



Implications of variations in stream specific conductivity for estimating baseflow using chemical mass balance and calibrated hydrograph techniques

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Abstract

Baseflow to rivers comprises regional groundwater and lower salinity intermediate water stores such as interflow, soil water, and bank return flows. Chemical mass balance (CMB) calculations based on the specific conductivity (SC) of rivers potentially estimates the groundwater contribution to baseflow. This study discusses

- 5 the application of the CMB approach in rivers from southeast Australia and assesses the feasibility of calibrating recursive digital filters (RDF) and sliding minima (SM) techniques based on streamflow data to estimate groundwater inflows. The common strategy of assigning the SC of groundwater inflows based on the highest annual river SC may not always be valid due to the long-term presence of lower salinity intermediate waters. Rather, using the river SC from low flow periods during drought years may be more realistic. If that is the case,
- 10 the estimated groundwater inflows may be lower than expected, which has implications for assessing contaminant transport and the impacts of near-river groundwater extraction. Probably due to long-term variations in the proportion of groundwater in baseflow, the RDF and SM techniques cannot generally be calibrated using the CMB results to estimate annual baseflow proportions. Thus, it is not possible to extend the estimates of groundwater inflows using those methods, although in some catchments reasonable estimates of
- 15 groundwater inflows can be made from annual streamflows. Short-term variations in the composition of baseflow also leads to baseflow estimates made using the CMB method being far more irregular than expected. This study illustrates that estimating baseflow, especially groundwater inflows, is not straightforward.





1. Introduction

- Documenting the sources of water in rivers is required to understand catchment hydrology and to manage and protect water resources (Brunke and Gonser, 1997; Winter, 1999; Sophocleous, 2002; McCallum et al., 2010; Cranswick and Cook, 2015; Stoelzle et al., 2020). If rivers receive substantial groundwater inflows, the groundwater may be a source of contaminants (Bardsley et al., 2015; Crabit et al., 2016) and streamflow may be significantly reduced if near-river groundwater extraction occurs (Gleeson and Richter, 2018). These impacts potentially adversely affect the utility of surface water resources and the riverine ecosystems. Understanding
- 25 the water sources in rivers is also important for flood forecasting and assessing impacts of climate or landuse change. While it is well understood that rivers interact with several catchment water stores (e.g. groundwater, soil water, shallow perched riparian water, and water temporarily stored in the riverbanks: McCallum et al., 2010; Cranswick and Cook, 2015; Rhodes et al., 2017; Cartwright et al., 2018; Cartwright and Irvine, 2020) understanding those interactions is difficult.
- 30 Streamflow may be broadly divided into quickflow and baseflow (Hall, 1968; Nathan and McMahon, 1990; Tallaksen, 1995; Yu and Schwartz, 1999; Eckhardt, 2005). Quickflow (also sometimes referred to as storm flow or surface runoff) largely represents water derived from precipitation that that contributes to streamflow soon after rainfall events. Baseflow represents water stored in the catchment that contributes to streamflow between precipitation events. Regional groundwater may be a significant component of baseflow in gaining rivers;
- 35 however, displaced soil water, interflow, bank return flows, snow melt, and/or water stored in floodplain pools can also be important (McCallum et al., 2010; Cranswick and Cook, 2015; Rhodes et al., 2017; Cartwright and Irvine, 2020; Stoelzle et al., 2020). Some of these components of baseflow (e.g., bank return waters and interflow) represent relatively recent rainfall whereas others, notably the regional groundwater, are generally much older. The composition of baseflow may differ seasonally or between wet and dry years.
- 40 Long-term (years to decades), sub-daily to daily measurements of streamflow (hydrographs) are available for many rivers globally. Giver their ubiquity, numerous techniques (e.g., graphical separation based on minimum discharge, rainfall-runoff models, and recursive digital filters) have been used to estimate baseflow from streamflow (e.g., Nathan and McMahon, 1990; Gustard et al., 1992; Eckhardt, 2005; Brodie et al., 2007; Aksoy





et al., 2008; Stoelzle et al., 2020). Groundwater and surface runoff generally have contrasting geochemistry,

- 45 which allows baseflow to be estimated by geochemical mass balance. Most geochemical parameters (such as major ions, stable and radioactive isotopes, dissolved gases, or nutrients) are not amenable to long-term autonomous measurements, meaning that their use is largely confined to short-term studies such as separating water sources over individual hydrograph peaks. Specific conductivity (SC) can, however, be readily measured at similar frequencies and timescales to streamflow and many rivers have both long-term SC and streamflow
- 50 data (Yu and Schwartz, 1999; Gonzales et al., 2009; Sanford et al., 2011; Miller et al., 2014, 2015, 2016; Cartwright et al., 2014; Rumsey et al., 2015; Hagedorn, 2020; Cartwright and Miller, 2021). While SC only provides a general indication of water geochemistry, it is a valuable parameter to estimate baseflow, especially in catchments where groundwater is saline.

Baseflow calculations based on river hydrographs commonly group all delayed waters into the baseflow

- 55 component (Nathan and McMahon, 1990). By contrast, because many near-river intermediate water stores (e.g., interflow, bank storage water, and water stored in floodplain pools) are less saline than regional groundwater, chemical mass balance (CMB) calculations are commonly assumed to reflect mainly groundwater inflows (Gonzales et al., 2009, Miller et al., 2014, 2015, 2016, Rumsey et al., 2015; Hagedorn, 2020); although the input of saline near-surface waters may also occur at the onset of high flows after prolonged dry periods. These
- 60 differences result in estimates of baseflow from CMB generally being lower than those based on analysis of river hydrographs (Cartwright et al., 2014; Lott and Stewart, 2016; Rammal et al., 2018; Saraiva Okello et al., 2018; Chen and Teegavarapu, 2019; Hagedorn, 2020). Some studies (e.g. Cartwright et al., 2014) used those differences to partition streamflow into groundwater inflows, intermediate stores, and surface runoff. Other studies (e.g., Stewart et al., 2007; Gonzales et al., 2009; Zhang et al., 2013; Rammal et al., 2018; Saraiva Okello
- 65 et al., 2018) have used the CMB to parameterise the recursive digital filters (RDF) and sliding minima (SM) techniques in order to use those to estimate groundwater inflows. Given that the different techniques have different errors and assumptions, this may be problematic (Yang et al., 2021). However, from a pragmatic viewpoint of extending estimates of groundwater inflows to time periods where there is no SC data or to similar catchments, such parameterisation efforts are valuable.



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70 **1.1. Conceptualisation of baseflow**

Baseflow is commonly conceived of as varying as shown in Figure 1. Total baseflow inflows are lower than surface runoff and the deeper catchment stores that contribute to baseflow, such as groundwater, are assumed to have longer wavelength and lower amplitude variations than the shallower intermediate stores. There is also a difference in the frequency that the different sources of baseflow are considered to be important. Groundwater inflows are generally considered be the dominant source of streamflow only during low summer flows, whereas the streams may be sustained mainly by baseflow from the combined catchment stores during low flow periods

throughout the year (Fig. 1).



Fig. 1. Conceptualisation of baseflow. Over the water year, baseflow may dominate streamflows during
successive low flow periods; however, groundwater inflows may be dominant only during low summer flows.
Both the groundwater inflows and total baseflow are conceived to vary smoothly.

Baseflow separation techniques based on streamflow data are based on this conceptualisation. Recursive digital filters separate smooth longer wavelength baseflow inputs from shorter wavelength quickflow (Nathan and McMahon, 1990; Chapman, 1999; Eckhardt, 2005). Likewise, graphical baseflow separation techniques consider that baseflow varies in a regular manner between periods of low discharge (Gustard et al., 1992; Aksoy et al., 2008; Stoelzle et al., 2020). By considering the time period over which different sources of baseflow may be the dominant source of river water, the sliding minimum technique has been adapted to separate the different

components of baseflow (Stoelzle et al., 2020). The variation of baseflow in Fig. 1 is consistent with our broader understanding of hydrogeology. Recharge generally occurs at slower rates than runoff and groundwater

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90 elevations change more slowly than river levels. The timescales that floodplain pools or riverbanks fill and drain are shorter than those over which groundwater responds but again are longer than the streamflow response.

Hydrograph separations carried out over individual discrete flow events using major ions, stable isotopes, and/or radioisotopes (Sklash and Farvolden, 1979; Uhlenbrook et al., 2002; Klaus and McDonnell, 2013; Tweed et al., 2016) also commonly conclude that baseflow varies smoothly over flow events. Many of those detailed studies

95 are from relatively small headwater catchments and it is less clear whether baseflow in larger rivers varies in a similar regular manner. Larger rivers aggregate water from numerous subcatchments, each of which may have a different contribution of baseflow at any given time. For example, bank storage waters may continue to contribute to some parts of catchments for many months but cease relatively quickly in other areas (McCallum et al., 2010; Cartwright and Irvine, 2020). Additionally, the discharge rate of groundwater depends on the

100 hydraulic gradient between the groundwater and the river which is likely to vary both temporally and spatially.

1.2. Objectives

This paper discusses some of the issues involved in estimating baseflow using streamflow and SC data. Firstly, it assesses how frequently rivers are fed predominantly by groundwater. Resolving this question is important for carrying out CMB calculations, especially understanding the length of the SC record that is required.

- 105 Secondly, it discusses whether CMB technique can be used to calibrate streamflow-based techniques to provide similar annual baseflow estimates. If this is feasible, it would permit groundwater inflows to be estimated at times or locations where SC data is not available. Finally, it assesses if groundwater inflows vary smoothly over both short (weeks to months) and longer (years to decades) timeframes. These questions are addressed using long-term streamflow and SC data from several perennial and intermittent rivers in Victoria (southeast
- 110 Australia). The results of this study are important for a broader understanding of how the quantity and composition of baseflow varies over time.





2. Materials and Methods

2.1. Data sources

The study uses data from gauging stations in the Barwon, Corangamite, Loddon and Goulburn catchments,

- 115 details of which are presented in the Supplement. The catchments upstream of the gauges have areas ranging from 5 to 2850 km². The Barwon, Corangamite, and Loddon catchments contain a range of intermittent to near-perennial relatively saline rivers while the Goulburn catchment contains rivers with lower salinities (Table 1). None of the chosen stations are impacted by major water storages or by near-river groundwater extraction. Daily mean streamflow (m³ sec⁻¹) and mean SC (electrical conductivity referenced to 25 °C in µS cm⁻¹) are from the
- 120 Department of Environment, Land, Water and Planning (2021). These two parameters are measured at identical locations and times, and the daily values represent the arithmetic means of measurements made at intervals of 15 minutes to four hours. The length of time over which continuous SC data have been measured varies; however, many stations have records between 1994 and 2020 and that period was adopted in this study. Streams in southeast Victoria record low flows over the austral summer to autumn (typically January to April). For this
- 125 study the water year was defined as commencing in September, which is when the peak flows occur. Previous studies in southeast Australia (Cartwright et al., 2014; Cartwright and Miller, 2021) used July as the start of the water year; however, some intermittent streams in the Loddon catchment have relatively high SC values in June and July. If the July date was retained, the calculated SC of baseflow in successive water years would occasionally be from the same flow period. Rainfall data is from the Bureau of Meteorology (2021). Correlations
- 130 are designated as being good with R² values ≥ 0.7 , moderate where $0.5 \ge R^2 < 0.7$, and poor where $R^2 < 0.5$.

2.2. Chemical mass balance

Baseflow (assumed to be mainly saline groundwater inflows) on day i (b_i in m³ sec⁻¹) was calculated from:

$$b_i = q_i \frac{s_{C_r} - s_{C_s}}{s_{C_b} - s_{C_s}} \tag{1}$$

(Yu and Schwartz, 1999), where SC_r , SC_b , and SC_s are the SC values of the river, baseflow, and surface runoff, 135 respectively. This method requires that: 1) SC_s and SC_b are well defined; 2) SC behaves conservatively; and 3)

there is a large contrast between SCr and SCb. The salinity of groundwater in these catchments is generally

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several orders of magnitude higher than that of rainfall (Supplement). Reactive species (e.g. NO_3^- or HCO_3^-) do contribute to SC; however, there is a robust correlation (R^2 values typically >0.95) between SC values and the concentration of conservative ions such as Cl in both groundwater and surface water (Cartwright et al., 2013,

- 140 2014, 2017). Initially a value of SC_s of 50 μ S cm⁻¹ was adopted, which corresponds to the lowest SC_r recorded at high streamflows in these catchments over the study period. SC_b . is based on the SC of the river during low flows using two methods for estimating SC_b were used. Firstly, daily SC_b values were estimated by interpolating between high SC_r values in successive water years (the *Variable SC* approach), which assumes that the river is entirely fed by groundwater each year during low flows (as in Fig. 1). Adopting the highest SC_r value as SC_b
- 145 risks outlier values caused by the flushing of solutes after prolonged dry spells being used (Miller et al., 2014), which results in b_i being underestimated. To overcome that potential problem, SC_b was assigned as the 99th percentile of SC_r (Miller et al., 2014, 2016; Rumsey et al., 2015). For the second set of calculations, baseflow was calculated using the highest annual SC_b from the variable SC calculations (the *Constant SC* approach). This may be a valid assumption if the SC of groundwater is relatively constant and the rivers are entirely fed by
- 150 groundwater only during low flow periods in drought years (with bank return waters and/or interflow providing some input at other times). The use of 99th percentiles and interpolation results in a small number of days where b_i calculated using Eq. (1) exceeds q_i; for these, b_i was set to q_i.

Baseflow and the baseflow index (BFI = $\sum b_i / \sum q_i$) for the individual water years and the entire records were calculated from the daily values. Periods of zero flow are distinguishable from missing data and these are

- 155 included ($q_i = 0$, $b_i = 0$ on those days). Some of the gauges record high SC_r values in zero flow periods, presumably from evaporated stagnant water at the gauge. These SC_r values are not considered in the calculation of SC_b. The streamflow records for most sites are near complete (>99%) and small (<5 day) gaps in streamflow were estimated by linear interpolation. As with streamflow, short gaps (<5 days) in SC_r were infilled by linear interpolation. For longer gaps, b_a was adjusted for the actual number of days of data (i.e. in a year with SC data
- 160 on 95% of the days $b_a = \sum b_i / 0.95$). To avoid excessive errors from missing data, only results for years where both SC and streamflow data (including zero flows) were recorded on >90% of the days prior to infilling of any gaps are reported.





2.3. Estimates of baseflow based on streamflow

Baseflow separation based on the Institute of Hydrology sliding minimum streamflow method (SM) (Gustard et al., 1992) as implemented in the USGS Groundwater toolbox (Barlow et al., 2017) was used with the streamflow data. Comprehensive descriptions of this method are provided by Gustard et al. (1992), Hisdal et al. (2004), Brodie et al. (2007), Aksoy et al. (2008), and Barlow et al. (2017). This method identifies significant streamflow minima that are plausibly where baseflow constitutes the total flow and interpolates baseflow between those minima. The factor (f) used to identify the minima or turning points in streamflow was set at 0.9

- 170 (which is the value generally used with this method). The minimum discharge is assessed over non-overlapping time periods (commonly referred to as the block size, N). Increasing N increases the spacing of the periods that the stream is assumed to be only fed by baseflow, which decreases the calculated BFI (Stewart et al., 2007; Stoelzle et al., 2020). N is commonly scaled to catchment size (Aksoy et al., 2008), although Stoelzle et al. (2020) used breakpoints in N vs. BFI trends to define N values for different baseflow components. Here the
- 175 approach of Stewart et al. (2007), which estimates N by bringing the BFI from this method into agreement with the BFI from the CMB method, is used. N is an integer and the value that produced the closest agreement was adopted. The BFI is significantly more sensitive to the value of N than f (Aksoy et al., 2008) and variations in f were not considered. As above only results for years where flow data was recorded on >90% of days prior to infilling are reported
- 180 The recursive digital filter:

$$b_{i} = \frac{(1 - BFI_{max})ab_{i-1} + (1 - a)BFI_{max}}{1 - aBFI_{max}}q_{i}$$
(2)

(Eckhardt, 2005) was also used to estimate baseflow. In Eq. (2), a is the recession constant that is estimated from the recession limbs of the hydrograph. Analysis of several hydrographs following Nathan and McMahon (1990) and Eckhardt (2005) indicate that a is typically ~0.93 and that value was adopted for all sites. BFI_{max} is the maximum value of the baseflow index that can be calculated using the filter. While BFI_{max} is commonly assigned using catchment characteristics, here the value of BFI_{max} that produces the same BFI as the CMB is

used, which is similar to the approach of Gonzales et al. (2009) and Saraiva Okello et al. (2018). The filter was





applied in a single pass with the condition that $b_i \le q_i$. Again, only results for years where flow data was recorded on >90% of the days are reported.

190 **3. Results**

3.1. Variation in streamflow and specific conductivity

Figure 2 shows the temporal variation of streamflow and SC records for one site in each catchment; the records for the other sites are similar. The main Barwon River sites are near perennial; however, some of the Barwon tributaries have more significant cease-to-flow periods with up to 59% of days of zero streamflow (Table 1).



Fig. 2a. Variations in rainfall (monthly running mean) in southeast Australia (data from Barwon Catchment, station 90008: Bureau of Meteorology, 2021). **2b-2e**. Variation in streamflow (Q) and SC for one station in the Barwon, Corangamite, Goulburn, and Loddon catchments (data from Department of Environment, Land, Water and Planning, 2021). SC_b is the SC of baseflow calculated by interpolation between annual maximum values.

200 The overall percentage of zero streamflow days in the other catchments are Corangamite 0-17%, Goulburn 64-33%, and Loddon 1-46%. SC_r values are highest in the late summers when streamflow is lowest. However, the maximum SC_r commonly varies between years. SC_r values are generally higher in years of low rainfall when total streamflows are lowest. This variability is also evident in the SC_r variations with streamflow (Fig 3). While





there are broad inverse correlations between SCr and streamflow, there is a wide range of SCr values at the lower

205 streamflows that reflects the year-on-year variability in stream salinity.



Fig. 3. Variation in streamflow (Q) and river SC for one station in the Barwon (3a), Corangamite (3b), Goulburn (3c), and Loddon (3d) catchments (data from Department of Environment, Land, Water and Planning, 2021).

3.2. Chemical mass balance estimates of baseflow

- 210 Values of BFI calculated using Eq. (1) and the two strategies for estimating SC_b are shown in Figs 4 and S1-S4 and Table 1. Total BFI calculated using the variable SC_b approach are higher (0.13-0.50) than those calculated using the constant SC_b value (0.04-0.37) and year BFI values are also higher. There is no *a priori* reason for assuming that rivers, even in relatively dry climates, are sustained wholly by groundwater inflows during low flows every year. Previous geochemical studies indicate that bank return flows are important in the Barwon
- 215 catchment (Cartwright et al., 2014; Howcroft et al., 2019) and they are likely to occur in most rivers (McCallum et al., 2010; Cranswick and Cook, 2015; Rhodes et al., 2017). Using a constant SC_b produces more regular yearly BFI vs. yearly streamflow trends (Figs 4, S1-S4; Table 1). Additionally, the constant SC_b value results in a better correlation of total and yearly BFI values from different sites in the same catchments. Sites on the same river (such as those in the Barwon catchment) would be expected to have similar yearly BFI values or





220 total BFI values that showed a coherent trend (e.g. systematically increasing or decreasing downstream). This is the case where a constant SC_b value is adopted but not where SC_b varies annually (Table 2).

There are several other uncertainties in these calculations. Given the high salinity of the baseflow in these catchments, BFI is relatively insensitive to SC_s . Allowing SC_s to vary between 25 and 75 μ S cm⁻¹ results in an uncertainty of total BFI of <5% and does not change the correlations. Uncertainties in SC_r values resulting from

225 logger errors is probably less than that of streamflow. For example, most high-quality commercial SC loggers quote a precision of <1%, whereas the precision of streamflow in southeast Australia largely resulting from errors in the rating curves was estimated as typically \pm 5% (McMahon and Peel, 2019). These uncertainties are difficult to assess but they do not significantly impact the BFI estimates.



Fig. 4. Variation in streamflow (Q) and river BFI calculated from CMB using the variable and constant SC calculations of SC_b for one station in the Barwon (**4a**), Corangamite (**4b**), Goulburn (**4c**), and Loddon (**4d**) catchments. Lines are power law fits with R^2 values indicated.





3.3. Baseflow estimates from streamflow variations

- As noted above, estimates of baseflow made using techniques based on streamflow data using default 235 parameters would be higher than those resulting from CMB, largely due to the presence of low SC intermittent waters in the baseflow component. Adjusting the SM technique by varying N in Eq. (2) and the RDF by varying BFI_{max} in Eq. (3) allows the BFI from these methods to be brought into agreement with those calculated using the CMB (Table 1). Despite the long-term BFI values being brought into agreement, the annual BFI values between the three techniques are commonly poorly correlated (Figs 5, S5-S8; Table 1). This lack of correlation
- 240 is apparent regardless of which strategy is adopted to calculate SC_b. There is little difference in the degree of disagreement at high or low BFI values (Figs 5, S5-S8), which precludes systematic differences in behaviour between low streamflow years that have generally higher BFI values and high streamflow years with lower BFI values. There is no significant difference in the correlation of BFI values and area, percentage flow, or the range of SC_r values (which precludes the possibility that groundwater inflows may be easier to calculate in more saline rivers).







Fig. 5. Comparison BFI calculated from the RDF and SM methods with the BFI from CMB using the variable and constant SC calculations of SC_b for one station in the Barwon (4a), Corangamite (5b), Goulburn (5c), and Loddon (5d) catchments. Dashed lines are the 1:1 relationship.

250 4. Discussion

The Victorian rivers used in this study have long and near complete records of SC and streamflow records and occur in regions where groundwater is commonly saline. This makes them ideal for assessing the CMB technique and comparing this with other methods of estimating baseflow.

4.1. Quantifying baseflow using chemical mass balance

255 The SC_r of these rivers are higher during low flow periods in low rainfall years compared with low flow periods in years of higher rainfall (Fig. 2). Rivers elsewhere show similar inverse correlations between annual SC values and rainfall (Hagedorn, 2020). The net SC of groundwater inflows may vary over time if groundwater from different parts of the catchment contributes differently to streamflow. However, given that bank storage waters





may contribute to streamflow for months or years and may only drain after several years of low flows
(McCallum et al., 2010; Cranswick and Cook, 2015; Cartwright and Irvine, 2020), it is more likely that regional groundwater only dominates baseflow during prolonged (multi-year) drier periods. If that is the case, there are several implications for quantifying groundwater contributions to rivers. Firstly, BFI estimates made using the variable SC_b approach may overestimate the groundwater contribution (Fig. 4, Table 1). Additionally, where SC_r is well correlated with streamflow, sporadically-measured SC values could be used to estimate groundwater inflows from the streamflow records (Miller et al., 2015). However, in the catchments discussed here, the year-on-year differences in stream salinity produces a broad range of SC_r values at any given streamflow which precludes that approach. Finally, river SC records need to include the dryer years to successfully apply the CMB method. The constant SC_b approach assumes that the SC groundwater is unvarying, which may also be an oversimplification. Adopting a hybrid approach that interpolated between the SC_r values in low flow years

would yields BFI estimates between the two sets of calculations. While this may be a more realistic model, it involves a significant amount of additional judgement in assigning SC_b values.

4.2. Short-term variations in baseflow

The RDF and SM techniques produce smoothly varying baseflow inputs (Fig. 6) that conform to our perceptions of how baseflow should vary (Fig. 1). This is the case both where these methods are used with their default 275 settings or where they have been modified to extract estimates of long-term baseflow or groundwater inputs (as in this study). By contrast, SC_r values in southeast Australian streams vary considerably over days to weeks (Cartwright and Miller, 2021) and this results in an irregular baseflow signal from the CMB method (Fig. 6). Similar irregular SC_r variations and baseflow signals occur elsewhere (Hagedorn, 2020; Yang et al., 2021) and most probably reflect variations in the baseflow components. The contribution of bank return waters, waters

280 draining from the floodplain, and interflow will vary in importance in different parts of the catchment over different timescales. Changes to the relative elevations of the water table and the rivers are likely to also be spatially variable. This variability in catchment processes potentially leads to the composition of baseflow being highly variable over short timescales. Whether the total baseflow input is relatively smooth and the variation in SC_r reflects the composition of baseflow or whether there are short-term variations in total baseflow is not





285 constrained by these data. The physical response of streamflow to rainfall (celerity) is commonly decoupled from the flow of water and solutes stored within catchments (McDonnell and Beven, 2014). It may be more realistic to conceive of the smooth baseflow variations as the physical response of the catchment rather than reflecting the input of water from specific stores.



290 **Fig. 6.** Baseflow fluxes estimated from the CMB and calibrated RDF and SM methods for a six-month period from gauging station 234201 in the Corangamite catchment.

4.3. Calibration of baseflow methods

Because long-term SC_r records are less common than streamflow records, the CMB method is sometimes used to calibrate other techniques to extend the estimates of groundwater inflows to times when SC data are not available or to similar catchments (Stewart et al., 2007; Gonzales et al., 2009; Saraiva Okello et al., 2018; Hagedorn, 2020). Yang et al. (2021) highlighted that different biases in the RDF and CMB techniques introduced problems for cross calibration. However, from a pragmatic viewpoint, such calibrations would be valuable if they were possible. In the catchments studied here, calibrating the RDF and SM techniques using the long-term BFI estimates from the CMB proved unsuccessful in estimating annual baseflow. This again

300 probably results from some of the intermediate stores of water (especially bank storage) contributing to streamflow over months to years. Additionally, yearly to decadal variations in groundwater recharge may result in long-term variations in the proportion of groundwater in the baseflow component and its salinity. This is certainly the case in southeast Australia where groundwater heads have not yet recovered following the prolonged droughts between 1996 and 2010 (Chen et al., 2016; Department of Environment, Land, Water and





305 Planning, 2021). In this study, the constant SC_b approach yields reasonable correlations between annual BFI and annual streamflow in some catchments (Figs 4, S1-S4; Table 1) that may be used to extend the baseflow estimates to periods when SC data are not available.

5. Conclusions

This study demonstrates some of the complexities in estimating baseflow. In particular, these rivers may only

- 310 be entirely fed by groundwater in dry years. Assuming that the rivers are sustained by groundwater at low flows each year or analysing only a few years of data from high rainfall periods may result in groundwater inflows being overestimated using the CMB method, which has implications for assessing inflows of contaminated groundwater or the impacts of near-river groundwater extraction on streams. Long-term variability and spatial heterogeneity in groundwater inflows also severely complicates efforts to calibrate hydrograph-based
- 315 techniques using the CMB method. The CMB calculations imply that groundwater input is irregular over short timescales (days to months); however, whether baseflow as whole varies smoothly is not clear. Understanding whether that is the case is important as separation techniques based on streamflow data assume a relatively smooth variation in baseflow. Detailed multi component geochemical studies in larger rivers that can separate different sources of water may help resolve this question.

320 6. Data Availability

All data is freely available from the Department of Environment, Land, Water and Planning Water Measurement site https://data.water.vic.gov.au/

7. Competing Interests

The author declares that he has no conflict of interest.

325 References

Aksoy, H., Unal, N.E., and Pektas, A.O.: Smoothed minima baseflow separation tool for perennial and intermittent streams, Hydrological Processes, 22, 4467-4476, 2008. https://doi.org/10.1002/hyp.7077

Bardsley, A.I., Hammond, D.E., Von Bitner, T., Buenning, N.H., and Townsend-Small, A.: Shallow Groundwater Conveyance of Geologically Derived Contaminants to Urban Creeks in Southern California,
Environmental Science and Technology, 49, 9610-9619, 2015. https://doi.org/10.1021/acs.est.5b01006





Barlow, P.M., Cunningham, W.L., Zhai, T., and Gray, M., 2017, U.S. Geological Survey Groundwater Toolbox version 1.3.1, a graphical and mapping interface for analysis of hydrologic data: U.S. Geological Survey Software Release, 26 May 2017, https://doi.org/10.5066/F7R78C9G

Brodie, R., Sundaram, B., Tottenham, R., Hostetler, S., and Ransley, T.: An overview of tools for assessing groundwater-surface water connectivity, Bureau of Rural Sciences, Canberra, 133 p., 2007.

Brunke, M., and Gonser, T.: The ecological significance of exchange processes between rivers and groundwater, Freshwater Biology, 37, 1-33, 1997. https://doi.org/10.1046/j.1365-2427.1997.00143.x

Bureau of Meteorology, 2021. Commonwealth of Australia Bureau of Meteorology climate data online. http://www.bom.gov.au/climate/data/. Accessed July 10, 2021

340 Cartwright, I., and Irvine, D.: The spatial extent and timescales of bank infiltration and return flows in an upland river system: Implications for water quality and volumes, Science of the Total Environment, 743, 140748, 2020. https://doi.org/10.1016/j.scitotenv.2020.140748

Cartwright, I., and Miller, M. P.: Temporal and spatial variations in river specific conductivity: Implications for understanding sources of river water and hydrograph separations, Journal of Hydrology, 593, 125895, 2021.
 https://doi.org/10.1016/j.jhydrol.2020.125895.

Cartwright, I., Atkinson, A.P., Gilfedder, B.S., Hofmann, H., Cendón, D.I., and Morgenstern, U.: Using geochemistry to understand water sources and transit times in headwater streams of a temperate rainforest, Applied Geochemistry, 99, 1-12, 2018. https://doi.org/10.1016/j.apgeochem.2018.10.018

Cartwright, I., Gilfedder, B., and Hofmann, H.: Transient hydrological conditions implied by chloride mass 350 balance in southeast Australian rivers, Chemical Geology, 357, 29-40, 2013. https://doi.org/10.1016/j.chemgeo.2013.08.028

Cartwright, I., Gilfedder, B., and Hofmann, H.: Contrasts between estimates of baseflow help discern multiple sources of water contributing to rivers, Hydrology and Earth System Sciences, 18, 15-30, 2014. https://doi.org/10.5194/hess-18-15-2014

355 Cartwright, I., Hofmann, H., Currell, M.J., and Fifield, L.K.: Decoupling of solutes and water in regional groundwater systems: The Murray Basin, Australia, Chemical Geology, 466, 466-478, 2017. https://doi.org/10.1016/j.chemgeo.2017.06.035

Chapman, T.: A comparison of algorithms for stream flow recession and baseflow separation, Hydrological Processes, 13, 701-714, 1999. https://doi.org/10.1002/(SICI)1099-1085(19990415)13:5<701::AID-360 HYP774>3.0.CO;2-2

Chen, H., and Teegavarapu, R.S.V.: Comparative Analysis of Four Baseflow Separation Methods in the South Atlantic-Gulf Region of the U.S., Water (Switzerland), 12, 12010120, 2019. https://doi.org/10.3390/w12010120

 Chen, J.L., Wilson, C.R., Tapley, B.D., Scanlon, B., and Güntner, A.: Long-term groundwater storage change in Victoria, Australia from satellite gravity and in situ observations, Global and Planetary Change, 139, 56-65, 2016. https://doi.org/10.1016/j.gloplacha.2016.01.002

Crabit, A., Cattan, P., Colin, F., and Voltz, M.: Soil and river contamination patterns of chlordecone in a tropical volcanic catchment in the French West Indies (Guadeloupe), Environmental Pollution, 212, 615-626, 2016. https://doi.org/10.1016/j.envpol.2016.02.055





Cranswick, R.H., and Cook, P.G.: Scales and magnitude of hyporheic, river-aquifer and bank storage exchange fluxes, Hydrological Processes, 29, 3084-3097, 2015. https://doi.org/10.1002/hyp.10421

Department of Environment Land Water and Planning, 2021. State Government Victoria, Department of Environment, Land, Water and Planning, Water Monitoring. https://data.water.vic.gov.au/. Accessed July 20, 2021.

Eckhardt, K.: How to construct recursive digital filters for baseflow separation, Hydrological Processes, 19, 507-515, 2005. https://doi.org/10.1002/hyp.5675

Gleeson, T., and Richter, B.: How much groundwater can we pump and protect environmental flows through time? Presumptive standards for conjunctive management of aquifers and rivers, River Research and Applications, 34, 83-92, 2018. https://doi.org/10.1002/rra.3185

Gonzales, A.L., Nonner, J., Heijkers, J., and Uhlenbrook, S.: Comparison of different base flow separation methods in a lowland catchment, Hydrology and Earth System Sciences, 13, 2055-2068, 2009. https://doi.org/10.5194/hess-13-2055-2009

Gustard, A., Bullock, A., and Dixon, J. M.: Low flow estimation in the United Kingdom, Institutute of Hydrology, Wallingford, UK. 108, 88, 1992.

Hagedorn, B.: Hydrograph separation through multi objective optimization: Revealing the importance of a temporally and spatially constrained baseflow solute source, Journal of Hydrology, 590, 125349, 2020. https://doi.org/10.1016/j.jhydrol.2020.125349

Hall, F. R.: Baseflow Recessions - A Review, Water Resources Research, 4, 973-983, 1968. https://doi.org/10.1029/WR004i005p00973

Hisdal, H., Tallaksen, L., Clausen, B., Peters, E., and Gustard, A.: Hydrological Drought Characteristics, in:
Hydrological Drought Processes and Estimation Methods for Streamflow and Groundwater, vol. 48, edited by:
Tallaksen, L. M. and van Lanen, H. A. J., Elsevier B.V., the Netherlands, 139–198, 2004.

Howcroft, W., Cartwright, I., and Cendón, D.I.: Residence times of bank storage and return flows and the influence on river water chemistry in the upper Barwon River, Australia, Applied Geochemistry, 101, 31-41, 2019. https://doi.org/10.1016/j.apgeochem.2018.12.026

395 Klaus, J., and McDonnell, J.J.: Hydrograph separation using stable isotopes: Review and evaluation, Journal of Hydrology, 505, 47-64, 2013. https://doi.org/10.1016/j.jhydrol.2013.09.006

Lott, D. A., and Stewart, M.T.: Base flow separation: A comparison of analytical and mass balance methods, Journal of Hydrology, 535, 525-533, 2016. https://doi.org/10.1016/j.jhydrol.2016.01.063

McCallum, J.L., Cook, P.G., Brunner, P., and Berhane, D.: Solute dynamics during bank storage flows and 400 implications for chemical base flow separation, Water Resources Research, 46 2010. https://doi.org/10.1029/2009WR008539

McDonnell, J.J., and Beven, K.: Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities and residence time distributions of the headwater hydrograph, Water Resources Research, 50, 5342-5350, 2014. https://doi.org/10.1002/2013WR015141

405 McMahon, T.A., and Peel, M.C.: Uncertainty in stage–discharge rating curves: application to Australian Hydrologic Reference Stations data, Hydrological Sciences Journal, 64, 255-275, 2019. https://doi.org/10.1080/02626667.2019.1577555





Miller, M.P., Johnson, H.M., Susong, D.D., and Wolock, D.M.: A new approach for continuous estimation of baseflow using discrete water quality data: Method description and comparison with baseflow estimates from 410 two existing approaches, Journal of Hydrology, 522, 203-210, 2015. https://doi.org/10.1016/j.jhydrol.2014.12.039

Miller, M.P., Susong, D.D., Shope, C.L., Heilweil, V.M., and Stolp, B.J.: Continuous estimation of baseflow in snowmelt-dominated streams and rivers in the Upper Colorado River Basin: A chemical hydrograph separation approach, Water Resources Research, 50, 6986–6999, 2014. https://doi.org/10.1002/2013WR014939

415 Miller, M.P., Tesoriero, A.J., Capel, P.D., Pellerin, B.A., Hyer, K.E., and Burns, D.A.: Quantifying watershedscale groundwater loading and in-stream fate of nitrate using high-frequency water quality data, Water Resources Research, 52, 330-347, 2016. https://doi.org/10.1002/2015WR017753

Nathan, R.J., and McMahon, T.A.: Evaluation of automated techniques for base flow and recession analyses. Water Resources Research, 26, 1465-1473, 1990. https://doi.org/10.1029/WR026i007p01465

420 Rammal, M., Archambeau, P., Erpicum, S., Orban, P., Brouyère, S., Pirotton, M., and Dewals, B.: Technical Note: An Operational Implementation of Recursive Digital Filter for Base Flow Separation, Water Resources Research, 54, 8528-8540, 2018. https://doi.org/10.1029/2018WR023351

Rhodes, K.A., Proffitt, T., Rowley, T., Knappett, P.S., Montiel, D., Dimova, N., Miller, G.R.: The importance of bank storage in supplying baseflow to rivers flowing through compartmentalized, alluvial aquifers. Water
Resources Research, 53, 10539–10557, 2017, https://doi.org/10.1002/2017WR021619.

Riis, T., Kelly-Quinn, M., Aguiar, F.Rumsey, C.A., Miller, M.P., Susong, D.D., Tillman, F.D., and Anning, D.W.: Regional scale estimates of baseflow and factors influencing baseflow in the Upper Colorado River Basin, Journal of Hydrology: Regional Studies, 4, 91-107, 2015. https://doi.org/10.1016/j.ejrh.2015.04.008

 Rumsey, C.A., Miller, M.P., Schwarz, G.E., Hirsch, R.M., and Susong, D.D.: The role of baseflow in dissolved
 solids delivery to streams in the Upper Colorado River Basin, Hydrological Processes, 31, 4705–4718, 2017. https://doi.org/10.1002/hyp.11390

Sanford, W.E., Nelms, D.L., Pope, J.P., and Selnick, D.L.: Quantifying components of the hydrologic cycle in Virginia using chemical hydrograph separation and multiple regression analysis, US Geological Survey Scientific Investigations Report, 5198, 152, 2011.

435 Saraiva Okello, A.M.L., Uhlenbrook, S., Jewitt, G.P.W., Masih, I., Riddell, E.S., and Van der Zaag, P.: Hydrograph separation using tracers and digital filters to quantify runoff components in a semi-arid mesoscale catchment, Hydrological Processes, 32, 1334-1350, 2018. https://doi.org/10.1002/hyp.11491

Sklash, M.G., and Farvolden, R.N.: The role of groundwater in storm runoff, Journal of Hydrology, 43, 45-65, 1979. https://doi.org/10.1016/S0167-5648(09)70009-7

440 Sophocleous, M.: Interactions between groundwater and surface water: the state of the science, Hydrogeology Journal, 10, 52-67, 2002. https://doi.org/10.1007/s10040-001-0170-8

Stewart, M., Cimino, J., and Ross, M.: Calibration of Base Flow Separation Methods with Streamflow Conductivity, Groundwater, 45, 17-27, 2007. https://doi.org/10.1111/j.1745-6584.2006.00263.x

Stoelzle, M., Schuetz, T., Weiler, M., Stahl, K., and Tallaksen, L.M.: Beyond binary baseflow separation: a delayed-flow index for multiple streamflow contributions, Hydrology and Earth System Sciences, 24, 849-867, 2020. https://doi.org/10.5194/hess-24-849-2020





Tallaksen, L.M.: A review of baseflow recession analysis, Journal of Hydrology, 165, 349-370, 1995. https://doi.org/10.1016/0022-1694(94)02540-R

Tweed, S., Munksgaard, N., Marc, V., Rockett, N., Bass, A., Forsythe, A.J., Bird, M.I., and Leblanc, M.:
 Continuous monitoring of stream δ¹⁸O and δ²H and stormflow hydrograph separation using laser spectrometry in an agricultural catchment, Hydrological Processes, 30, 648-660, 2016. https://doi.org/10.1002/hyp.10689

Uhlenbrook, S., Frey, M., Leibundgut, C., and Maloszewski, P.: Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales, Water Resources Research, 38, 311-3114, 2002. https://doi.org/10.1029/2001WR000938

455 Winter, T.C.: Relation of streams, lakes, and wetlands to groundwater flow systems, Hydrogeology Journal, 7, 28-45, 1999. https://doi.org/10.1007/s100400050178

Yang, W., Xiao, C., Zhang, Z., and Liang, X.: Can the two-parameter recursive digital filter baseflow separation method really be calibrated by the conductivity mass balance method?, Hydrol. Earth Syst. Sci., 25, 1747-1760, 2021. https://doi.org/10.5194/hess-25-1747-2021

460 Yu, Z., and Schwartz, F.W.: Automated calibration applied to watershed-scale flow simulations, Hydrological Processes, 13, 191-209, 1999. https://doi.org/10.1002/(SICI)1099-1085(19990215)13:2<191::AID-HYP706>3.0.CO;2-N

Zhang, R., Li, Q., Chow, T.L., Li, S., and Danielescu, S.: Baseflow separation in a small watershed in New Brunswick, Canada, using a recursive digital filter calibrated with the conductivity mass balance method,
Hydrological Processes, 27, 2659-2665, 2013. https://doi.org/10.1002/hyp.9417





Tables

Table 1. Summary of baseflow estimates from southeast Australia.

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Station ^a	Area	%Flow	Max SC ^b	BFI ^c	BFI ^c	R ^{2 d}	R ^{2 d}	R ² e	R ² e	R ^{2 e}	R ² e
			µS cm ⁻¹	CMBc	CMBv	Q-	Q-	CMBc-	CMBv-	CMBc-	CMBv-
			•			CMBc	CMBv	SM	SM	RDF	RDF
Barwon Catchment											
233200	2713	100	3309	0.34 ^f	0.42	0.70	0.67	0.55	0.57	0.14	0.31
233201	1052	96	4740	0.17	0.32	0.65	0.18	0.11	0.10	0.01	0.07
233211	88	33	25762	0.11	0.15	0.76	0.78	0.13	0.03	0.00	0.05
233213	839	99	2475	0.37	0.50	0.79	0.71	0.73	0.55	0.44	0.60
233218	1269	95	11200	0.10	0.20	0.77	0.14	0.20	0.47	0.03	0.10
233223	57	50	7622	0.11	0.13	0.90	0.88	0.69	0.70	0.38	0.41
233224	593	98	3494	0.17	0.34	0.66	0.44	0.52	0.29	0.20	0.25
233247	864	97	4190	0.19	0.36	0.67	0.10	0.51	0.27	0.12	0.28
233250	5	41	12959	0.09	0.16	0.60	0.06	0.08	0.05	0.01	0.02
Corangar	nite Cat	chment									
234200	324	83	4547	0.22	0.26	0.93	0.89	0.65	0.72	0.31	0.14
234201	1158	100	11922	0.17	0.21	0.95	0.92	0.79	0.81	0.43	0.46
234209	45	86	7372	0.16	0.30	0.78	0.61	0.35	0.32	0.09	0.21
234212	231	99	21790	0.08	0.15	0.88	0.70	0.79	0.62	0.48	0.55
Goulburn	Catchn	nent									
405212	337	77	2370	0.15	0.37	0.81	0.48	0.10	0.25	0.02	0.00
405226	787	69	498	0.30	0.42	0.30	0.29	0.40	0.25	0.21	0.28
405240	609	70	1650	0.26	0.28	0.82	0.70	0.14	0.26	0.01	0.24
405246	164	36	690	0.21	0.43	0.53	0.31	0.04	0.01	0.00	0.00
Loddon Catchment											
407211	1850	74	16862	0.05	0.11	0.82	0.72	0.87	0.84	0.00	0.09
407239	137	56	2679	0.05	0.14	0.89	0.78	0.50	0.45	0.01	0.01
407252	2850	99	36918	0.13	0.25	0.69	0.18	0.01	0.05	0.00	0.26
407284	650	54	28667	0.04	0.13	0.31	0.01	0.11	0.05	0.12	0.52
407288	124	69	12507	0.13	0.18	0.86	0.41	0.23	0.08	0.29	0.01
407289	nm	98	1869	0.24	0.31	0.00	0.04	0.00	0.01	0.00	0.00

a: Department of Environment, Land, Water and Planning (2021)

b: Maximum SC over the monitoring period

c: BFI from the Constant (CMBc) and Variable (CMBv) CMB methods

475 d: Correlations between streamflow (Q) and BFI from the Constant (CMBc) and Variable (CMBv) CMB methods

e: Correlations of BFI between the Constant (CMBc) and Variable (CMBv) CMB methods and the RDF and SM methods calibrated to the BFI from the CMB

f: Normal type $R^2 < 0.5$, *italic* type $0.5 \ge R^2 < 0.7$, bold type $R^2 \ge 0.7$

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Single SC _b ^a						Variable	SC_b^a			
Station	223200	223201	223218	223244	223247	223200	223201	223218	223244	223247
Year										
1994-1995	0.53		0.13	0.19		0.64		0.37	0.35	
1995-1996	0.26		0.05	0.11	0.16	0.32		0.17	0.22	0.34
1996-1997	0.24		0.07	0.11	0.16	0.32		0.32	0.32	0.40
1997-1998	0.54		0.14	0.25	0.22	0.68		0.35	0.56	0.47
1998-1999	0.43		0.10	0.16		0.48	0.71	0.20	0.35	
1999-2000	0.58	0.25	0.19	0.28	0.26	0.61	0.31	0.32	0.62	0.53
2000-2001	0.31	0.16	0.09	0.19	0.16	0.36	0.28	0.13	0.34	0.28
2001-2002	0.33	0.17	0.08	0.17	0.18	0.40	0.38	0.17	0.31	0.29
2002-2003	0.49	0.22	0.13	0.23	0.25	0.54	0.36	0.27	0.44	0.48
2003-2004	0.38	0.20	0.10	0.23	0.21	0.41	0.38	0.21	0.43	0.45
2004-2005	0.34	0.16	0.09	0.16	0.18	0.42	0.55	0.24	0.34	0.46
2005-2006	0.45	0.24	0.14	0.24	0.24	0.62	0.35	0.31	0.52	0.59
2006-2007	0.58	0.21	0.14	0.22	0.23	0.69	0.17	0.17	0.39	0.32
2007-2008	0.33	0.17	0.08	0.14	0.19	0.37	0.34	0.09	0.32	0.20
2008-2009	0.53	0.27	0.15	0.28	0.24	0.65	0.47	0.29	0.56	0.38
2009-2010	0.41	0.23	0.12	0.24	0.24	0.54	0.23	0.26	0.44	0.45
2010-2011	0.26	0.18	0.09	0.17	0.18	0.30	0.34	0.19	0.33	0.25
2011-2012	0.33	0.15	0.09	0.16	0.16	0.43	0.27	0.20	0.33	0.31
2012-2013	0.28	0.16	0.07	0.16	0.18	0.38	0.33	0.12	0.35	0.29
2013-2014	0.31	0.16	0.08	0.18	0.17	0.39	0.41	0.13	0.39	0.37
2014-2015	0.39	0.20	0.12	0.23	0.23	0.51	0.33	0.25	0.36	0.45
2015-2016	0.51	0.26	0.19	0.31	0.26	0.59	0.18	0.25	0.35	0.38
2016-2017	0.39	0.18	0.08	0.18		0.49	0.23	0.10	0.23	
2017-2018	0.38	0.17	0.10	0.20		0.48	0.32	0.13	0.30	
2018-1019	0.38	0.20	0.11	0.23	0.24	0.45	0.56	0.15	0.35	0.40
2019-2020	0.33	0.17	0.11	0.23	0.25	0.46		0.24	0.50	0.55
R ^{2 b}		0.70	0.74	0.57	0.63		0.05	0.33	0.38	0.27

Table 2. Comparison of annual BFI estimates from the Barwon River.

a: CMB calculations using the single and variable SC values of baseflow b: Correlation of annual BFI with station 223200; normal type $R^2 < 0.5$, *italic* type $0.5 \ge R^2 < 0.7$, bold type R^2 485 ≥0.7