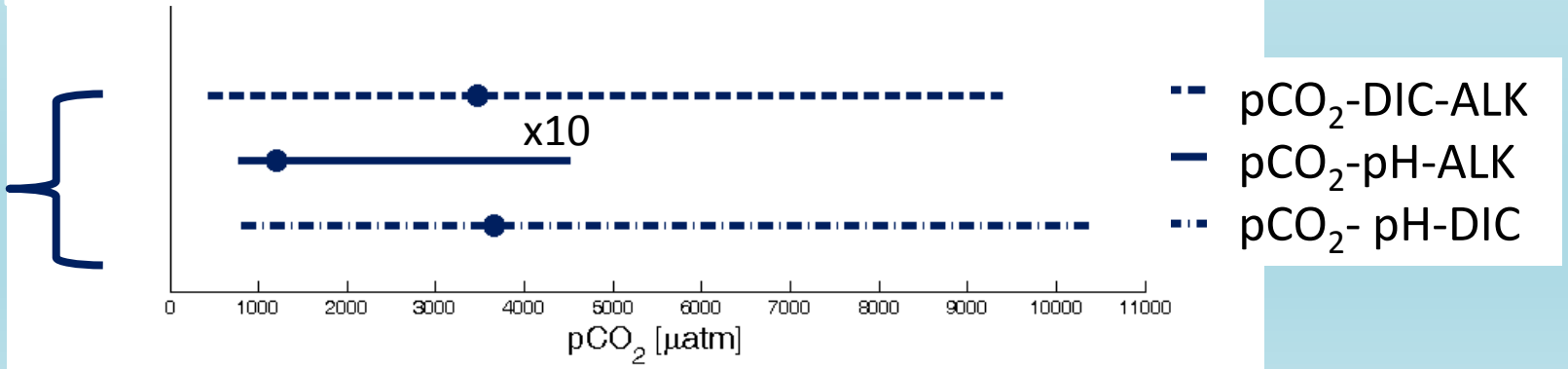
STEP 2: Random Error Propagation Through Carbonate Equilibrium Constant Models

pCO_2 – pH – ALK gives unrealistic pCO_2 estimates in low ALK lakes

Low ALK

ALK ~ **12.5** µeq L^{-1}

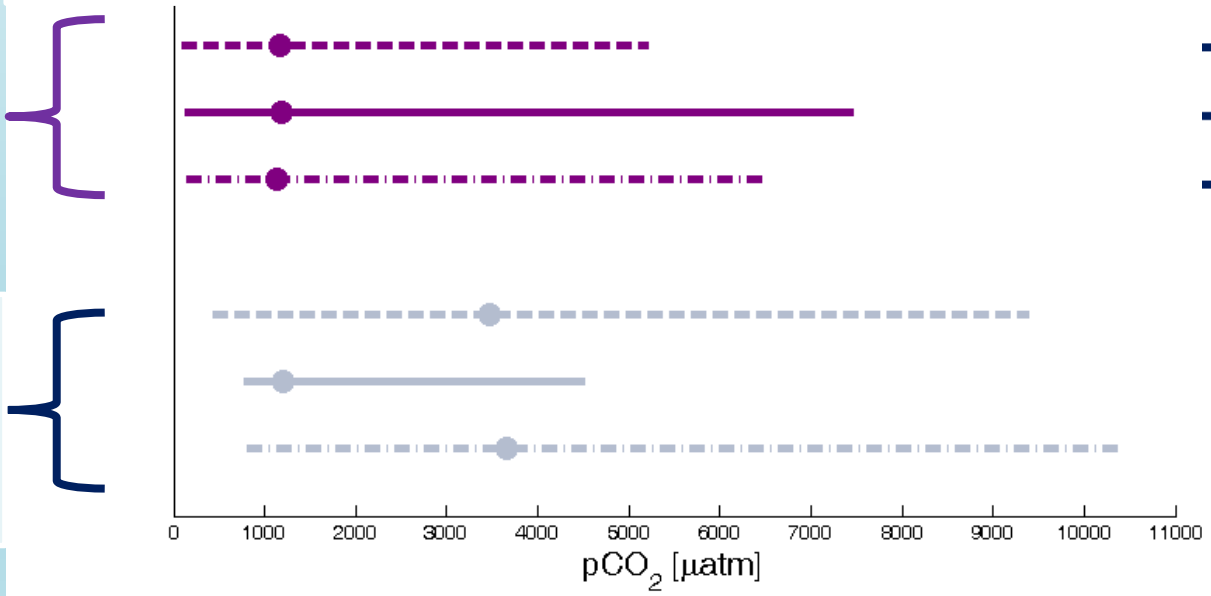
DOC ~ **14.2** mg L^{-1}



Similar pCO_2 estimates in med-ALK regardless of model used

Med ALK
ALK ~ **544** µeq L^{-1}
DOC ~ **4.5** mg L^{-1}

Low ALK
ALK ~ **12.5** µeq L^{-1}
DOC ~ **14.2** mg L^{-1}

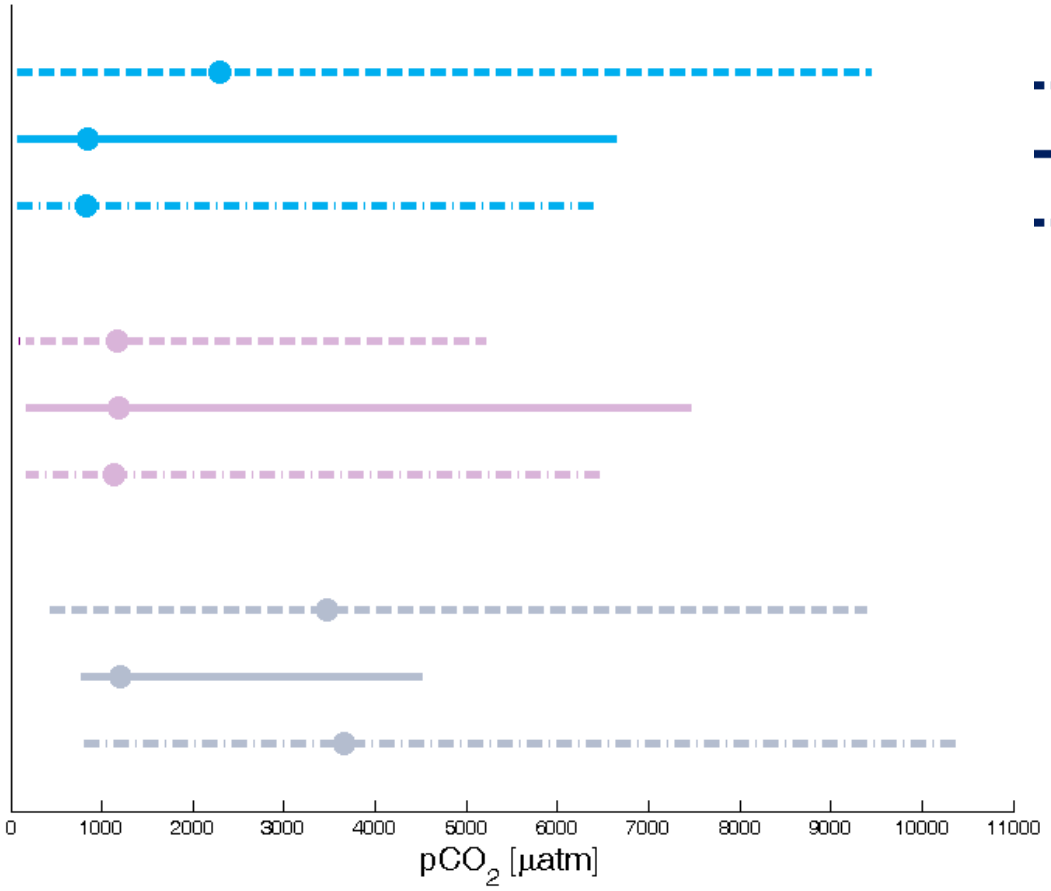


pH-based models give similar pCO_2 estimates in high ALK lakes

High ALK
ALK ~**3470** µeq L^{-1}
DOC ~ **9.4** mg L^{-1}

Med ALK
ALK ~ **544** µeq L^{-1}
DOC ~ **4.5** mg L^{-1}

Low ALK
ALK ~ **12.5** µeq L^{-1}
DOC ~ **14.2** mg L^{-1}



- pCO_2-DIC-ALK
- pCO_2-pH-ALK
- pCO_2- pH-DIC

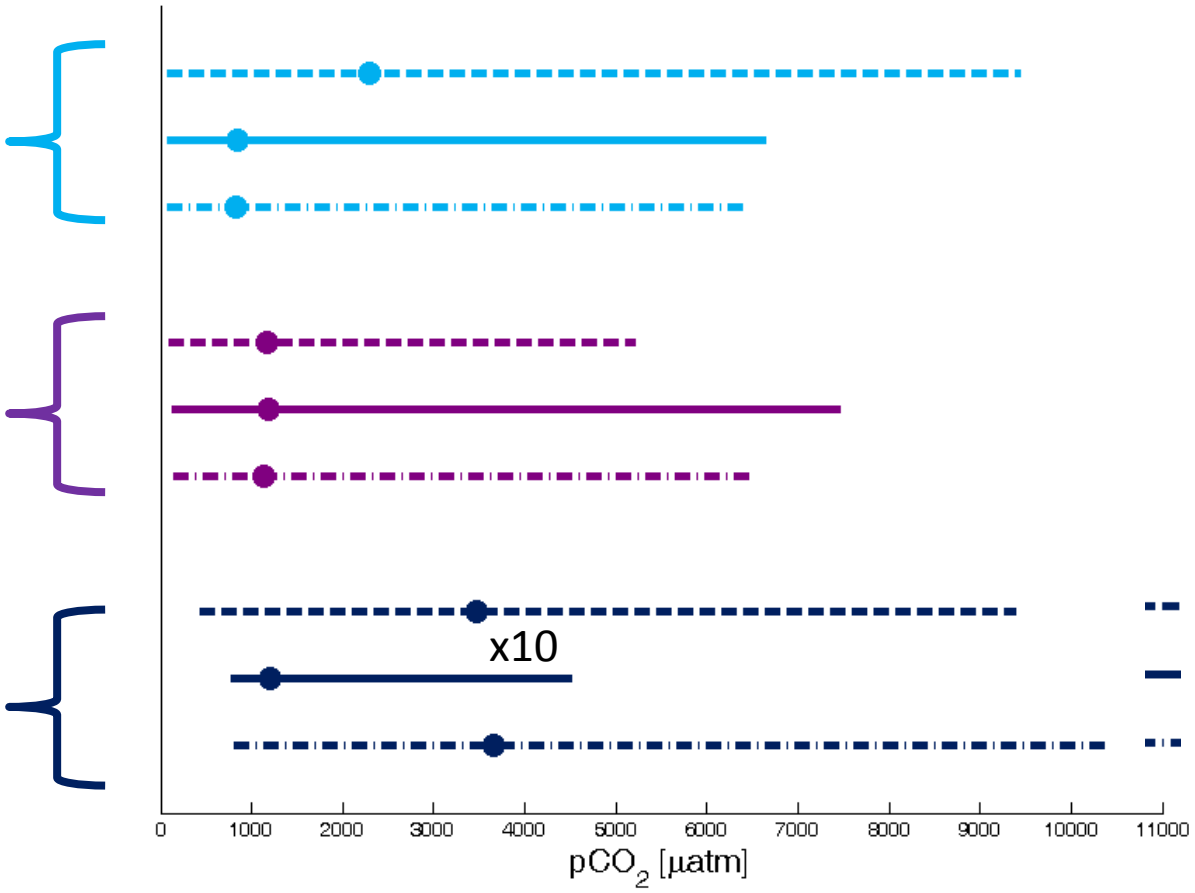
Wide breath and skewed distribution of estimated pCO_2

- Possible difficulty in constraining CO_2 concentrations

High ALK
ALK ~**3470** µeq L^{-1}
DOC ~ **9.4** mg L^{-1}

Med ALK
ALK ~ **544** µeq L^{-1}
DOC ~ **4.5** mg L^{-1}

Low ALK
ALK ~ **12.5** µeq L^{-1}
DOC ~ **14.2** mg L^{-1}



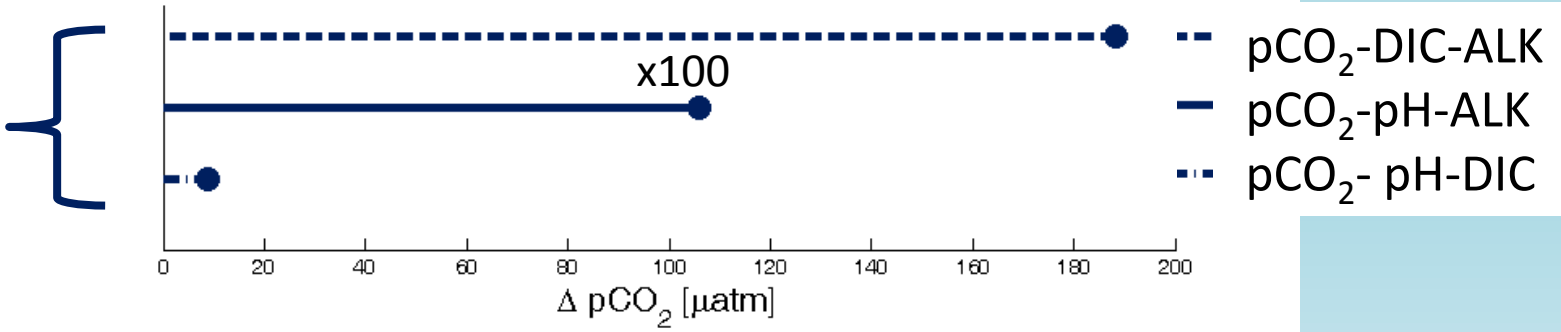
pCO_2 bias due to random error

Low ALK

ALK ~ **12.5** µeq L^{-1}

DOC ~ **14.2** mg L^{-1}

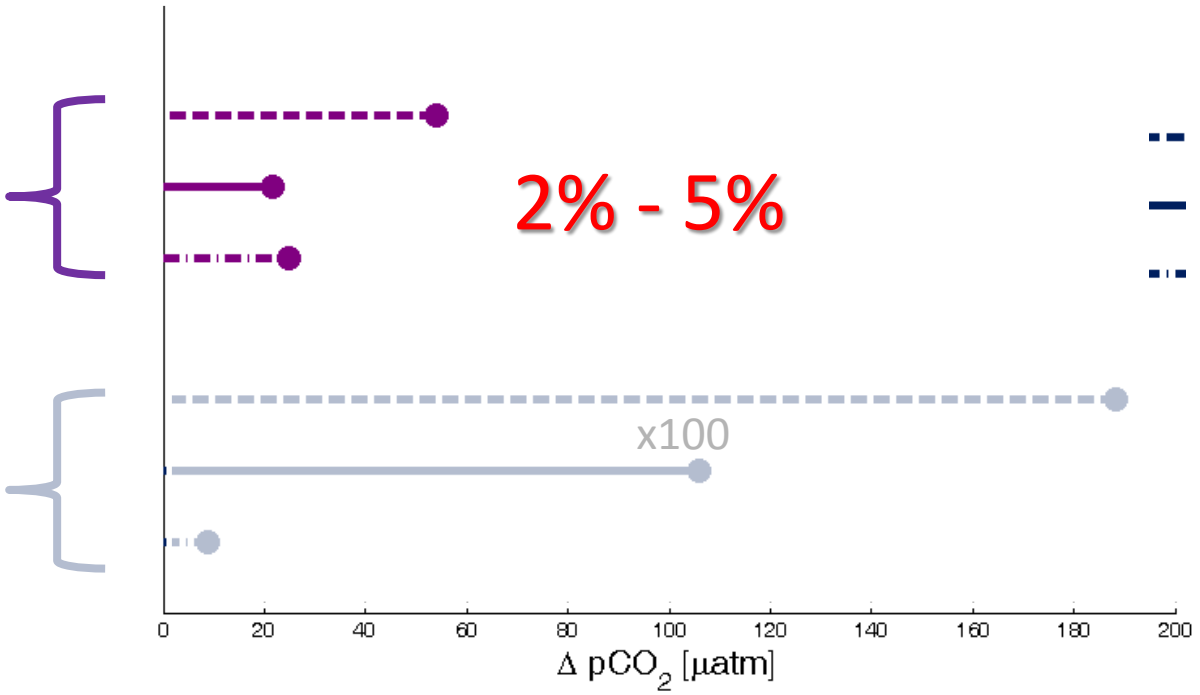
0.2% - 88%



pCO_2 bias due to random error

Med ALK
ALK ~ **544** µeq L^{-1}
DOC ~ **4.5** mg L^{-1}

Low ALK
ALK ~ **12.5** µeq L^{-1}
DOC ~ **14.2** mg L^{-1}



pCO_2 bias due to random error

High ALK
ALK ~**3470** µeq L^{-1}
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Med ALK
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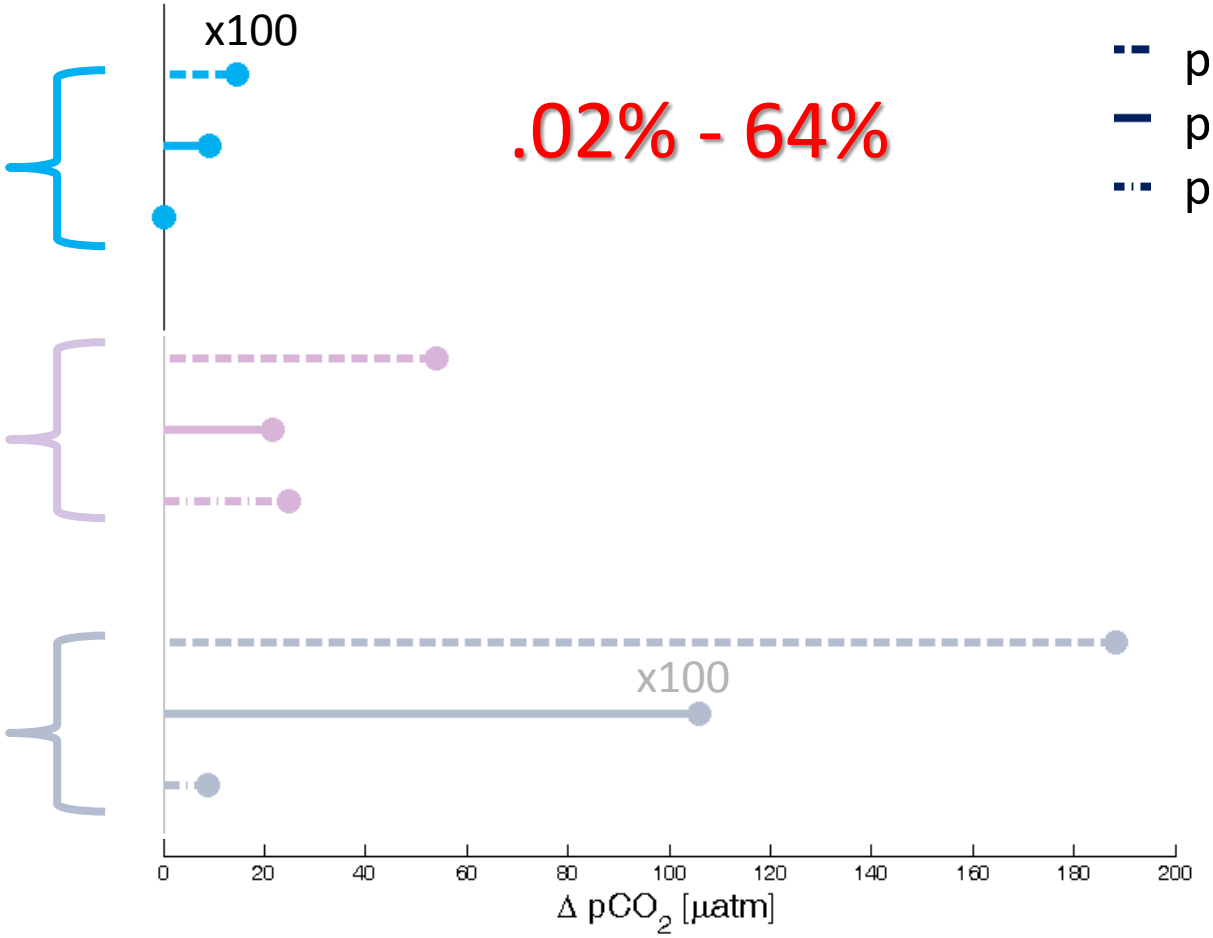
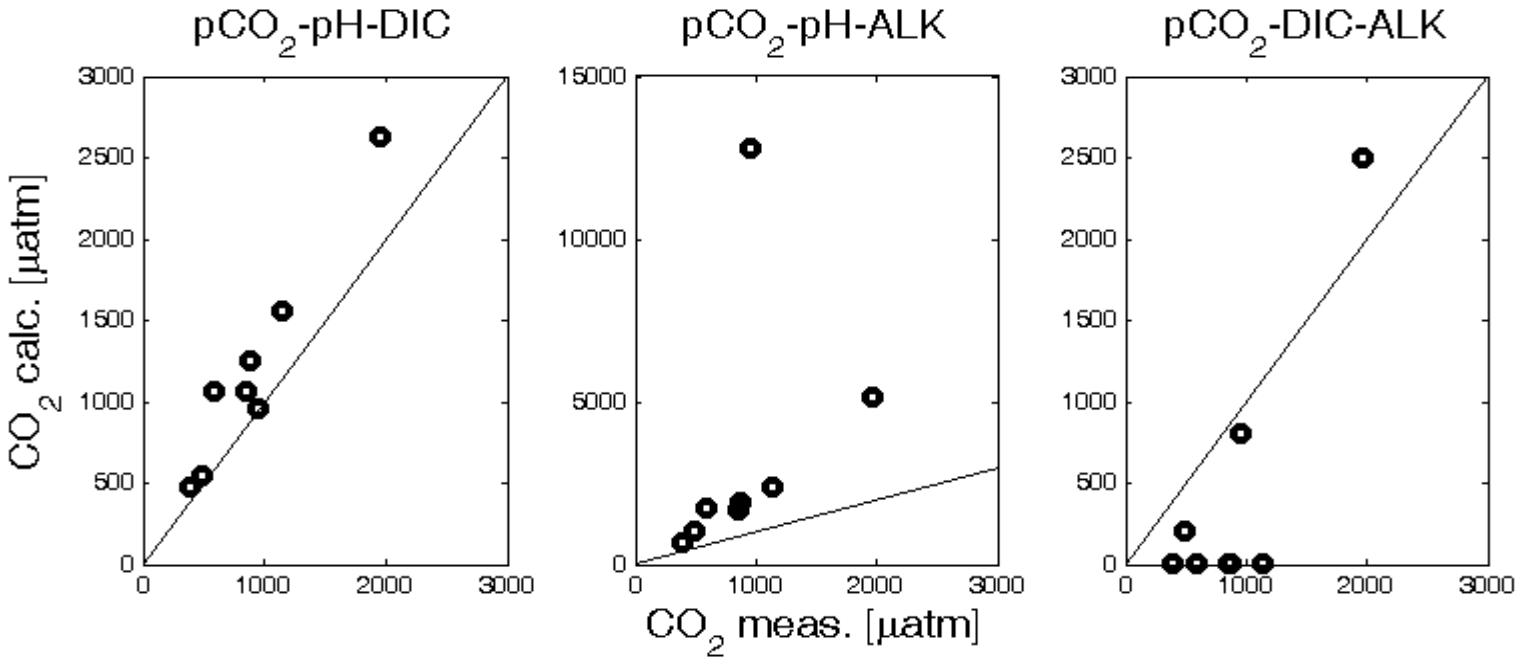


Random error is not the largest source of uncertainty



RMSE = **364** µatm

Low ANC = 9.0
Med ANC = 25.0
High ANC = 0.17

RMSE = **4410** µatm

Low ANC = 10,590
Med ANC = 22.0
High ANC = 9.0

RMSE = **675** µatm

Low ANC = 188.0
Med ANC = 54.0
High ANC = 1,456

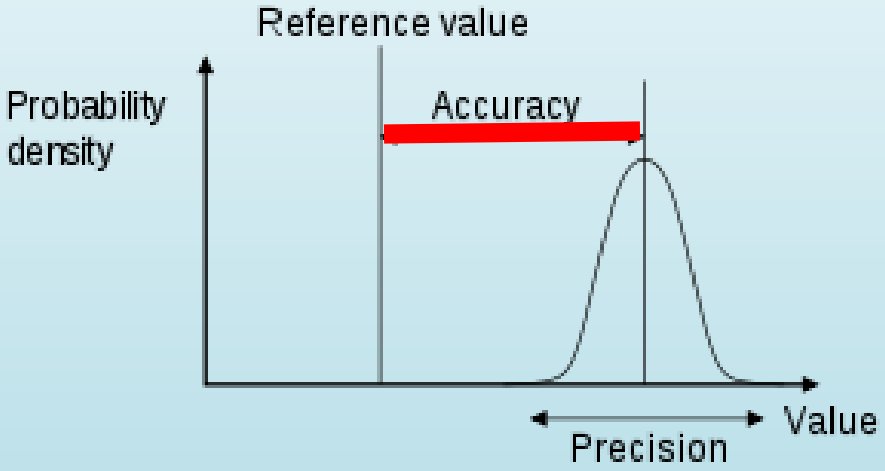
Take home messages

- There is no one perfect carbonate equilibrium model applicable for all lake groups, but model pCO_2-pH-DIC seems to be least affected by random error

- Carbonate equilibrium models cannot be blindly used to estimate CO_2 concentrations and C flux from inland waters

- Random parameter errors are not the largest sources of uncertainty in the pCO_2 calculation but need to be considered during data analysis and interpretation
  - Conservative estimates of uncertainty in CO_2
  - Need to quantify other sources of uncertainty

Next steps:
Quantify systematic errors



Systematic error affects **accuracy**

- Instrumental errors
- Methodological limitations
- Personal errors

Random error affects **precision**

- Caused by many hard to control variables

Image source: Wiki

Acknowledgements

- Funding:
  - NSF DEB-0845166
  - NTL-LTER
  - CCR
  - Birge Grant

- NTL – LTER base crews (Boulder Junction and Madison)

- Members of Stanley Lab and Desai Lab

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