Isotope analytical uncertainty propagation

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Here I (1) state the uncertainty propagation rules plainly, (2) apply them to our mass-balance model equation and calculate the results, and finally (3) I explore the the derivation of Genereux's (1998) isotopic tracer component uncertainty equations and how they, sadly, differ to my arithmetic propagation in section (2).

1 Uncertainty propagation rules

Our uncertainty rules are as follows. Let q be some quantity, and u_q be its uncertainty, where q is a function of variables x, y and z.

For **constants**

$$\begin{aligned} q &= Bx \\ \frac{u_q}{q} &= \frac{u_x}{x} \end{aligned} \tag{1.1}$$

For **sums**

$$\begin{aligned} q &= x \pm y \pm z \\ u_q &= \sqrt{u_x^2 + u_y^2 + u_z^2} \end{aligned} \tag{1.2}$$

And for **products/quotients**

$$\begin{aligned} q &= xyz \\ \frac{u_q}{|q|} &= \sqrt{\left(\frac{u_x}{x}\right)^2 + \left(\frac{u_y}{y}\right)^2 + \left(\frac{u_z}{z}\right)^2} \end{aligned} \tag{1.3}$$

2 Ruan's propagation

Derivation

Let p_E be the proportion of streamflow derived from rainfall according to an isotope E, where

$$p_E = \frac{E_{streamflow} - E_{baseflow}}{E_{rain} - E_{baseflow}} \tag{2.1}$$

As such, for our analysis, we propagate the uncertainty as follows, relying on our known uncertainty in measuring isotope values u_E

$$\begin{aligned} p_E &= \frac{E_{streamflow} - E_{baseflow}}{E_{rain} - E_{baseflow}} \\ \therefore u_{p_E} &= |p_E| \sqrt{\left(\frac{u_{[E_{streamflow} - E_{baseflow}]}}{E_{streamflow} - E_{baseflow}}\right)^2 + \left(\frac{u_{[E_{rain} - E_{baseflow}]}}{E_{rain} - E_{baseflow}}\right)^2} \end{aligned}$$

where

$$u_{[E_{streamflow} - E_{baseflow}]} = u_{[E_{rain} - E_{baseflow}]} = \sqrt{u_E^2 + u_E^2}$$

such that

$$u_{p_E} = |p_E| \sqrt{\left(\frac{\sqrt{u_E^2 + u_E^2}}{E_{streamflow} - E_{baseflow}}\right)^2 + \left(\frac{\sqrt{u_E^2 + u_E^2}}{E_{rain} - E_{baseflow}}\right)^2} \tag{2.2}$$

We then average $p_{\delta^2 H}$ and $p_{\delta^{18} O}$, each with their own uncertainty derived above, as follows

$$\begin{aligned} p &= \frac{p_{\delta^{18} O} + p_{\delta^2 H}}{2} \\ \therefore u_p &= |p| \frac{\sqrt{u_{p_{\delta^{18} O}} + u_{p_{\delta^2 H}}}}{p_{\delta^{18} O} + p_{\delta^2 H}} \end{aligned} \tag{2.3}$$

Application to Liesbeek study

For our study, we combined long term analytical precision and accuracy using Equation 1.2

$$
\begin{aligned}
u_{\delta^{18}O} &= \sqrt{0.07^2 + 0.13^2} \\
&= 0.1476482 \\
u_{\delta^2 H} &= \sqrt{0.2^2 + 1.5^2} \\
&= 1.5132746
\end{aligned}
$$

As such, we calculate our p_E values using Equation 2.1 as

$$
\begin{aligned}
p_{\delta^{18}O} &= \frac{-4.7860375 - -2.2142798}{-4.794164 - -2.2142798} \\
&= 0.99685 \\
p_{\delta^2 H} &= \frac{-20.4562927 - -6.0803734}{-20.092425 - -6.0803734} \\
&= 1.0259682
\end{aligned}
$$

and their uncertainties using Equation 2.2

$$
\begin{aligned}
u_{p_{\delta^{18}O}} &= |0.99685|\sqrt{\left(\frac{\sqrt{0.1476482^2 + 0.1476482^2}}{-4.7860375 - -2.2142798}\right)^2 + \left(\frac{\sqrt{0.1476482^2 + 0.1476482^2}}{-4.794164 - -2.2142798}\right)^2} \\
&= 0.114281 \\
u_{p_{\delta^2 H}} &= |1.0259682|\sqrt{\left(\frac{\sqrt{1.5132746^2 + 1.5132746^2}}{-20.4562927 - -6.0803734}\right)^2 + \left(\frac{\sqrt{1.5132746^2 + 1.5132746^2}}{-20.092425 - -6.0803734}\right)^2} \\
&= 0.2188186
\end{aligned}
$$

We then use Equation 2.3 to derive p proper

$$
\begin{aligned}
p &= \frac{0.99685 + 1.0259682}{2} \\
&= 1.0114091 \\
\therefore u_p &= |1.0114091|\frac{\sqrt{0.114281 + 0.2188186}}{0.99685 + 1.0259682} \\
&= 0.1234319
\end{aligned}
$$

Thus, we can conclude that, following this method, the Liesbeek River streamflow during our storm constituted 101% ± 12.3% rain-water.

3 Genereux's propagation

Knowing Equations 1–3, applying them to Equation 4 Genereux got

$$u_{p_E} = \sqrt{\left(u_{E_{baseflow}} \frac{E_{rain} - E_{streamflow}}{(E_{rain} - E_{baseflow})^2}\right)^2 + \left(u_{E_{rain}} \frac{E_{streamflow} - E_{baseflow}}{(E_{rain} - E_{baseflow})^2}\right)^2 + \left(u_{E_{streamflow}} \frac{-1}{E_{rain} - E_{baseflow}}\right)^2}$$

Since we know that, for our analyses, we have identical analytical uncertainty for any measurement of an isotope E, such that

$$u_{E_{streamflow}} = u_{E_{rain}} = u_{E_{baseflow}} = u_E$$

With this approach, I get $p_{\delta^{18}O} = 0.99685 \pm 0.1594934$ and $p_{\delta^2 H} = 1.0259682 \pm 0.1413952$, such that following (2.3) $p = 1.0114091 \pm 0.1065724$.

Problem: u_p from (2.2) $\neq$ that from (3.2)

References

Genereux (1998) *Water Resources Research* 34(4):915–919