Isotope analytical uncertainty propagation

Ruan van Mazijk

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**

$$q = Bx \tag{1.1}$$
$$\frac{u_q}{q} = \frac{u_x}{x} \tag{1}$$

For **sums**

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

And for **products/quotients**

$$q = xyz \tag{1.3}$$
$$\frac{u_q}{|q|} = \sqrt{\left(\frac{u_x}{x}\right)^2 + \left(\frac{u_y}{y}\right)^2 + \left(\frac{u_z}{z}\right)^2} \tag{3}$$

2 Ruan's propagation

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

$$p_E = \frac{E_{streamflow} - E_{baseflow}}{E_{rain} - E_{baseflow}} \tag{4}$$

$$\therefore u_{p_E} = |p_E| \sqrt{\left(\frac{u_{[E_{streamflow} - E_{baseflow}]}}{E_{streamflow} - E_{baseflow}}\right)^2 + \left(\frac{u_{[E_{rain} - E_{baseflow}]}}{E_{rain} - E_{baseflow}}\right)^2} \tag{5}$$

where

$$u_{[E_{streamflow} - E_{baseflow}]} = u_{[E_{rain} - E_{baseflow}]} = \sqrt{u_E^2 + u_E^2} \tag{6}$$

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

$$p = \frac{p_{\delta^{18} O} + p_{\delta^2 H}}{2} \tag{2.3}$$

$$\therefore u_p = |p| \frac{\sqrt{u_{p_{\delta^{18} O}} + u_{p_{\delta^2 H}}}}{p_{\delta^{18} O} + p_{\delta^2 H}} \tag{7}$$

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

$$u_{\delta^{18} O} = \sqrt{0.07\text{Ğ}^2 + 0.13\text{Ğ}^2} \tag{8}$$

$$= 0.1476482\text{Ğ} \tag{9}$$

$$u_{\delta^2 H} = \sqrt{0.2\text{Ğ}^2 + 1.5\text{Ğ}^2} \tag{10}$$

$$= 1.5132746\text{Ğ} \tag{11}$$

As such, we calculate our p_E values using (2.1)

$$p_{\delta^{18} O} = \frac{-4.7860375\text{Ğ} - -2.2142798\text{Ğ}}{-4.794164\text{Ğ} - -2.2142798\text{Ğ}} \tag{12}$$

$$= 0.99685 \tag{13}$$

$$p_{\delta^2 H} = \frac{-20.4562927\text{Ğ} - -6.0803734\text{Ğ}}{-20.092425\text{Ğ} - -6.0803734\text{Ğ}} \tag{14}$$

$$= 1.0259682 \tag{15}$$

and their uncertainties (using (2.2))

$$u_{p_{\delta^{18}O}} = |0.99685|\sqrt{\left(\frac{\sqrt{0.1476482Ğ^2 + 0.1476482Ğ^2}}{-4.7860375 - -2.2142798}\right)^2 + \left(\frac{\sqrt{0.1476482Ğ^2 + 0.1476482Ğ^2}}{-4.794164 - -2.2142798}\right)^2} \quad (16)$$

$$= 0.114281Ğ \quad (17)$$

$$u_{p_{\delta^{2}H}} = |1.0259682|\sqrt{\left(\frac{\sqrt{1.5132746Ğ^2 + 1.5132746Ğ^2}}{-20.4562927 - -6.0803734}\right)^2 + \left(\frac{\sqrt{1.5132746Ğ^2 + 1.5132746Ğ^2}}{-20.092425 - -6.0803734}\right)^2} \quad (18)$$

$$= 0.2188186Ğ \quad (19)$$

We then use (2.3) to derive p proper

$$p = \frac{0.99685 + 1.0259682}{2} \quad (20)$$

$$= 1.0114091 \quad (21)$$

$$\therefore u_p = |1.0114091|\frac{\sqrt{0.114281Ğ + 0.2188186Ğ}}{0.99685 + 1.0259682} \quad (22)$$

$$= 0.1234319 \quad (23)$$

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 (1.1)–(1.3), applying them to (2.1) Genereux got

$$u_{p_E} = \sqrt{\left(u_{E_{baseflow}}\frac{E_{rain} - E_{streamflow}}{(E_{rain} - E_{baseflow})^2}\right)^2 + \left(u_{E_{rain}}\frac{E_{streamflow} - E_{baseflow}}{(E_{rain} - E_{baseflow})^2}\right)^2 + \left(u_{E_{streamflow}}\frac{-1}{E_{rain} - E_{baseflow}}\right)^2} \quad (3.1)$$

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

$$u_{E_{streamflow}} = u_{E_{rain}} = u_{E_{baseflow}} = u_E \quad (24)$$

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