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Technical note: Uncertainty in multi-source partitioning using large tracer data sets

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Abstract

The availability of large tracer data sets opened up the opportunity to investigate multiple source contributions to a mixture. However, the source contributions may be uncertain and apart from Bayesian approaches to estimate such source uncertainty only sound methods for two and three sources. We expand these methods developing an uncertainty estimation method for four sources based on multiple tracers as input data. Taylor series approximation is used to solve the set of linear mass balance equations. We illustrate the method with an example from hydrology, where we use a large tracer set from four water sources contributing to streamflow in a tropical, high-elevation catchment. However, our uncertainty estimation method can be generalized to any number of tracers across a range of disciplines.

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1. Introduction

Tracer applications have dramatically increased over recent years across a wide range of disciplines (West et al., 2010). Applications in hydrology (Hooper, 2003; James and Roulet, 2006; Kirchner and Neal, 2013), ecology (Phillips and Gregg, 2003; Semmens et al., 2009b), anthropology (Ehleringer et al., 2008), conservation biology (Bicknell et al., 2014), nutrition (Magaña-Gallegos et al., 2018), environmental and ecosystem science (Bartov et al., 2013; Granek et al., 2009), and erosion and sediment transportation (Davies et al., 2018) have been the most prominent. Such a widespread use of tracers was mainly facilitated by novel analytical techniques that provide high sensitive, rapid multi-element analysis at lower cost (Falkner et al., 1995). For example, the use of inductively coupled plasma mass spectrometry (ICP-MS) as one of the leading analytical techniques for elemental analysis (Helaluddin et al., 2016), led to the availability and use of large tracers sets (elements) in hydrological studies (Barthold et al., 2017; Belli et al., 2017; Correa et al., 2018; Kirchner and Neal, 2013; Mimba et al., 2017). Trace elements together with water stable isotopes (novel Cavity Ringdown Laser Absorption Spectroscopy paved the way: (Berman et al., 2009; Lis et al., 2008)) as well as physical-chemical water parameters (e.g. electrical conductivity and pH) are now often used to improve understanding of hydro-geochemical cycles, flow pathways and runoff generation in hydrology. Furthermore, mixing models based on mass balance equations are widely-applied to identify the dominant sources and their dynamics as components of a mixture.

In hydrological mixing models the composition of the stream is assumed to be an integrated mixture of signatures of different sources (Christophersen et al., 1990). The proportional contributions of n+1 sources to the stream can be uniquely determined using n different tracers (Christophersen & Hooper, 1992). Bayesian methods have been developed to identify multiple (> 3) sources and compute their contributions to a mixture in a two-dimensional space (Parnell et al., 2010; Stock et al., 2018). In this case a unique solution is not feasible and a higher uncertainty is attributed to the model (Phillips and Gregg, 2001, 2003). On the other hand, End Member Mixing Analysis (EMMA) (Hooper, 2003) was developed to use multiple tracers as input, and therefore, allows for a multi-dimensional space that potentially increases the number of identifiable sources (Barthold et al., 2011; Inamdar et al., 2013; Liu et al., 2004). Additionally, the use of multiple tracers can avoid bias and subjectivity in the input information. Therefore, EMMA provides a robust and complete conceptualization of catchment functioning and source interactions during runoff generation (Iwasaki et al., 2015). However, despite its benefits, the EMMA approach lacks a formal methodology to assess the uncertainty of multiple end-members (Delsman et al., 2013) and to assess individual uncertainties in the calculation of source contributions to a stream.

To our knowledge, the uncertainty estimation of source contributions to streams is based on Gaussian error propagation (Genereux, 1998) and was so far only calculated using one or two tracers simultaneously (MixSIAR: Parnell et al., 2010; Phillips & Gregg, 2001; Semmens, Moore, et al., 2009). Alternatively, when the number of sources is higher, the uncertainty is usually based on the sum of analytical errors, elevation effects and the spatial variability of end-member concentrations (Uhlenbrook and Hoeg, 2003). Hence, we propose a novel and robust methodology to estimate the uncertainty of individual end-member (source) contributions to streams (mixture) based on a multi-tracer set in a three-dimensional space defined by a Principal Component Analysis. We outline and explain the step by step

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development of the mathematical procedure and give an example application including MatLab codes using a large multi-tracer data set from an experimental catchment in Ecuador.

2. Uncertainty estimation method development

In this section, we extend the method for uncertainty estimation presented in Phillips and Gregg, (2001). Let $\mathcal{C} = \{A, B, C, D, M\}$ be the set of end-members used. In the following $x \in \mathcal{C}$, $y \in \{\overline{\delta}, \overline{\lambda}, \overline{\phi}\}$ and $z \in \{A, M, C\}$. If the system is composed of Eq. (1)

$$\begin{cases} \overline{\delta}_A f_A & + & \overline{\delta}_B f_B & + & \overline{\delta}_C f_C & + & \overline{\delta}_D f_D & = & \overline{\delta}_M \\ \overline{\lambda}_A f_A & + & \overline{\lambda}_B f_B & + & \overline{\lambda}_C f_C & + & \overline{\lambda}_D f_D & = & \overline{\lambda}_M \\ \overline{\phi}_A f_A & + & \overline{\phi}_B f_B & + & \overline{\phi}_C f_C & + & \overline{\phi}_D f_D & = & \overline{\phi}_M \\ f_A & + & f_B & + & f_C & + & f_D & = & 1 \end{cases} \qquad \text{Eq.(1)}$$

and has solution[1] for $f_A, f_B, f_C, f_D > 0$, they take the following form:

$$\begin{aligned} f_A &= \frac{(\Phi_M - \Delta_M)(\Lambda_C - \Delta_C) - (\Lambda_M - \Delta_M)(\Phi_C - \Delta_C)}{(\Phi_A - \Delta_A)(\Lambda_C - \Delta_C) - (\Lambda_A - \Delta_A)(\Phi_C - \Delta_C)} = \frac{Num}{Den} \\ f_C &= \frac{(\Delta_M - \Lambda_M) - (\Delta_A - \Lambda_A) f_A}{(\Delta_C - \Lambda_C)} \\ f_B &= \Delta_M - (\Delta_C f_C + \Delta_A f_A) \\ f_D &= 1 - (f_C + f_B + f_A) \end{aligned} \qquad \text{Eq.(2)}$$

where

$$\Delta_x = \frac{\overline{\delta}_x - \overline{\delta}_D}{\overline{\delta}_B - \overline{\delta}_D}, \Lambda_x = \frac{\overline{\lambda}_x - \overline{\lambda}_D}{\overline{\lambda}_B - \overline{\lambda}_D}, \Phi_x = \frac{\overline{\phi}_x - \overline{\phi}_D}{\overline{\phi}_B - \overline{\phi}_D}. \qquad \text{Eq.(3)}$$

The partial derivatives of (2) are given by:

[1] The system has a solution if the vector of source M is on the polyhedron generated by the vectors of sources A, B, C, D such that $\sum_x f_x = 1$.

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$$\begin{aligned}
\frac{\partial f_A}{\partial y_x} &= \frac{1}{Den^2}\Bigg[\left[(\Lambda_C-\Delta_C)\left(\frac{\partial\Phi_M}{\partial y_x}-\frac{\partial\Delta_M}{\partial y_x}\right)+(\Phi_M-\Delta_M)\left(\frac{\partial\Lambda_C}{\partial y_x}-\frac{\partial\Delta_C}{\partial y_x}\right)\right.\\
&\left.-(\Phi_C-\Delta_C)\left(\frac{\partial\Lambda_M}{\partial y_x}-\frac{\partial\Delta_M}{\partial y_x}\right)-(\Lambda_M-\Delta_M)\left(\frac{\partial\Phi_C}{\partial y_x}-\frac{\partial\Delta_C}{\partial y_x}\right)\right]Den\\
&-\left[(\Lambda_C-\Delta_C)\left(\frac{\partial\Phi_A}{\partial y_x}-\frac{\partial\Delta_A}{\partial y_x}\right)+(\Phi_A-\Delta_A)\left(\frac{\partial\Lambda_C}{\partial y_x}-\frac{\partial\Delta_C}{\partial y_x}\right)\right.\\
&\left.-(\Phi_C-\Delta_C)\left(\frac{\partial\Lambda_A}{\partial y_x}-\frac{\partial\Delta_A}{\partial y_x}\right)-(\Lambda_A-\Delta_A)\left(\frac{\partial\Phi_C}{\partial y_x}-\frac{\partial\Delta_C}{\partial y_x}\right)\right]Num\Bigg]\\
\frac{\partial f_C}{\partial y_x} &= \frac{1}{(\Delta_C-\Lambda_C)^2}\Bigg[\left[\left(\frac{\partial\Delta_M}{\partial y_x}-\frac{\partial\Lambda_M}{\partial y_x}\right)-\left(\frac{\partial\Delta_A}{\partial y_x}-\frac{\partial\Lambda_A}{\partial y_x}\right)f_A-(\Delta_A-\Lambda_A)\frac{\partial f_A}{\partial y_x}\right](\Delta_C-\Lambda_C)\\
&-\left(\frac{\partial\Delta_C}{\partial y_x}-\frac{\partial\Lambda_C}{\partial y_x}\right)[(\Delta_M-\Lambda_M)-(\Delta_A-\Lambda_A)f_A]\Bigg],\\
\frac{\partial f_B}{\partial y_x} &= \frac{\partial\Delta_M}{\partial y_x}-\frac{\partial\Delta_C}{\partial y_x}f_C-\Delta_C\frac{\partial f_C}{\partial y_x}-\frac{\partial\Delta_A}{\partial y_x}f_A-\Delta_A\frac{\partial f_A}{\partial y_x},\\
\frac{\partial f_D}{\partial y_x} &= -\frac{\partial f_C}{\partial y_x}-\frac{\partial f_B}{\partial y_x}-\frac{\partial f_A}{\partial y_x}
\end{aligned} \qquad \text{Eq.(4)}$$

where

$$\frac{\partial\Delta_z}{\partial w_x}=0,\ w\in\{\bar\lambda,\bar\phi\};\ \frac{\partial\Lambda_z}{\partial w_x}=0,\ w\in\{\bar\delta,\bar\phi\};\ \frac{\partial\Phi_z}{\partial w_x}=0,\ w\in\{\bar\delta,\bar\lambda\}. \qquad \text{Eq.(5)}$$

$$\frac{\partial\Delta_z}{\partial\bar\delta_x} = (\bar\delta_B-\bar\delta_D)^{-1}\begin{cases}1 & z\in\{A,C,M\}\text{ and }x=z\\ -\Delta_z & z\neq B\text{ and }x=B\\ \Delta_z-1 & z\neq D\text{ and }x=D\\ 0 & otherwise\end{cases}, \qquad \text{Eq.(6)}$$

$$\frac{\partial\Lambda_z}{\partial\bar\lambda_x} = (\bar\lambda_B-\bar\lambda_D)^{-1}\begin{cases}1 & z\in\{A,C,M\}\text{ and }x=z\\ -\Lambda_z & z\neq B\text{ and }x=B\\ \Lambda_z-1 & z\neq D\text{ and }x=D\\ 0 & otherwise\end{cases}\quad\text{and} \qquad \text{Eq.(7)}$$

$$\frac{\partial\Phi_z}{\partial\bar\phi_x} = (\bar\phi_B-\bar\phi_D)^{-1}\begin{cases}1 & z\in\{A,C,M\}\text{ and }x=z\\ -\Phi_z & z\neq B\text{ and }x=B\\ \Phi_z-1 & z\neq D\text{ and }x=D\\ 0 & otherwise\end{cases}. \qquad \text{Eq.(8)}$$

For example, for f_A we have

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$$\begin{aligned}
\frac{\partial f_A}{\partial \bar{\delta}_x} &= \frac{1}{Den^2}\left[\left[\frac{\partial \Delta_M}{\partial \bar{\delta}_x}(\Phi_C-\Lambda_C)-\frac{\partial \Delta_C}{\partial \bar{\delta}_x}(\Phi_M-\Lambda_M)\right]Den \right.\\
&\quad \left. -\left[\frac{\partial \Delta_A}{\partial \bar{\delta}_x}(\Phi_C-\Lambda_C)-\frac{\partial \Delta_C}{\partial \bar{\delta}_x}(\Phi_A-\Lambda_A)\right]Num\right].\\
\frac{\partial f_A}{\partial \bar{\lambda}_x} &= \frac{1}{Den^2}\left[\frac{\partial \Lambda_C}{\partial \bar{\lambda}_x}(\Phi_M-\Delta_M)-\frac{\partial \Lambda_M}{\partial \bar{\lambda}_x}(\Phi_C-\Delta_C)\right]Den\\
&\quad -\left[\frac{\partial \Lambda_C}{\partial \bar{\lambda}_x}(\Phi_A-\Delta_A)-\frac{\partial \Lambda_A}{\partial \bar{\lambda}_x}(\Phi_C-\Delta_C)\right]Num\right].\\
\frac{\partial f_A}{\partial \bar{\phi}_x} &= \frac{1}{Den^2}\left[\left[\frac{\partial \Phi_M}{\partial \bar{\phi}_x}(\Lambda_C-\Delta_C)-\frac{\partial \Phi_C}{\partial \bar{\phi}_x}(\Lambda_M-\Delta_M)\right]Den \right.\\
&\quad \left. -\left[\frac{\partial \Phi_A}{\partial \bar{\phi}_x}(\Lambda_C-\Delta_C)-\frac{\partial \Phi_C}{\partial \bar{\phi}_x}(\Lambda_A-\Delta_A)\right]Num\right].
\end{aligned} \qquad \text{Eq.(9)}$$

Using Eq. (9) the first-order Taylor series approximation for the variance of f_A evaluated at the mean can be calculated (Taylor, 1982) by:

$$\sigma_{f_A}^2 = \sum_x \left(\frac{\partial f_A}{\partial \bar{\delta}_x}\right)^2 \sigma_{\bar{\delta}_x}^2 + \sum_x \left(\frac{\partial f_A}{\partial \bar{\lambda}_x}\right)^2 \sigma_{\bar{\lambda}_x}^2 + \sum_x \left(\frac{\partial f_A}{\partial \bar{\phi}_x}\right)^2 \sigma_{\bar{\phi}_x}^2 = \sum_y \sum_x \left(\frac{\partial f_A}{\partial y_x}\right)^2 \sigma_{y_x}^2. \qquad \text{Eq.(10)}$$

To calculate γ_A (the Satterthwaite (1946) approximation for the degrees of freedom), we define $f_{Ay_x} = c_A\left(\frac{\partial f_A}{\partial y_x}\right)^2$. In this case, we get:

$$\gamma_A = \frac{\left(\sum_y \sum_x f_{Ay_x}\sigma_{y_x}^2\right)^2}{\sum_y \sum_x \frac{\left(f_{Ay_x}\sigma_{y_x}^2\right)^2}{n_{y_x}-1}}. \qquad \text{Eq.(11)}$$

Note that whatever the value of c_A is, Eq. (11) leads to:

$$\gamma_A = \frac{\left(\sum_y \sum_x \left(\frac{\partial f_A}{\partial y_x}\right)^2 \sigma_{y_x}^2\right)^2}{\sum_y \sum_x \frac{\left(\left(\frac{\partial f_A}{\partial y_x}\right)^2 \sigma_{y_x}^2\right)^2}{n_{y_x}-1}}$$

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and if we set $f^*_{Ay_x} = \left(\frac{\partial f_A}{\partial y_x}\right)^2$ then the numerator of the last equation can be replaced by $\left(\sigma^2_{f_A}\right)^2$. In other words, we can use Eq. (10) and the derivatives (9) to estimate the value of γ_A resulting in $f_{Ay_x} = c_A f^*_{Ay_x}$. Of course, it is required that c_A is constant w.r.t. y_x. Then,

$$\gamma_A = \frac{\left(\sigma^2_{f_A}\right)^2}{\sum_y \sum_x \frac{\left(\left(\frac{\partial f_A}{\partial y_x}\right)^2 \sigma^2_{y_x}\right)^2}{n_{y_x} - 1}} \qquad \text{Eq.(12)}$$

Let $w \in \mathcal{C} \setminus \{A\}$. The first-order Taylor series approximation for the variance of f_w, can be calculated by (as above):

$$\sigma^2_{f_w} = \sum_x \left(\frac{\partial f_w}{\partial \bar{\delta}_x}\right)^2 \sigma^2_{\delta_x} + \sum_x \left(\frac{\partial f_w}{\partial \bar{\lambda}_x}\right)^2 \sigma^2_{\lambda_x} + \sum_x \left(\frac{\partial f_w}{\partial \bar{\phi}_x}\right)^2 \sigma^2_{\phi_x} = \sum_y \sum_x \left(\frac{\partial f_w}{\partial y_x}\right)^2 \sigma^2_{y_x}. \qquad \text{Eq.(13)}$$

If we construct γ_w as γ_A, we get:

$$\gamma_w = \frac{\left(\sum_y \sum_x f^*_{wy_x} \sigma^2_{y_x}\right)^2}{\sum_y \sum_x \frac{\left(f^*_{wy_x} \sigma^2_{y_x}\right)^2}{n_{y_x} - 1}}$$

where $f_{wy_x} = c_w f^*_{wy_x}$ and $f^*_{wy_x} = \left(\frac{\partial f_w}{\partial y_x}\right)^2$ with c_w constant w.r.t. y_x, then we finally get:

$$\gamma_w = \frac{\left(\sigma^2_{f_w}\right)^2}{\sum_y \sum_x \frac{\left(\left(\frac{\partial f_w}{\partial y_x}\right)^2 \sigma^2_{y_x}\right)^2}{n_{y_x} - 1}} \qquad \text{Eq.(14)}$$

3. Application

3.1. Study site and data

This methodology was tested using data from a high elevation (3,500 - 3,900 m a.s.l.) tropical catchment (7.53 km^2) located in southern Ecuador (3°4′38″S, 79°15′30″O). The mean annual precipitation for this study site is 1,300 mm (Padrón et al., 2015), the mean annual discharge is 860 mm yr^{-1}. The catchment is of a volcanic origin and dominated by volcanic Histosol (24%) and Andosol (72%) soils (IUSS Working Group WRB, 2015), both with high percentage of organic matter content (450 and 310 g kg, respectively) (Quichimbo et al., 2012) and large water-holding capacities (Buytaert et al., 2006). Histosols are primarily located at the valleys and covered by cushion plants, while Andosol soils are predominated on the hillslopes under a cover of tussock grass. Nearly-saturated conditions of the riparian zone are observed year-round, and a spring is located in the north-western part of the catchment. Streamwater samples were collected weekly from March 2013 to April 2014 (n=270) and at a higher frequency during experimental campaigns. We also collected bi-weekly water samples from 4 potential water source end-members: rainfall (RF), soil water from Andosols (AN) and Histosols (HS) and spring water (SW) (n ~ 30). The above-mentioned waters sources (RF, AN, HS and SW), were previously identified as end-members (Correa et al., 2017, 2018) (Table 1). A multi-tracer (14 tracers) data set of conservative tracers was obtained from each water sample (Na, Mg, Al, Si, K, Ca, Rb, Sr, Ba, Ce, V, Y, Nd) at the Institute for Landscape Ecology and Resource Management of the Justus Liebig University using an ICP-MS (Agilent 7500ce, Agilent Technologies) and the electrical conductivity (EC) was measured in situ. More detailed information on the study site and data set can be found in Correa et al. (2017, 2018).

3.2. Source water uncertainty estimation

Using the classic EMMA approach (Christophersen and Hooper, 1992), end-members (source) and stream (mixture) data were projected into a three-dimensional space (Correa et al., 2018) visualized in Figure 1. The resulting median and standard deviation of end-members and stream coordinates are shown in Table 1.

The uncertainty of each of the four end-member contributions to the stream was determined using the above developed first-order Taylor series approximation from Eq. 14 (MatLab code in (Correa et al., 2019). The variance for each end-member fraction can be calculated using partial derivatives and the 95% confidence intervals (as recommended by Phillips and Gregg (2001)) constructed as $f_{EM1} \pm t_{0.05,\gamma}\, \sigma_{fEM1}$. The $t_{0.05,\gamma}$ depicts the Student's t for α=0.05 (two-tailed) and γ degrees of freedom. The γ degrees of freedom represents the Satterthwaite (1946) approximation for the related degrees of freedom with σ_{fEM1} and can be calculated as follows:

$$\gamma_{EM1} = \frac{\left(\sigma_{f_{EM1}}^2\right)^2}{\sum_y \sum_x \frac{\left(\left(\frac{\partial f_{EM1}}{\partial y_x}\right)^2 \sigma_{y_x}^2\right)^2}{n_{y_x} - 1}} \quad \text{Eq.(15)}$$

Note that Eq. (14) is an adaptation of Eq. (15) for this particular end-member configuration with x = EM1, EM2, EM3, EM4 and SW, y = δ, λ and ϕ, n= number of samples. The δ, λ and ϕ represent the median of the projected water samples from end-members and stream in U1, U2 and U3, respectively. The f_{EM1} gives w the proportion of EM1 in SW and $\sigma_{f_{EM1}}^2$, the variances of the EM1. A similar procedure should be used for all end-members. The resulting uncertainty estimates for each source end-member are shown in Table 2.

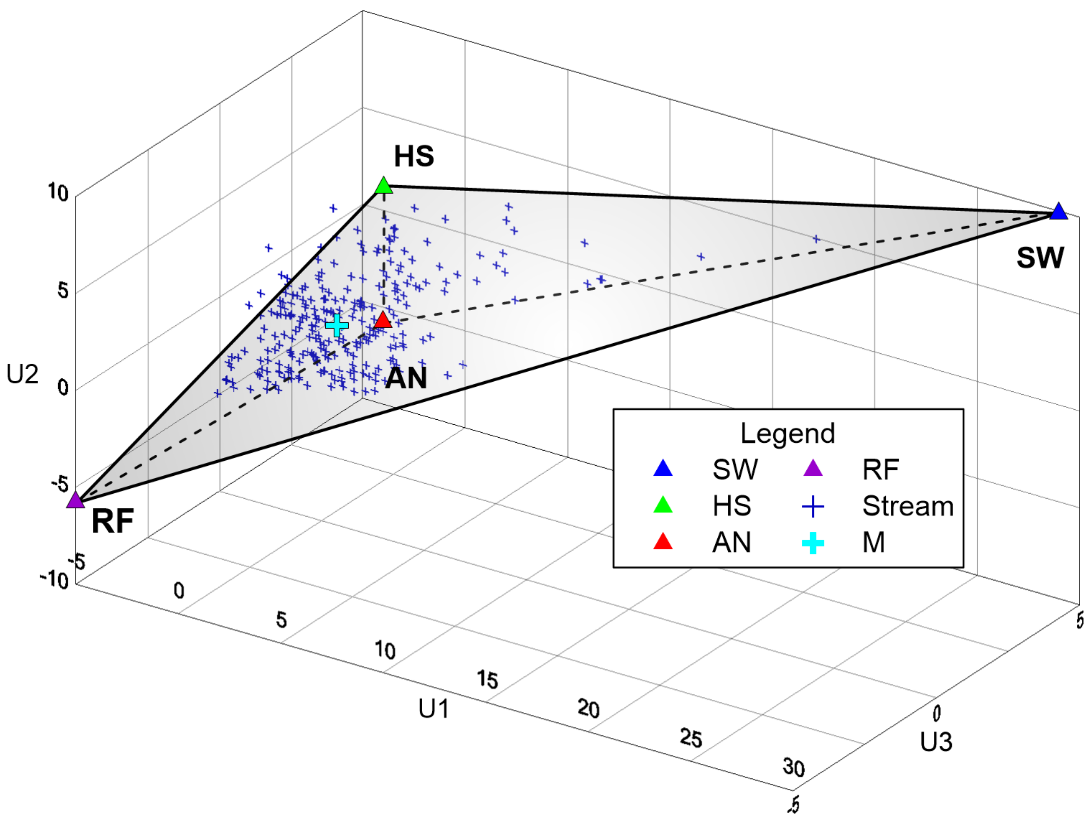

Figure 1. Three-dimensional mixing space generated using stream data, where the median of end-members are projected. U1 represents 59.6% of the variance, U2 19.7%, and U3 7.4% (From PCA); RF, rainfall; AN, Andosols; HS, Histosols; SW, spring water; M, median of stream data (mixture)

4. Summary and remarks

Our methodology developed to calculate the contribution of sources to the mixture and its associated uncertainty (based on multiple tracer sets) has been shown to be effective in a real application case. The simplicity of the methodology, the MatLab code provided and the illustrative example facilitates its understanding and future scientific applications. We are confident that the use of this methodology will help the scientific community that is increasingly using large tracer sets in its research to obtain robust results.

5. Code and data availability

A MatLab code to calculate the fractions of end-members contribution to the mixture and their associated uncertainties is freely available in https://zenodo.org/record/2649201. As well as input data (used in this study) as an example for the code run and an instruction note.

6. Author contribution

AC and CB conceptualized the methodology. AC was responsible for the data collection and analysis. DO AC programmed and evaluated the MatLab code with collected data. AC wrote the manuscript with contributions from all co-authors.

7. Competing interests

The authors declare that they have no conflict of interest

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Discussions

Table 1. Median and standard deviation (std.dev.) of end-members and stream projected in three-dimensional space for the study period 2013–2014.

End-member		Coordinates*			Naming
		U1	U2	U3	in equations
SW (n = 25)	median	26,25	7,29	7,00	A
	std.dev.	0,46	0,36	0,39	
HS (n = 33)	median	0,23	5,48	1,97	B
	std.dev.	0,85	1,29	0,69	
AN (n = 37)	median	-2,24	-3,93	3,71	C
	std.dev.	0,55	0,58	0,45	
RF (n = 36)	median	-5,38	-6,10	-4,84	D
	std.dev.	0,27	0,56	0,15	
Stream (n = 257)	median	-0,61	-1,04	0,94	M
	std.dev.	2,06	1,10	0,66	

* Coordinates of end-members and stream (mixture) medians in three- axes. n represents the sample size

Table 2. Uncertainty of individual end-member contributions to the stream.

	EM1 SW	EM2 HS	EM3 AN	EM4 RF
Fraction of end-members contribution	0.06	0.30	0.35	0.29
Upper 95% confidence limit	0.21	0.57	0.58	0.46
Lower 95% confidence limit	0.00	0.03	0.12	0.12