

Abstract

This study compares geochemical and physical methods of estimating baseflow in the upper reaches of the Barwon River, southeast Australia. Estimates of baseflow from physical techniques such as local minima and recursive digital filters are higher than those based on chemical mass balance using continuous electrical conductivity (EC). Between 2001 and 2011 the baseflow flux calculated using chemical mass balance is between 1.8×10^3 and 1.5×10^4 MLyr⁻¹ (15 to 25 % of the total discharge in any one year) whereas recursive digital filters yield baseflow fluxes of 3.6×10^3 to 3.8×10^4 MLyr⁻¹ (19 to 52 % of discharge) and the local minimum method yields baseflow fluxes of 3.2×10^3 to 2.5×10^4 MLyr⁻¹ (13 to 44 % of discharge). These differences most probably reflect how the different techniques characterise baseflow. Physical methods probably aggregate much of the water from delayed sources as baseflow. However, as many delayed transient water stores (such as bank return flow or floodplain storage) are likely to be geochemically similar to surface runoff, chemical mass balance calculations aggregate them with the surface runoff component. The mismatch between geochemical and physical estimates is greatest following periods of high discharge in winter, implying that these transient stores of water feed the river for several weeks to months. Consistent with these interpretations, modelling of bank storage indicates that bank return flows provide water to the river for several weeks after flood events. EC vs. discharge variations during individual flow events also imply that an inflow of low EC water stored within the banks or on the floodplain occurs as discharge falls. The joint use of physical and geochemical techniques allows a better understanding of the different components of water that contribute to river flow, which is important for the management and protection of water resources.

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Documenting the sources of water in rivers and streams is critical to our overall understanding of hydrological processes and for the management of groundwater and surface water resources (e.g., Yu and Schwartz, 1999; Uhlenbrook et al., 2002; Eckhardt, 2005; Gonzales et al., 2009; Kirchner, 2009). If rivers receive substantial groundwater inflows, groundwater extraction may significantly reduce river flow during periods of low rainfall with consequent impacts on riverine ecosystems or the utility of surface water resources. Managing surface water and groundwater resources thus requires a sound knowledge of the likely quantities of groundwater that rivers receive. Understanding the relative contributions of groundwater and surface water to river discharge is also important to assessing potential impacts of climate change and for flood forecasting (Winter, 1999, 2000). While it is well understood that groundwater and surface water systems interact, it is difficult to robustly measure the fluxes of groundwater to gaining streams (Winter, 1999, 2000; Sophocleous, 2002).

A non-generic division of river discharge following a rainfall event is into quickflow (water that contributes to river flow soon after the rainfall event) and baseflow (longer term flow through the unsaturated and saturated zone that sustains the river between rainfall events) (e.g., Hall, 1968; Nathan and McMahon, 1990; Yu and Schwartz, 1999; Eckhardt, 2005; Brodie et al., 2007). As discussed by Hall (1968), Brodie et al. (2007), and Schwartz (2007) these two components may include water from several sources. The quickflow component is commonly dominated by event water but can also include older water displaced from soils or the unsaturated zone (Anderson and Burt, 1980; Wittenberg and Sivapalan, 1999; Kirchner, 2009). In gaining river systems baseflow will include inputs from regional groundwater and but may also include interflow, the return of water from bank storage, or draining of pools on the floodplain (Chen et al., 2006; McCallum et al., 2010). This potential presence of multiple sources of water complicates our understanding of groundwater-surface water interaction.

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

5 Many techniques have been applied to quantifying the water balance in rivers (comprehensive recent reviews are provided by Winter, 1999; Sophocleous, 2002; Brodie et al., 2007; Schwartz, 2007; Cook, 2012). Discharge records represent the most comprehensive and abundant surface water datasets available. Commonly, discharge is recorded at sub-daily to daily intervals at one or more gauges in a catchment and records may extend for several decades or longer. Several techniques, such as graphical separation, rainfall-runoff models, and baseflow filters have arisen to estimate baseflow fluxes from discharge records (e.g., Nathan and McMahon, 1990; Eckhardt, 2005, 2008; Brodie et al., 2007; Aksoy et al., 2009). Automated graphical baseflow separation algorithms such as fixed block, sliding block, or local minima methods define baseflow as the minimum discharge over a given period of time, the duration of which is governed by catchment size (e.g., Sloto and Crouse, 1996; Aksoy et al., 2009). Digital filtering techniques assume that baseflow has a longer wavelength response than quickflow and may be estimated by passing a low pass digital filter across the river hydrograph (e.g., Nathan and McMahon, 1990; Eckhardt, 2005). While these techniques are relatively simple to apply and can be automated, there remains a degree of subjectivity (e.g., a range of digital filters exist). Some of the digital filters are tuneable so that estimates of baseflow fluxes can be brought into agreement with those from other techniques where catchment specific knowledge exists (Eckhardt, 2005). The estimates of baseflow fluxes yielded by these techniques include all delayed water not just groundwater inflows (Nathan and McMahon, 1990; Brodie et al., 2007).

15 There is an increasing volume of river geochemistry data. This includes electrical conductivity (EC), major ions, stable and radiogenic isotopes, gases, nutrients, and contaminants. Providing groundwater and surface water has different concentrations of a given geochemical component and the behaviour of component species is well known (e.g., whether it behaves conservatively and any rates of degassing or decay), geochemistry may be used to estimate groundwater inflows to rivers (Cook, 2012). Given that some delayed sources of water such as bank storage are likely to be geochemically similar to the surface water from which they are derived, chemical mass

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

balances may yield estimates of groundwater inflows rather than the total baseflow flux (McCallum et al., 2010). During single flow events there may be also different concentration vs. discharge relationships on the rising limb of the hydrograph compared with the falling limb (Evans and Davies, 1998; Hornberger et al., 2001). Such hysteresis loops have been used to assess how the sources of water supplying the river vary over time.

Most geochemical datasets represent surveys along rivers at specific times, often at low flow conditions (e.g., Mullinger et al., 2007; Cartwright et al., 2011; Cook, 2012); thus while they constrain the spatial variability of groundwater inflows and fluxes they commonly do not constrain temporal variability. By contrast many calculations of baseflow fluxes based on river discharge use daily or sub daily data from a single gauge. This approach captures the temporal variations but aggregates the behaviour of the entire catchment upstream of the gauge. Some studies have used time series of geochemical data; however, these are commonly collected over short time periods (e.g. Evans and Davies, 1998; Yu and Schwartz, 1999; Gonzales et al., 2009) or at relatively long intervals (e.g. Ahearn et al., 2004).

1.1 Objectives

The objectives of this paper are to contrast estimates of baseflow fluxes based on daily river discharge and electrical conductivity (EC) data in the upper Barwon River, southeast Australia. Although EC is only a general indicator of water chemistry, it can be measured continuously on timescales comparable to those of river discharge. Thus, EC records permit a direct comparison between physical and geochemical methods for estimating baseflow fluxes. Specifically our aims are to compare the estimated baseflow fluxes at different flow conditions and use these to assess the importance of different water stores that contribute to baseflow. The results of this work will allow better understanding of the information that may be gleaned from physical and chemical estimates of baseflow fluxes. Understanding the contribution of different water sources

to rivers over time will also aid in the management of connected groundwater-surface water systems.

1.2 Data sources

River discharge, groundwater geochemistry, and river geochemistry data are from the Victoria Water Resources Data Warehouse (2012), Cartwright et al. (2013), and unpublished Department of Primary Industry data. River EC and discharge is monitored continuously on a sub daily basis (typically 30 to 60 min) at several sites in the Barwon River and EC records extend from 1989 for some gauges to 2012.

2 Local geology and hydrogeology

The Barwon River catchment occupies $\sim 2700 \text{ km}^2$ of southern Victoria, Australia (Fig. 1), and includes three major river systems the Barwon, Leigh, and Moorabool Rivers (Corangamite Catchment Management Authority, 2005). This study focuses on the upper catchment of the Barwon River upstream of the Winchelsea gauging station (Fig. 1). The headwaters of the Barwon River largely comprises native eucalypt forest and plantation forestry; however much of the upper catchment has been cleared for grazing. The headwaters of the Barwon River drain the northern slopes of the Otway Ranges where the surface geology comprises Mesozoic-Cainozoic sediments of the Gelibrand Marl, Clifton Hill Formation, and the Eumeralla Formation (Witebsky et al., 1995; Corangamite Catchment Management Authority, 2005; Petrides and Cartwright, 2006; Dahlhaus et al., 2008). The remainder of the upper catchment comprises basaltic flows and pyroclastic deposits of the Pliocene-Pleistocene Newer Volcanics Province that are interbedded with Tertiary marine and freshwater sediments. The eruption of the basalts buried the pre-existing landscape blocking drainage courses and forming lakes and wetlands in depressions in the lava surface. Many of these lakes and wetlands are the sites of shallow groundwater discharge or throughflow systems and are

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



brackish to hypersaline (Dahlhaus et al., 2008; Tweed et al., 2011). Holocene alluvial deposits are developed along the river courses.

Regional groundwater in the deeper Mesozoic-Cainozoic aquifers flows from the recharge area in the Otway Ranges to the northeast, approximately parallel to the river flow (Witebsky et al., 1995; Petrides and Cartwright, 2006). Flow in the shallower basaltic and alluvial aquifers is broadly in the same direction (Corangamite Catchment Management Authority, 2005; Dahlhaus et al., 2008). The total dissolved solids (TDS) content of groundwater in the shallow aquifers generally increases down catchment and much of the shallow groundwater in the upper Barwon River has TDS contents of 3500 to 13 000 mgL⁻¹ (Witebsky et al., 1995; Petrides and Cartwright, 2006; Water Resources Data Warehouse, 2012). There are several instances of shallow (< 10 m) groundwater and soil water with much higher salinities (TDS up to 68 000 mgL⁻¹) in low-lying regions on the river floodplains (Fig. 1). These high groundwater salinities result from recharge of water that has undergone evapotranspiration in the poorly drained wetlands and marshes on the upper floodplain (Cartwright et al., 2013). Total discharges of the upper Barwon River between 1974 and 2011 were between 2200 and 330 000 ML yr⁻¹ (Water Resources Data Warehouse, 2012). The upper Barwon River increases in salinity along its length due to the influxes of saline groundwater combined with the flushing of saline wetlands on the floodplain (Cartwright et al., 2013). River EC values at Forrest in the uppermost catchment are typically < 200 µS cm⁻¹ whereas TDS contents at Winchelsea are up to 3200 mgL⁻¹ (Water Resources Data Warehouse, 2012).

3 Flow and EC variation

This study analyses flow and EC between 2001 and 2011, which represents the length of the EC record at the Winchelsea gauge. Although a longer flow and EC record (from 1989) exists for the Inverleigh gauge (Fig. 1), the inflows of anomalously saline groundwater (TDS up to 50 000 mgL⁻¹) in the region between the Winchelsea and Inverleigh

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



gauges (Corangamite Catchment Management Authority, 2005) may complicate the results of chemical mass balance techniques.

On average 50 to 60% of the annual rainfall in the upper Barwon catchment is received in the austral winter between July and October; January and February typically each receive 0 to 5% of the annual rainfall. Average rainfall at Winchelsea between 2001 and 2011 was 652 mm yr^{-1} , which is close to the long-term (1904 to 2011) average of 630 mm yr^{-1} (Bureau of Meteorology, 2012). This period comprises a number of years of below average rainfall (notably 2006 to 2009) that occurred during a regional drought period in southeast Australia together with years of above average rainfall (e.g., 2001 and 2010 to 2011). Annual potential evapotranspiration in the upper Barwon catchment is 1000 to 1100 mm yr^{-1} and potential evapotranspiration rates exceed average rainfall for the period between November and May (Bureau of Meteorology, 2012). The variation in evapotranspiration and rainfall leads to a strong seasonality of flows in the Barwon River with a period of low discharge in late summer (generally between February and April) and a period of higher flows in winter (generally between June and October). The groundwater system also responds to rainfall. In particular there is an annual rise of the water table following high rainfall periods in winter, which corresponds to the main period of recharge. The hydraulic heads and water table levels in the catchment were lower during the drought period in the mid 2000's than in the preceding or subsequent years (Water Resources Data Warehouse, 2012).

Annual discharge at Winchelsea between 2001 and 2011 ranges from 8.1×10^3 to $1.5 \times 10^5 \text{ ML yr}^{-1}$ with a total discharge over this period of $5.4 \times 10^4 \text{ ML}$ (Table 1). There are periods of no discharge, notably in December 2006 to February 2007 and February to April 2009. These time periods represent the summers of low rainfall years when several of the gauges in the Barwon and adjacent rivers also recorded no or very little discharge (Water Resources Data Warehouse, 2012). This indicates that the river had ceased flowing rather than the data reflecting malfunctioning of the gauge. Years 2001, 2002, and 2006 will be used to illustrate the patterns of flow and EC variation (Figs. 2–4). 2001 had the highest annual discharge in this period, 2002 represents

Contrasts between
chemical and
physical estimates of
baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

a year where the discharge in the upper Barwon River was close to the long-term median value, and 2006 is the year with lowest discharge between 2001 and 2011. Rainfall in 2001, 2002, and 2006 was 807 mm yr^{-1} , 654 mm yr^{-1} , and 428 mm yr^{-1} , respectively. The maximum discharge between 2001 and 2011 was 7318 ML day^{-1} and the median discharge (Q_{50}) was 21.6 ML day^{-1} (Fig. 5). The maximum and median discharges are 7318 and 91.6 ML day^{-1} in 2001, 1126 and 33.2 ML day^{-1} in 2002, and 1013 and 7.9 ML day^{-1} in 2006 (Fig. 5).

EC values between 2001 and 2011 ranged between 100 and $4200 \mu\text{Scm}^{-1}$ (Fig. 6); however, EC values $> 3500 \mu\text{Scm}^{-1}$ are mainly recorded during periods of very low or no discharge. These higher EC values probably reflect evaporation when the river is stagnant, and for the majority of the monitoring period EC values are $< 3200 \mu\text{Scm}^{-1}$. The discharge at Winchelsea in 2002 varied between 5 and 1125 ML day^{-1} and EC varied between 300 and $2790 \mu\text{Scm}^{-1}$ (Figs. 3, 6). Total discharge for this year was $4.0 \times 10^4 \text{ ML yr}^{-1}$ (Table 1). Higher discharges occurred during a discrete flow event in February 2002 and a series of high flow events between June and October. River discharges were lowest (as low as 6 ML day^{-1}) in March to April but remained generally high ($> 100 \text{ ML day}^{-1}$) between the flow events in June to October. EC values were highest (up to $2790 \mu\text{Scm}^{-1}$) during the March to April low flow period and were generally below $2000 \mu\text{Scm}^{-1}$ throughout June to October, even during periods of low flow. The variation in discharge and EC for 2001 and 2006 are similar. The highest EC values are generally recorded during the low discharge periods in February to April and are lower during periods of higher discharge later in the years. The river discharge between the flood peaks remains higher in the winter months than over the summers.

While EC is broadly inversely correlated with discharge (Fig. 6), EC vs. discharge variations for several of the major flow events in 2002 define clockwise hysteresis loops (i.e. EC is lower at any given discharge on the falling limb of the hydrograph than on the rising limb) (Fig. 7). For the event between days 170 and 200 in 2002 (number 2 on Fig. 3), gauges elsewhere in the catchment (Kildean Lane, Ricketts Marsh, and Inverleigh) record similar clockwise hysteresis loops (Fig. 8).

4 Estimating baseflow

4.1 Graphical separation techniques

The baseflow flux to rivers may be estimated by graphical methods. Sloto and Crouse (1996) and Askoy et al. (2009) describe a local minimum method where the baseflow flux is assumed to vary linearly between minimum discharges that occur within a window of specified number of days ($0.5[2N^* - 1]$). The number of days after which surface water runoff ceases (N) scales to catchment area, and the empirical relationship $N = A^{0.2}$ is generally adopted where A is area in square miles (Sloto and Crouse, 1996). $2N^*$ is the odd integer nearest to $2N$. For the Winchelsea gauge $A = 1270 \text{ km}^2$ (490 mi^2) and $2N^* = 7$. The analysis of the hydrograph was completed between the minimum discharges proceeding January 2001 and following December 2011 to allow baseflow fluxes for the entire 2001 to 2011 period to be calculated.

For 2001, 2002, and 2011 the smoothed minimum technique predicts that baseflow fluxes are close to total discharge during the March to April low flow periods that corresponds to the low rainfall period at the end of summer (Figs. 2–4). Baseflow fluxes increase during the higher discharge periods of July to October; this is the period of groundwater recharge that causes a rise in the water table and increased groundwater flows towards the river. The predicted variations in baseflow flux in the upper Barwon River from the smoothed minimum method correspond to the general perception of how baseflow varies with rainfall and river discharge (e.g. Brodie et al., 2007). For 2001, 2002, and 2006 the baseflow fluxes estimated by this technique were $2.5 \times 10^4 \text{ ML yr}^{-1}$ ($\sim 20\%$ of total discharge), $1.8 \times 10^4 \text{ ML yr}^{-1}$, ($\sim 44\%$ of total discharge), and $3.2 \times 10^3 \text{ ML yr}^{-1}$ ($\sim 39\%$ of total discharge). For the period between 2001 and 2011 the smoothed minimum technique yields a total baseflow volume of $1.4 \times 10^5 \text{ ML}$ ($\sim 27\%$ of the volume of water discharged by the upper Barwon River) (Table 1).

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.2 Digital filters

Baseflow was estimated for the Barwon River the using the following digital filters:

$$b_k = ab_{k-1} + \frac{1+a}{2} (y_k - y_{k-1}) \quad (1)$$

(Lyne and Hollick, 1979; Nathan and McMahon, 1991) and

$$b_k = \frac{(1 - \text{BFI}_{\max})ab_{k-1} + (1 - a)\text{BFI}_{\max}y_k}{1 - a\text{BFI}_{\max}} \quad (2)$$

(Eckhardt, 2005, 2008). While there are other possible digital filters (e.g., the Schwartz, 2007 filter that takes into account differences in baseflow fluxes on the rising and falling limbs of the hydrographs), these two are readily implemented and have been applied in many studies. In Eqs. (1, 2), b_k is the baseflow flux on day k , y_k is total discharge on day k , and a is the recession constant that is estimated from the recession limbs of the hydrographs by calculating $y_{k+1} = ay_k$ for every stream discharge value that is part of a recession period of at least five days (Nathan and McMahon, 1991; Eckhardt, 2005, 2008). For the Barwon River, $a = 0.95$. The Lyne and Hollick filter was applied in three passes (forward, backwards, forwards) as proposed by Nathan and McMahon (1991). In the Eckhardt filter, BFI_{\max} is the maximum value of the baseflow index (the long-term ratio of baseflow to river discharge) that can be modelled by the algorithm. The value of BFI_{\max} is subjective; Eckhardt (2005, 2008) suggest values of 0.7 to 0.8 for perennial streams on porous aquifers and values as low as 0.2 to 0.25 for perennial streams on crystalline basement. In this study, given that the upper Barwon is a perennial river hosted within porous aquifers, an initial BFI_{\max} value of 0.75 was used. Both filters were applied with the condition that $b_k \leq y_k$.

The Lyne and Hollick filter produces a predicted variation in baseflow fluxes that is similar to that of the smoothed minimum method (Figs. 2–4; Table 1). The overall baseflow flux calculated using this method for 2001, 2002, and 2006 is $3.8 \times 10^4 \text{ MLyr}^{-1}$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(~ 30 % of total discharge), $2.1 \times 10^4 \text{ MLyr}^{-1}$ (~ 52 % of the total discharge), and $3.6 \times 10^3 \text{ MLyr}^{-1}$ (~ 44 % of total discharge), respectively. For the period between 2001 and 2011 this filter yields a net volume of baseflow of $1.9 \times 10^5 \text{ ML}$ (~ 35 % of the total volume of water discharged by the upper Barwon River) (Table 1).

The estimated baseflow flux from the Eckhardt filter with $\text{BFI}_{\text{max}} = 0.75$ is significantly higher ($2.7 \times 10^4 \text{ MLyr}^{-1}$ or 69 % of total discharge in 2002) than that of the smoothed minimum method or the Lyne and Hollick filter (Table 1, Figs. 2–4). For the period between 2001 and 2011 the Eckhardt filter yields baseflow fluxes of 5.2×10^3 to $7.1 \times 10^4 \text{ MLyr}^{-1}$ that correspond to ~ 31 to ~ 50 % of annual discharge. The net baseflow volume between 2001 and 2011 is estimated as $3.2 \times 10^5 \text{ ML}$ or ~ 59 % of the total of water discharged by the upper Barwon River (Table 1). The predicted variation in baseflow fluxes is also less attenuated, with higher baseflow fluxes during each of the high flow events than estimated by the other physical methods. Reducing BFI_{max} to 0.4 results in more attenuated baseflow fluxes that are similar to those estimated by the Lyne and Hollick filter and the smoothed minimum method (Figs. 2–4, Table 1).

4.3 Chemical mass balance

Baseflow was also estimated using geochemical mass balance based on the river EC values at Winchelsea via:

$$b(f) = \frac{\text{EC}_r - \text{EC}_{\text{sw}}}{\text{EC}_{\text{gw}} - \text{EC}_{\text{sw}}} \quad (3)$$

(Yu and Schwartz, 1999) where $b(f)$ is the fraction of baseflow contributing to total discharge, EC_r is the EC of the river, EC_{sw} is the EC of the surface runoff, and EC_{gw} is the EC of the groundwater (Brodie et al., 2007). The mass balance calculations assume that the tracer behaves conservatively. Groundwater and surface water EC values in the upper Barwon catchment are dominantly a function of the concentrations of Cl and Na, which are largely governed by the degree of evapotranspiration (Cartwright

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2013). Thus, to a first approximation EC can be assumed to behave conservatively. The EC of most groundwater in the upper Barwon catchment ranges from 1000 to 20 000 μScm^{-1} with local occurrences of highly saline groundwater (EC up to 76 000 μScm^{-1} : Water Resources Data Warehouse, 2012; Department of Primary Industries, unpublished data; Cartwright et al., 2013). However, the distribution of shallow groundwater bores is insufficient to make a precise estimate of the EC of near-river groundwater. Thus, in common with other studies (e.g., Gonzales et al., 2009), the highest EC recorded in the Barwon River at Winchelsea during the low flow periods when the river is most likely to be fed mainly or entirely by groundwater inflows will be used as the groundwater component. The highest EC recorded at Winchelsea between 2001 and 2011 when there is above zero discharge is 3200 μScm^{-1} and this is used as the average EC of the groundwater. The EC of surface runoff was assumed to be 15 μScm^{-1} which is appropriate for local rainfall (Cartwright et al., 2013). Stable isotope data from the Barwon River at a variety of flow conditions between 2011 and 2012 preclude significant in-river evaporation occurring during periods where the river is flowing (Cartwright et al., 2013), which implies that evaporation in the river does not increase EC values.

The baseflow fluxes calculated using chemical mass balance for 2001, 2002, and 2006 are $1.5 \times 10^4 \text{ MLyr}^{-1}$ ($\sim 12\%$ of total discharge), $9.9 \times 10^3 \text{ MLyr}^{-1}$ ($\sim 25\%$ of total discharge) and $1.8 \times 10^3 \text{ MLyr}^{-1}$ ($\sim 22\%$ of total discharge), respectively (Figs. 2–4, Table 1). These are lower than those calculated using the smoothed minimum technique or either of the two digital filters. Between 2001 and 2011 the volume of baseflow estimated using chemical mass balance is $8.8 \times 10^4 \text{ ML}$ which corresponds to 16% of the water discharged from the upper Barwon River over this period (Table 1).

In the chemical mass balance, the minimum EC that the groundwater can have is that of the maximum EC recorded in the river (otherwise $b(f)$ in Eq. 3 exceeds 1). Lower baseflow estimates would be produced if the groundwater had higher EC values than was assumed (which is possible given the recorded groundwater EC values in the catchment). Surface runoff may have a higher EC than that of rainfall due to

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

dissolution of solutes during overland flow and the minimum EC recorded in the river is $\sim 100 \mu\text{Scm}^{-1}$ (Fig. 6). Increasing the assumed EC of the surface water again reduces the estimated annual baseflow fluxes; for surface water with an EC of $100 \mu\text{Scm}^{-1}$, the annual baseflow fluxes are $\sim 8\%$ lower. Given these constraints the baseflow fluxes estimated from the chemical mass balance are likely to be maxima.

5 Discussion

Estimates of annual baseflow fluxes in the upper Barwon River made using physical methods are generally higher than those from chemical mass balance (Fig. 9). The difference between the physical and chemical approaches most probably points to a fundamental difference in how each method aggregates the different sources of water rather than an error in any single formulation. The differences between the methods may help improve our understanding of what constitutes baseflow at any particular time. Baseflow fluxes from the digital filters, local minimum method, and the EC mass balance generally agree during the low flow periods in February to March. However, the differences between estimated baseflow fluxes are large during the period of higher winter flows. The variation in baseflow fluxes calculated from the chemical mass balance is also less attenuated than that of the physical methods. Specifically, baseflow fluxes from chemical mass balance are higher than those from the physical techniques on the rising limbs of the hydrographs. This trend also manifests itself in differences between measured and predicted EC in individual flow events. If groundwater was the only contribution of baseflow, the EC of the river may be predicted from the calculated proportion of baseflow contributing to total stream flow. Assuming that groundwater has an EC of $3200 \mu\text{Scm}^{-1}$ and rainfall has an EC of $15 \mu\text{Scm}^{-1}$, the predicted variation in EC over individual discharge episodes (Fig. 7) is larger than the observed variation. Within individual episodes, the predicted EC value on the rising limb of the hydrograph is lower than observed while it is higher on the falling limb.

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5.1 Potential other transient water stores

The above observations imply that other transient water stores aside from surface runoff and regional groundwater inflow are important in the upper Barwon River. As noted above, the floodplain of the upper Barwon contains numerous saline marshes and wetlands. Flushing of this saline water into the river during the onset of overland flow may produce relatively high EC values on the rising limbs of the hydrographs with the consequence that chemical mass balance overestimates the baseflow component at those times. The input of older water prior to the event water entering the river has been noted elsewhere (e.g., Waddington et al., 1993; Brassard et al., 2000).

Bank storage may be an important transient water store on the falling limb of the hydrographs (e.g., Hall, 1968; Chen et al., 2006; McCallum et al., 2010). Water recharged into the banks at high river stage will return to the river as river levels fall thus providing a component of delayed or slow flow over a period of weeks to months. The physical techniques are likely to record bank return flows as part of the baseflow component since it provides a delayed input relative to the surface water flows. However, as the water within river banks is likely to have a much lower EC than the regional groundwater, the geochemical mass balance techniques may not account for this component. The upper Barwon River also develops pools and billabongs on its floodplain during flood events. Drainage of water from these surface water stores back into the river following high river stages may also provide a delayed component of water to rivers that is geochemically similar to surface runoff.

To test the impact of bank storage we used a two-dimensional MODFLOW model of a fully penetrating river similar to the HydroGeoSphere model of McCallum et al. (2010). The model grid was 1000 m × 5 m and has uniform porosity of 0.2 and a dispersivity of 0.1 m. The lower boundary is a no flow boundary and one of the lateral boundaries away from the river is a constant head boundary; for simplicity the river is modelled using variable heads at the other lateral boundary rather than a river or stream package. Horizontal hydraulic conductivities (K_h) were varied from 10^{-5} to

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

10^{-2} m s^{-1} and vertical hydraulic conductivities were 10 % of K_h . Initially there is a horizontal head gradient of 5×10^{-4} toward the river. To simulate a flood peak the head level at the river boundary was increased by 3 m over 2 days, the high head levels were maintained for 2 days, and heads subsequently decreased exponentially over 10 days; this produces a flood peak similar in size and duration to those observed on the Barwon River. Geochemical transport was modelled using a conservative tracer with an initial normalised concentration of 1 in the aquifer and 0 in the river. The time required for the tracer concentration in the aquifer at the river boundary to recover to between 0.5 and 0.9 of its initial value following the flood peak is a few days to several weeks (Fig. 10). In the model the river begins to receive water from the aquifer 6 to 7 days after the flood peak and these initial flows from the aquifer into the river have substantially lower tracer concentrations than the water flowing into the river prior to the flood peak. The study of McCallum et al. (2010) that used different porosities, dispersivities, and flood peaks reached similar conclusions. That study also showed that varying parameters such as porosity, river penetration, or dispersivity does not make a significant difference to the results. Horizontal hydraulic conductivities of the Newer Volcanics Province basalts range from 10^{-4} to 10^{-2} m s^{-1} (Dahlhaus et al., 2008) suggesting that bank return water may infiltrate the river for several days to weeks following flood events, and that during a period of successive flood events the water infiltrating the river may always contain a significant portion of bank water. As the bank water is derived from the river and likely has a much lower EC than regional groundwater, the EC of the river between the flood peaks will be lower than over prolonged low flow periods when the banks have drained and the baseflow comprises mainly high EC regional groundwater.

Support for the presence of water components that are geochemically similar to surface water but which has a delayed input to the river is also provided by the EC vs. discharge hysteresis loops. The observed variation in EC over an individual flow event is much smaller than that predicted from either the baseflow filter or local minima technique (Fig. 7), resulting in flatter hysteresis loops. Additionally, the EC of the river on the falling limb of hydrograph is lower than on the rising limb. These observations

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

are consistent with the return of low EC water from river banks or the floodplain to the river as the surface water flows decline (cf., Evans and Davies, 1998). Other gauges in the upper Barwon River show similar hysteresis loops (Fig. 8), implying that these flow-discharge relationships are common throughout the catchment.

5 If the physical methods are assumed to reflect total delayed flow to the river and the chemical mass balance the groundwater inflow, the magnitude of the mismatch between the methods may be used to estimate the relative contribution of bank storage and/or other transient water stores. For 2002, the total estimate is 7600 to 10 200 MLyr⁻¹ or 19 to 27 % of the total river discharge. As these calculations do not
10 take into account the potential flushing of high EC water from the floodplain during the early stages of discharge events, which may cause the chemical mass balance techniques to overestimate baseflow at those times, they are minimum estimates. As shown by Fig. 9, there is no clear relationship between annual river discharge and the relative divergence between the physical and chemical baseflow estimates. This possibly
15 reflects that generation of bank storage and other transient stores of water depend on the timing and frequency of high runoff events rather than total annual discharge.

The ratio of discharge exceeded 90 % of the time to the median discharge (Q_{90}/Q_{50}) on flow duration curves (Fig. 5) has been proposed as an estimate of the proportion of stream flow derived from groundwater storages (Nathan and McMahon, 1990; Brodie, 2007). Q_{90}/Q_{50} for the 2001 to 2011 discharge data is 13%, which is similar to the
20 estimate of the proportion of baseflow from the chemical mass balance. As with other techniques, there is no compelling reason why the flow duration curve provides an accurate estimate of groundwater inflows; nevertheless, the shape of the low discharge part of the flow duration curve and the observation that the river occasionally ceases
25 to flow implies that the upper Barwon River does not have high groundwater inflows.

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

6 Conclusions

This study illustrates that geochemical and physical methods of estimating baseflow yield contrasting results. The contrast most probably relates to how the different methods characterise the water sources to rivers. For example, the physical methods of estimating baseflow may aggregate all delayed water sources as baseflow components. Many of these delayed water sources (such as bank flow or floodplain storage) will have a geochemistry that is similar to that of surface runoff and geochemical mass balance techniques aggregate them with the surface runoff. These stores of water impact the catchment for several weeks to months following rainfall events and during periods of high-rainfall may dominate the non-surface water component of river flow. The high salinity of groundwater and the consequent high salinity of the upper Barwon River emphasises the mismatch between the different methods, in catchments where there is less contrast between groundwater and surface water salinity, the effects may not be so obvious.

This study amplifies the conclusions made elsewhere that assigning the origins of the quickflow and baseflow components may not be simple (e.g., Hall, 1968; Anderson and Burt, 1980; Brodie et al., 2007; Schwartz, 2007; McCallum et al., 2010) and also illustrates that the components of water contributing to baseflow may change throughout the year. Records of surface water geochemistry are gradually becoming more common, making it viable to use comparisons between chemical mass balance and physical techniques to better understand the changing sources of water that is input into rivers over discharge events.

The results of this study have implications for managing groundwater and surface water resources. There is a recognition that neglecting the groundwater inflows to rivers may lead to double allocation of water resources (i.e., some of the surface water allocation may represent groundwater that has been separately allocated). However, the use of physical methods alone may result in overestimation of regional groundwater inputs

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

to rivers if a significant part of the baseflow component is from water stores such as bank return flow or draining of surface pools on the floodplain.

Acknowledgements. We would like to thank the Department of Sustainability and Environment for their ongoing support of the Victorian Water Resources Data Warehouse without which studies such as this would not be possible. This work was supported by the P3 program of the ARC-NWI funded National Centre for Groundwater Research and Training.

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HESD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Cook, P. G.: Estimating groundwater discharge to rivers from river chemistry surveys, *Hydrol. Process.*, online first, doi:10.1002/hyp.9493, 2012.
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Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Table 1. Summary of baseflow estimates for the upper Barwon River.

	Discharge ($\times 10^4$ MLyr $^{-1}$)	M ^a	Baseflow Fluxes ($\times 10^4$ MLyr $^{-1}$)			
			RDF ^b	Ek (0.4) ^c	Ek (0.75) ^d	CMB ^e
2001	13	2.5	3.8	4.1	7.1	1.5
% ^h		20	30	32	56	12
2002	4.0	1.8	2.1	1.6	2.7	0.99
%		44	52	42	69	25
2003	6.5	1.6	2.4	2.2	3.9	1.2
%		24	37	39	61	19
2004	5.8	2.2	2.4	2.2	3.6	0.90
%		39	42	39	63	16
2005	3.4	1.1	1.3	1.1	2.	0.60
%		32	39	32	60	18
2006	0.81	0.32	0.36	0.31	1.8	0.18
%		39	44	39	64	22
2007	3.8	0.50	0.73	0.98	1.9	4.8
%		16	19	25	48	12
2008	0.89	0.40	0.41	0.34	.62	2.3
%		45	46	39	70	25
2009	2.7	0.69	1.0	0.98	1.7	0.53
%		25	37	36	63	20
2010	7.3	2.1	2.5	2.1	4.5	1.1
%		29	34	36	61	15
2011	3.9	0.89	1.3	1.4	2.3	0.69
%		23	33	37	60	18
Total ^g	Discharge	Total Baseflow Volumes ($\times 10^4$ ML)				
	($\times 10^4$ ML)	M	RDF	Ek (0.4)	Ek (0.75)	CMB
2001–2011	54	14	19	19	32	8.8
%		27	35	35	59	16

a: smoothed minima (Sloto and Crouse, 1996)

b: Nathan and McMahon (1990) implementation of the Lyne and Hollick (1979) recursive digital filter

c: Ekhardt (2005) digital filter with $BF_{\max}^{-1} = 0.4$

d: Ekhardt (2005) digital filter with $BF_{\max}^{-1} = 0.75$

e: chemical mass balance (Yu and Schwartz, 1999)

f: baseflow as a percent of total discharge

g: total baseflow and discharge volumes between 2001 and 2011

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

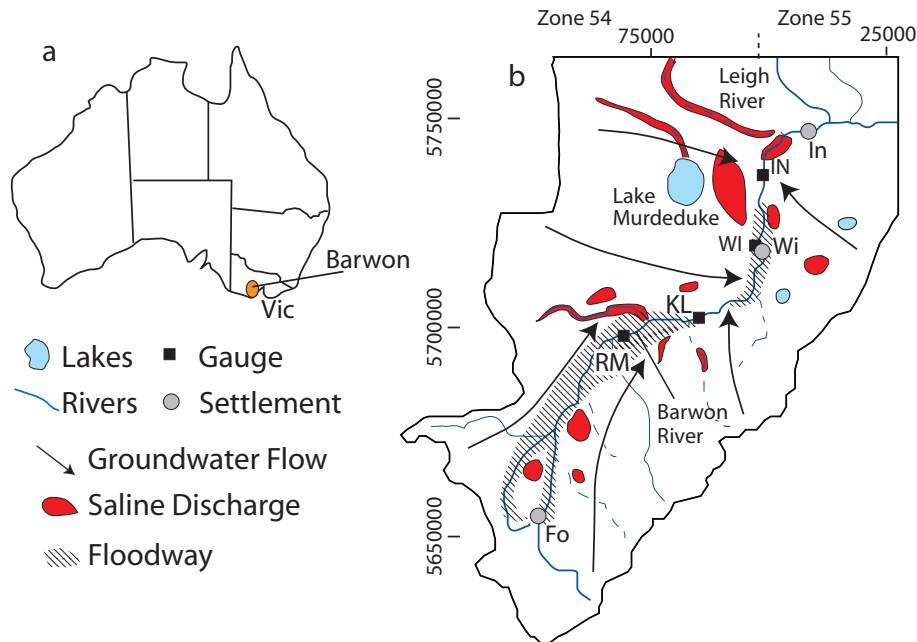


Fig. 1. (a) Location of upper Barwon Catchment in Australia (Vic = Victoria). (b) Hydrology of the upper Barwon Catchment showing groundwater flow directions, location of gauges (IN = Inverleigh; KL = Kildean Lane; RM = Ricketts Marsh; WI = Winchelsea), saline discharge sites, and settlements (Fo = Forrest; In = Inverleigh; Wi = Winchelsea). Data from Corangamite Catchment Management Authority (2005) and Water Resources Data Warehouse (2012).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

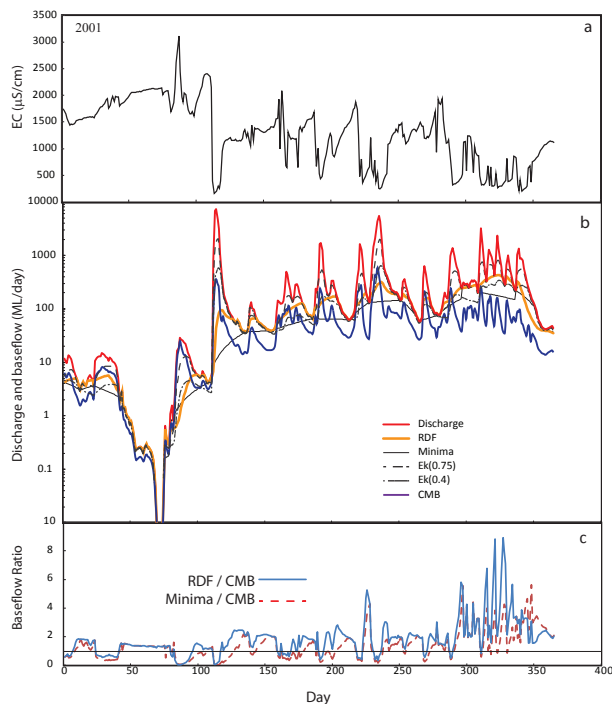


Fig. 2. (a) Variation in EC in the upper Barwon River at Winchelsea in 2001. (b) Variation in discharge of the Barwon River at Winchelsea in 2001 and estimated baseflow calculated by the Nathan and McMahon (1990) implementation of the Lyne and Hollick (1979) digital filter (RDF), smoothed minima (Sloto and Crouse, 1996) (minima), the Ekhardt (2005) digital filter with $BFI_{max} = 0.75$ (Ek(0.75)) and 0.4 (Ek(0.4)), and chemical mass balance (CMB). (c) Ratio of baseflows derived by smoothed minima and the Lyne and Hollock (1979) digital filter to that estimated by chemical mass balance. Days are from 1 January. Data from Water Resources Data Warehouse (2012).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

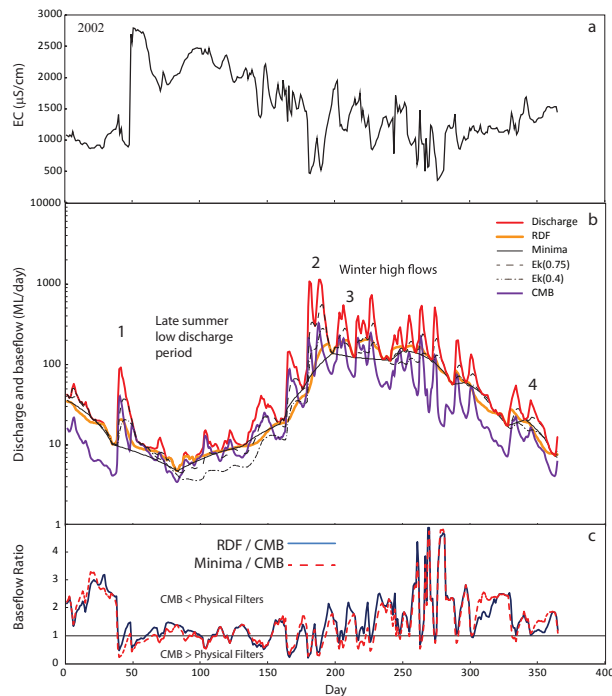


Fig. 3. (a) Variation in EC in the upper Barwon River at Winchelsea in 2002. (b) Variation in discharge of the Barwon River at Winchelsea in 2002 and estimated baseflow calculated by the Nathan and McMahon (1990) implementation of the Lyne and Hollick (1979) digital filter (RDF), smoothed minima (Sloto and Crouse, 1996) (Minima), the Ekhardt (2005) digital filter with $\text{BFI}_{\text{max}} = 0.75$ (Ek(0.75)) and 0.4 (Ek(0.4)), and chemical mass balance (CMB). (c) Ratio of baseflows derived by smoothed minima and the Lyne and Hollock (1979) digital filter to that estimated by chemical mass balance. Days are from 1 January. Data from Water Resources Data Warehouse (2012).

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

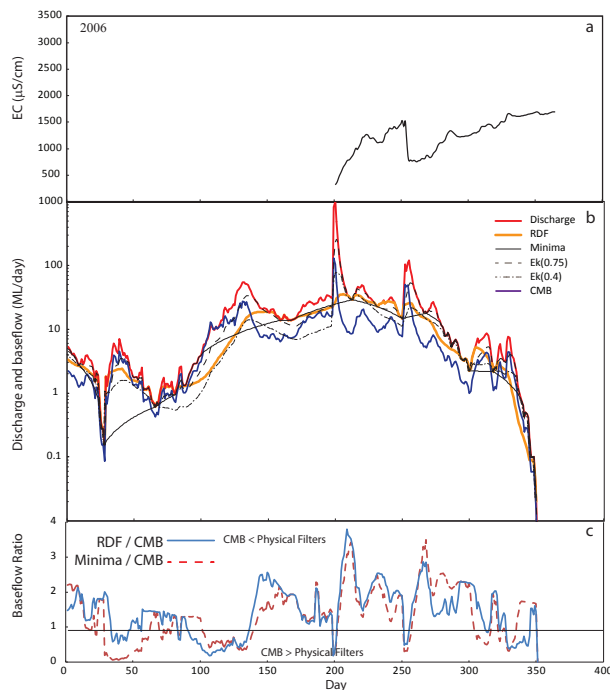


Fig. 4. (a) Variation in EC in the upper Barwon River at Winchelsea in 2006. (b) Variation in discharge of the Barwon River at Winchelsea in 2001 and estimated baseflow calculated by the Nathan and McMahon (1990) implementation of the Lyne and Hollick (1979) digital filter (RDF), smoothed minima (Sloto and Crouse, 1996) (Minima), the Ekhardt (2005) digital filter with $BFI_{max} = 0.75$ (Ek(0.75)) and 0.4 (Ek(0.4)), and chemical mass balance (CMB). (c) Ratio of baseflows derived by smoothed minima and the Lyne and Hollick (1979) digital filter to that estimated by chemical mass balance. Days are from 1 January. Data from Water Resources Data Warehouse (2012).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

HESSD

10, 5943–5974, 2013

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

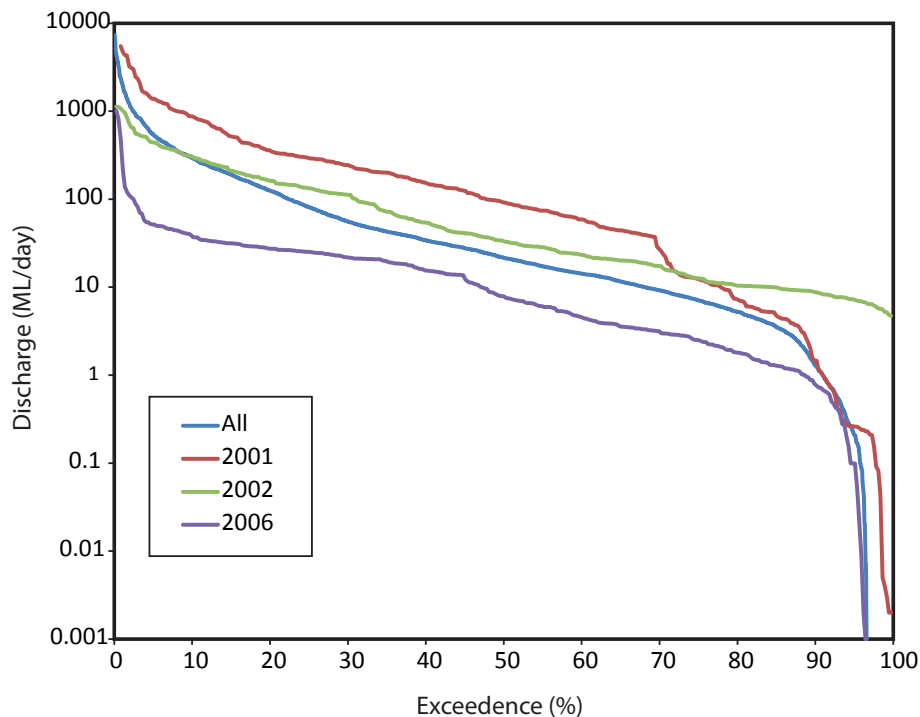
[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Fig. 5. Flow duration curve for the upper Barwon River in 2001, 2002, 2006, and for all years between 2001 and 2011. Data from Water Resources Data Warehouse (2012).

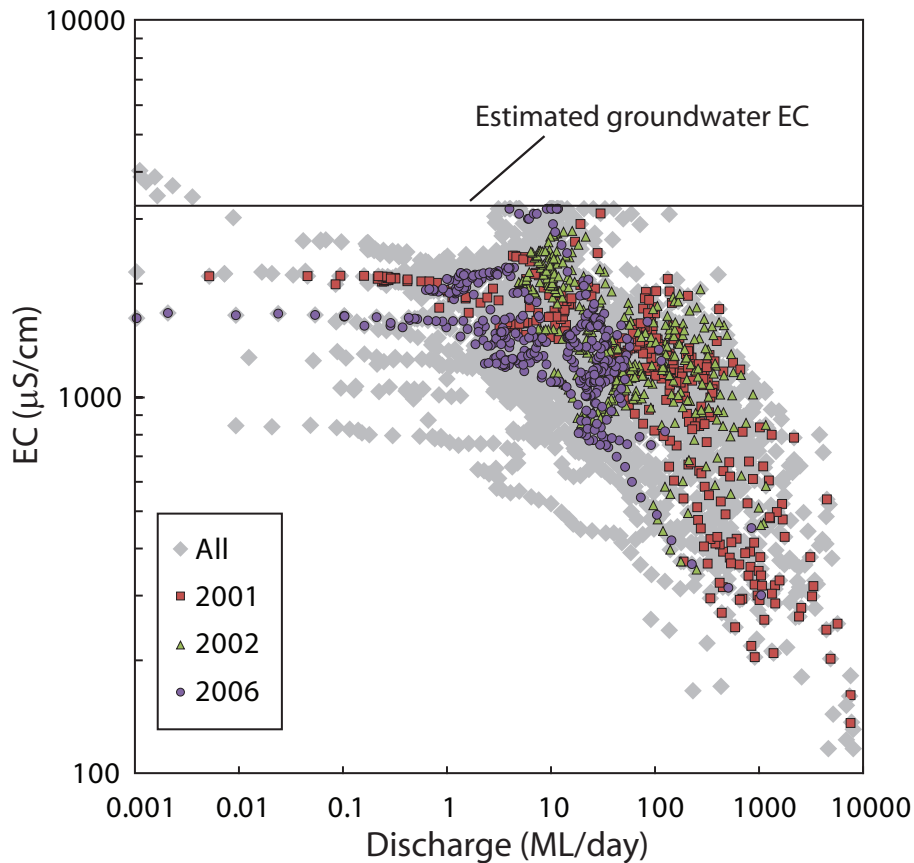


Fig. 6. EC vs. Discharge for the upper Barwon River between 2001 and 2011. Data from Water Resources Data Warehouse (2012).

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

[Title Page](#)

[Abstract](#) | [Introduction](#)

[Conclusions](#) | [References](#)

[Tables](#) | [Figures](#)

[⏪](#) | [⏩](#)

[⏴](#) | [⏵](#)

[Back](#) | [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



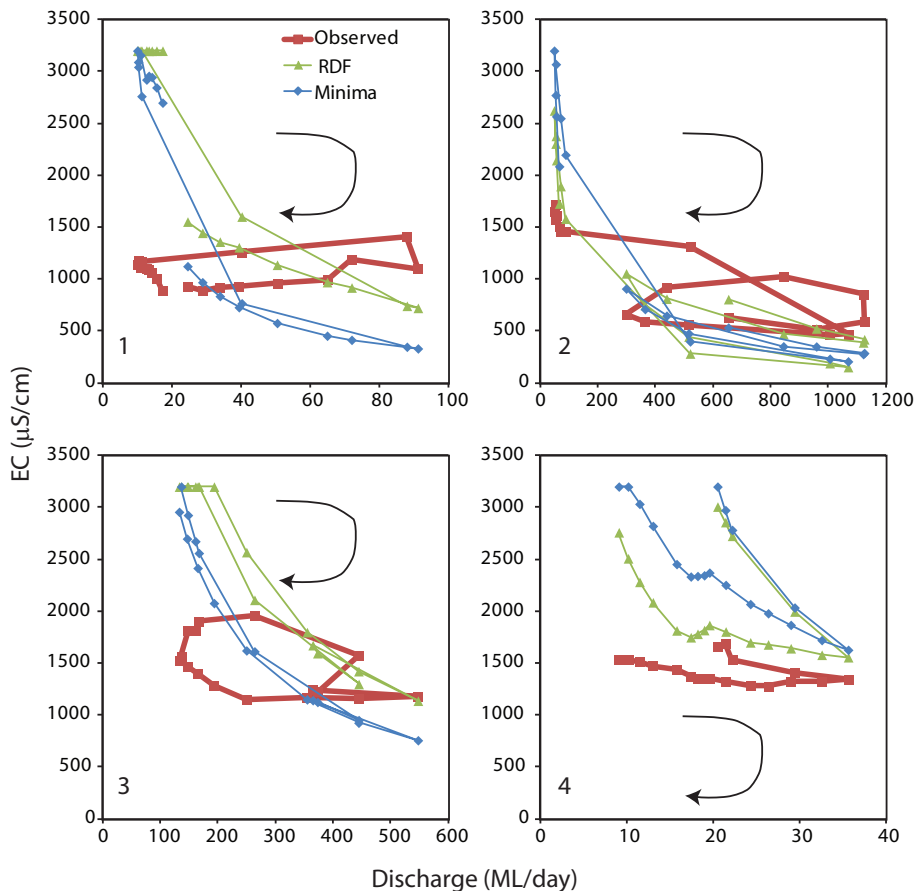


Fig. 7. EC vs. Discharge hysteresis loops for discharge events in 2002 at Winchelsea. Arrows show changes with time, numbers correspond to events on Fig. 3b. RDF and Minima indicate the calculated EC vs. Discharge relationships made using the baseflow estimates from the Lyne and Hollock digital filter and the smoothed minima technique, respectively.

[Title Page](#)
[Abstract](#) [Introduction](#)
[Conclusions](#) [References](#)
[Tables](#) [Figures](#)
[⏪](#) [⏩](#)
[⏴](#) [⏵](#)
[Back](#) [Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Contrasts between
chemical and
physical estimates of
baseflow**

I. Cartwright et al.

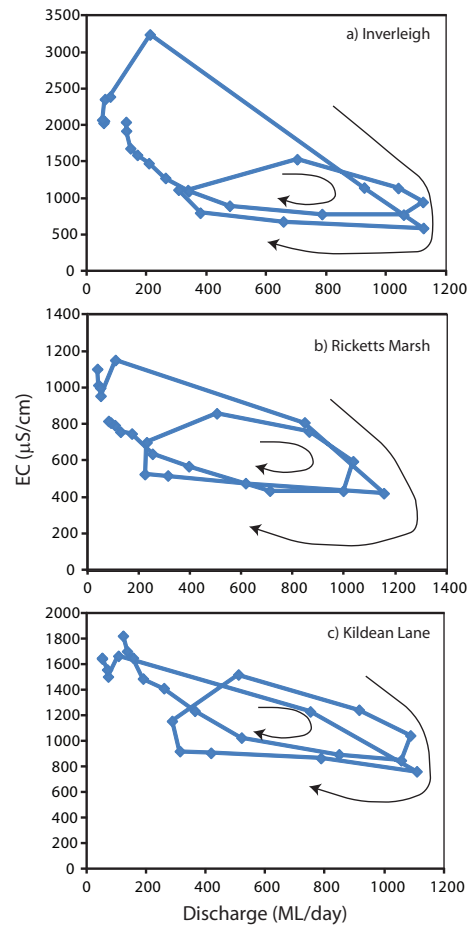


Fig. 8. EC vs. Discharge hysteresis loops for discharge events on days 170–200 in 2002 at Inverleigh, Ricketts Marsh, and Kildean Lane (Fig. 1), arrows show changes with time. This event corresponds to event 2 on Fig. 3.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Contrasts between chemical and physical estimates of baseflow

I. Cartwright et al.

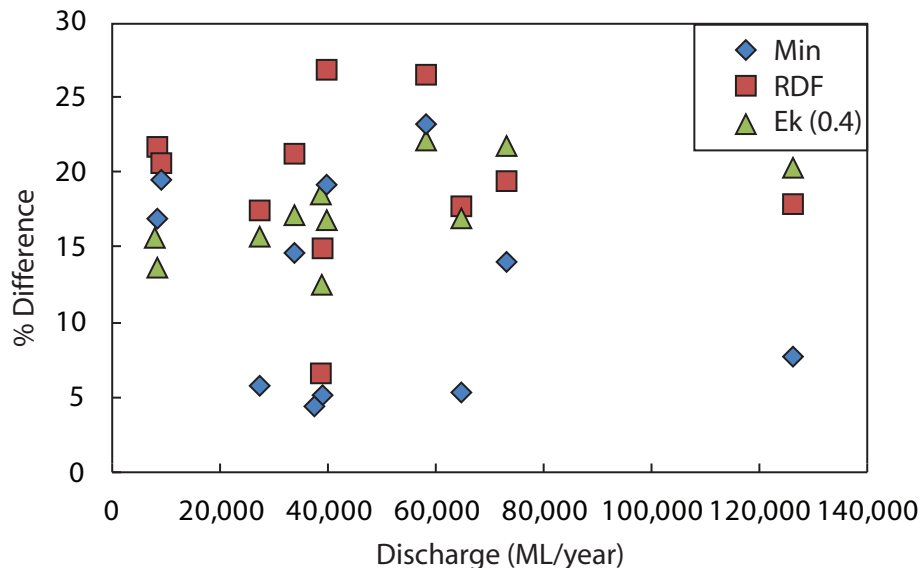


Fig. 9. Summary of the percentage difference of the estimated baseflow from the chemical mass balance technique and the smoothed minima (Min), the Lyne and Hollick digital filter (RDF) and the Eckhardt filter with $BFI_{\max} = 0.4$ (Ek(0.4)). Data from Table 1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Contrasts between
chemical and
physical estimates of
baseflow**

I. Cartwright et al.

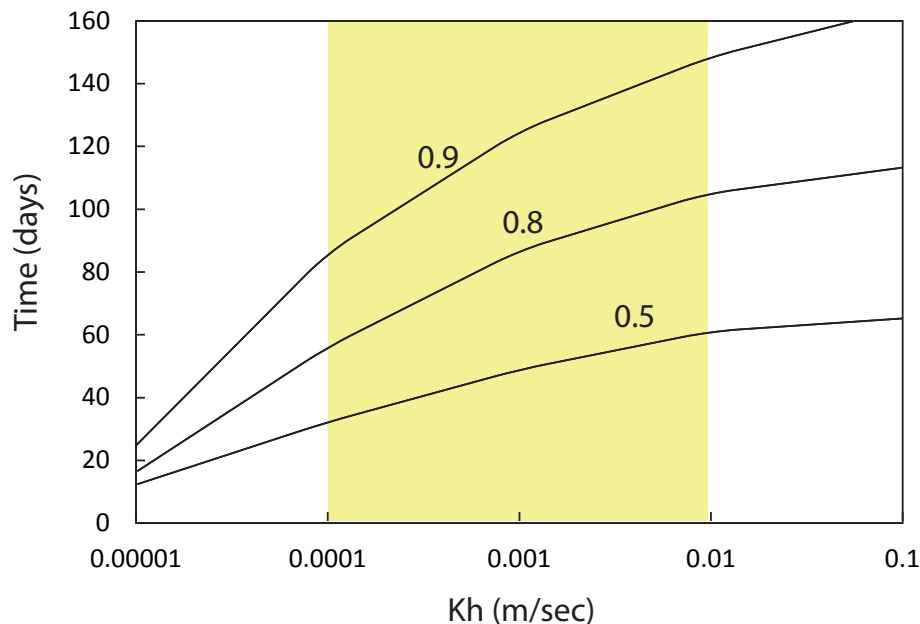


Fig. 10. Time required for compositions in the aquifer next to a river to recover to 0.5, 0.8, and 0.9 of their initial values following a flood event estimated using the MODFLOW model as discussed in the text. Shaded box is the range of estimated hydraulic conductivities in the Newer Volcanic Province basalts.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)