Sensitivity Analysis and Quantification of Uncertainty for Isotopic Mixing Relationships in Carbon Cycle Research

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Abstract

- Quantifying and understanding the uncertainty in isotopic mixing relationships is critical to isotopic applications in carbon cycle studies at all spatial and temporal scales. Studies associated with the North American Carbon Program will depend on stable isotope approaches. An important application of isotopic mixing relationships is determination of the isotopic content of large-scale respiration ($\delta^{13}C_R$) via an inverse relationship (a Keeling plot, Keeling 1958) between atmospheric CO_2 concentrations ($[CO_2]$) and carbon isotope ratios of CO2 ($\delta^{13}C$). Alternatively, a linear relationship between $[CO_2]$ and the product of $[CO_2]$ and $\delta^{13}C$ (a Miller/Tans plot, Miller & Tans, 2003) can also be applied.
- We used an extensive dataset from the Niwot Ridge Ameriflux Site of $[CO_2]$ and $\delta^{13}C$ in forest air to examine contrasting approaches to determine $\delta^{13}C_R$ and its uncertainty. These included Keeling isotopic mixing relationships, Miller-Tans isotopic mixing relationships, Model I, and Model II regressions.
- Our analysis confirms previous observations that increasing the range of measurements ($[CO_2]$ range) reduces the uncertainty associated with $\delta^{13}C_R$. For carbon isotope studies, uncertainty in the isotopic measurements rather than the uncertainty in $[CO_2]$ has a greater effect on the uncertainty of $\delta^{13}C_R$. Reducing the uncertainty of isotopic measurements decreases the uncertainty of $\delta^{13}C_R$ even when the $[CO_2]$ range of samples is small (< 20 ppm). We conclude improvement in isotope (rather than CO_2) measuring capability is needed to substantially reduce uncertainty in $\delta^{13}C_R$. We also find for carbon isotope studies no inherent advantage to using either a Keeling or a Miller-Tans approach to determine $\delta^{13}C_R$.

Isotopic Mixing Relationships

- Assume a measured CO_2 concentration (C_M) is drawn from mixing a respiratory (C_R) and a background (C_B) pool of carbon. Using conservation of mass of CO_2 and $^{13}CO_2$, it is possible to determine the isotopic signature of ecosystem respiration ($\delta^{13}C_R$) via a Keeling mixing relationship or a Miller-Tans mixing relationship after a suitable arrangement of the conservation equations.

$$C_M = C_B + C_R$$

$$\delta_M C_M = \delta_B C_B + \delta_R C_R$$

Keeling (1958)

$$\delta_M = C_B(\delta_B - \delta_R)\frac{1}{C_M} + \delta_R$$

Miller and Tans (2003)

$$\delta_M C_M = C_B(\delta_B - \delta_R) + \delta_R C_M$$

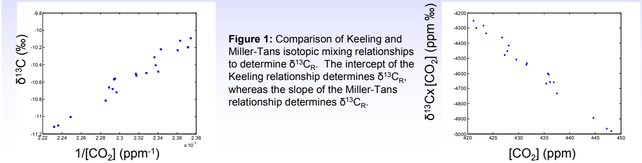


Figure 1: Comparison of Keeling and Miller-Tans isotopic mixing relationships to determine $\delta^{13}C_R$. The intercept of the Keeling relationship determines $\delta^{13}C_R$, whereas the slope of the Miller-Tans relationship determines $\delta^{13}C_R$.

Linear Regression & Uncertainty Propagation

- For any data that one needs to fit to a best fit line, one can find the residual of the data points to the hypothetical best fit line.
- For Ordinary Least Squares (OLS) Regression (Model I Regression), it is assumed there is no error in the independent variable.
- For Orthogonal Distance (Model II) Regression (ODR) it is assumed that both variables have error.
- Geometric Mean Regression (GMR) is another Model II regression technique. For two variables *x* and *y*, the slope of a GMR regression is the square root of the product of the OLS slope of *y* versus *x* and the inverse of the OLS slope of *x* versus *y*.
- Current practice recommends using a GMR regression with uncertainties in intercept estimated from an OLS regression. (Pataki et al 2003)
- It is possible to develop an analytical equation for the variance of the slope or intercept of a linear regression formula that depends on the data set along with the errors associated with the independent and dependent variables. (Zobitz et al, in preparation).

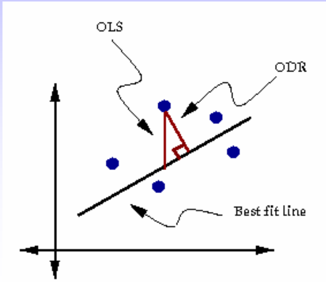


Figure 4: Data points (blue) are fitted to a best fit line, which is the line that minimizes the sum of the square residuals. For Ordinary Least Squares (OLS), the residual (shown in red) is the vertical distance from each data point. For Geometric Mean Regression (GMR), a vertical and horizontal residual is calculated. For Orthogonal Distance Regression (ODR) the residual is the perpendicular distance from the best fit line.

Perturbations to a "perfect" data set

- By taking a data set of $[CO_2]$ and isotope data, we can generate a "perfect" data set without error in the observations of CO_2 and isotopes.
- This perfect data set was perturbed by adding noise with known magnitude and probability distribution to each variable. We then randomly sub-sampled the perturbed data (n=20 samples, 5000 separate runs). From this a Keeling or Miller/Tans and OLS or ODR regression was calculated.
- By using the theoretical framework outlined, results indicate decreasing error in the isotopic sample greatly improved accuracy in $\delta^{13}C_R$.

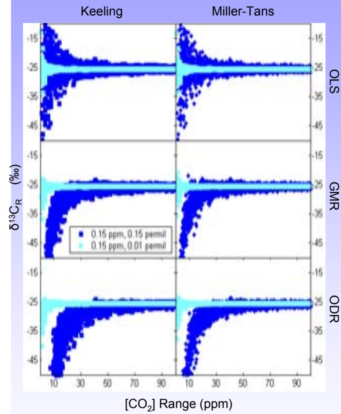


Figure 5: $\delta^{13}C_R$ determined by Keeling (left panels) or Miller-Tans (right panels) regressions by subsampling a data set with known error. The dark blue points show a simulation with data perturbed by a standard deviation of .15 ppm in CO_2, .15 ‰ in $\delta^{13}C$. The light blue points show a simulation with data perturbed by a standard deviation of .15 ppm in CO_2, .01 ‰ in $\delta^{13}C$.

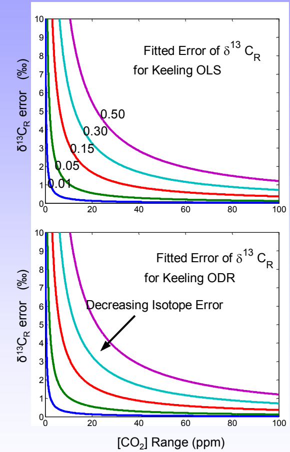


Figure 6: Error in $\delta^{13}C_R$ as a function of CO_2 range for both OLS and ODR using Keeling regressions. The numbers on the top graph represent the standard deviation of the $\delta^{13}C$ error added to the "perfect" data set. In these simulations, the standard deviation in CO_2 error added was .15 ppm.

Increased Uncertainty at Low Sampling Ranges

- For CO_2 carbon isotope studies, a wide sample range is important to obtain estimates of $\delta^{13}C_R$ that have acceptable uncertainty. In particular, as sampling range decreases, error in $\delta^{13}C_R$ increases.

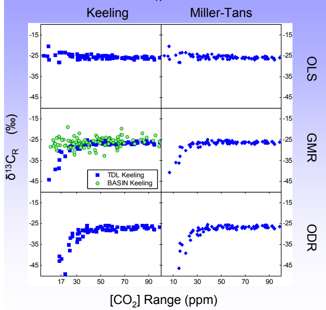
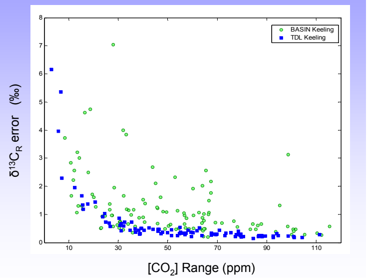


Figure 2: (Left) Comparison of $\delta^{13}C_R$ versus CO_2 range using Keeling or Miller-Tans isotopic mixing relationships and Model I or Model II regression schemes using data collected by tunable diode laser spectroscopy (Bowling et al in review). Superimposed on the Keeling GMR panel is BASIN data from Pataki et al 2003. Note the systematic negative bias for Model II regression.

Figure 3: (Right) Comparison of standard error of the intercept of $\delta^{13}C_R$ versus CO_2 range using data from Pataki et al 2003 and data collected by tunable diode laser spectroscopy. The BASIN data (http://basinisotopes.org/) were collected from 137 Keeling plots from 37 sites in many biomes (Pataki et al 2003). $\delta^{13}C_R$ was calculated using a Keeling GMR regression.



Contributing Factors to Uncertainty

CO_2 Signal (ppm)	Uncertainty in CO_2 (ppm)	CO_2 SNR	$\delta^{13}C$ Signal (‰)	Uncertainty in $\delta^{13}C$ (‰)	$\delta^{13}C$ SNR	OLS $\delta^{13}C_R$ Uncertainty (‰)
50	0.15	333.33	2.50	0.15	16.67	0.71
				0.05	50.00	0.23
				0.01	250.00	0.05
				0.0075	333.33	0.04
				0.0005	5000.00	0.03
	0.10	5000		0.15	16.67	0.69
				0.05	50.00	0.23
				0.01	250.00	0.05
				0.0075	333.33	0.04
				0.0005	5000.00	0.02

Table 1: Results of simulations where CO_2 and $\delta^{13}C$ was perturbed with a controlled amount of noise. The uncertainty in $\delta^{13}C_R$ at a specific CO_2 range was found from graphs similar to Figure 6. Results in red represent uncertainty levels from Bowling et al (in review). Results in blue are from uncertainty levels in Miller & Tans (2003). Note that uncertainty in $\delta^{13}C_R$ is controlled by uncertainty in measured $\delta^{13}C$ instead of CO_2. GMR and ODR are omitted here because they give similar results to OLS $\delta^{13}C_R$ uncertainty.

Conclusions

- The uncertainty in $\delta^{13}C_R$ is primarily controlled by uncertainty in measured $\delta^{13}C$, not CO_2.
- The analytical uncertainty of $\delta^{13}C$ relative to the measured signal is poor compared to that for CO_2 with present instrumentation.
- There is no inherent advantage to using either Keeling or Miller-Tans mixing relationships to determine $\delta^{13}C_R$.
- Model II regressions result in a systematic negative bias in $\delta^{13}C_R$. We advocate Model I regression instead.

References

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Acknowledgments

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