

1 **Identifying flood recharge and inter-aquifer connectivity using multiple isotopes in**
2 **subtropical Australia**

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13 **Abstract**

14 An understanding of hydrological processes is vital for the sustainable management of
15 groundwater resources, especially in areas where an aquifer interacts with surface water
16 systems or where aquifer-interconnectivity occurs. This is particularly important in areas that
17 are subjected to frequent drought/flood cycles, such as the Cressbrook Creek catchment in
18 southeast Queensland, Australia. In order to understand the hydrological response to
19 flooding and to identify inter-aquifer connectivity, multiple isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H
20 and ^{14}C) were used in this study in conjunction with a comprehensive hydrochemical
21 assessment, based on data collected six months after severe flooding in 2011. The relatively
22 depleted stable isotope signatures of the flood-generating rainfall ($\delta^2\text{H}$: -30.2 to -27.8‰,
23 $\delta^{18}\text{O}$: -5.34 to -5.13 ‰ VSMOW) were evident in surface water samples ($\delta^2\text{H}$: -25.2 to -
24 23.2‰, $\delta^{18}\text{O}$: -3.9 to -3.6‰ VSMOW), indicating that these extreme events were a major
25 source of recharge to the dam in the catchment headwaters. Furthermore, stable isotopes
26 confirmed that the flood generated significant recharge to the alluvium in the lower part of
27 the catchment, particularly in areas where interactions between surface waters and
28 groundwater were identified and where diffuse aquifer recharge is normally limited by a
29 thick (approximately 10 m) and relatively impermeable unsaturated zone. However, in the
30 upper parts of the catchment where recharge generally occurs more rapidly due to the
31 dominance of coarse-grained sediments in the unsaturated zone, the stable isotope signature
32 of groundwater resembles the longer-term average rainfall values ($\delta^2\text{H}$: -12.6, $\delta^{18}\text{O}$: -3.4‰
33 VSMOW), highlighting that recharge was sourced from smaller rainfall events that occurred
34 subsequent to the flooding. Interactions between the bedrock aquifers and the alluvium were

1 identified at several sites in the lower part of the catchment based on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; this was
2 also supported by the hydrochemical assessment, which included the modelling of
3 evaporation trends and saturation indices. The integrated approach used in this study
4 facilitated the identification of hydrological processes over different spatial and temporal
5 scales, and the method can be applied to other complex geological settings with variable
6 climatic conditions.

7

8 *Keywords: Groundwater/surface-water interactions, inter-aquifer connectivity,*
9 *hydrochemistry, isotopes, groundwater recharge*

10

11 **1 Introduction**

12 Alluvial aquifers are natural reservoirs of groundwater, buffering baseflow in river systems
13 and providing a reliable water supply during drier climatic phases (Winter et al., 1998).
14 Moreover, interactions between alluvial aquifers and their connected streams are essential
15 for the maintenance of healthy surface water and groundwater ecosystems (Boulton et al.,
16 1998; Hancock et al., 2005; Boulton et al., 2010; Anibas et al., 2012). Sustainable
17 management of these alluvial aquifers is critical, but to enable this, a good understanding of
18 recharge processes is required, together with an appreciation of the different groundwater
19 sources and the spatial variability of this recharge (Hrachowitz et al., 2011; Dogramaci et al.,
20 2012).

21 While it is generally recognised that recharge is variable over time, the influence of
22 episodic climatic events such as flooding are not very well understood. This is particularly
23 the case in alluvial aquifers where total recharge is often dominated by flood-related influxes
24 (e.g. Workman and Serrano, 1999). In these alluvial systems, recharge rates are commonly
25 elevated during floods, as a result of: (1) the enhanced permeability of the creek-bed during
26 the flood, due to scouring of the clogging layer by high velocity flows (e.g. Cendón et al.,
27 2010; Simpson and Meixner, 2012); (2) enlarged pathway between surface-and groundwater,
28 due to the increased width of the creek and the interface between groundwater and the creek
29 across which interaction can occur (e.g. Lange, 2005); and (3) the increased head gradient
30 between the creek and the stream (e.g. Rushton and Tomlinson, 1979). Owing to this
31 reliance on infrequent flooding and large rainfall events, alluvial aquifers are likely to be
32 severely impacted by the predicted changes in climatic patterns, such as the projected
33 increased frequency and severity of droughts and floods (Parry et al., 2007). This forecasted
34 climate change will impact on river flows (Arnell and Gosling, 2013) and groundwater

1 recharge processes (Green et al., 2011; Barron et al., 2012; Dawes et al., 2012). This is
2 particularly relevant for alluvial systems which are connected to ephemeral or intermittent
3 streams, as interactions between these streams and the alluvial aquifers are highly dependent
4 on antecedent rainfalls (Hughes et al., 2011).

5 The study area is a small subtropical catchment in southeast Queensland, Australia,
6 which was subject to severe climate extremes in recent years, including an extended drought
7 from the late 1990s through to approximately 2009, followed by heavy rains, which
8 culminated in a 1% annual exceedance probability (AEP) flood in January 2011 (Babister
9 and Retallick, 2011). This event provided a unique opportunity to study groundwater
10 recharge processes that result from episodic flooding.

11 Seepage to the alluvium from the underlying bedrock aquifers is potentially an
12 important source of recharge for the alluvium, but this process has not been verified. The
13 influx of poor quality groundwater, which is often associated with bedrock aquifers in the
14 study area, may negatively impact on the water-quality of the alluvial aquifer. Therefore, it is
15 important to identify and monitor areas where bedrock seepage occurs.

16 The objective of this study is to demonstrate how multiple environmental isotopes
17 ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H and ^{14}C) in combination with a comprehensive hydrochemical
18 assessment can be applied to: (1) assess the significance of floods as a major recharge
19 source; (2) identify recharge processes and connectivity between surface water and
20 groundwater; and (3) identify areas where the alluvium is recharged by the underlying highly
21 diverse bedrock (inter-aquifer connectivity). Multiple isotopes are increasingly being used to
22 identify inter-aquifer connectivity (e.g. Dogramaci and Herczeg, 2002; Raiber et al., 2009,
23 Cartwright et al., 2010a, 2012; Costelloe et al., 2012;; Baudron et al., 2014); nevertheless,
24 studies of this kind are still challenging due to the complexity of the hydrochemical
25 interactions that result from inter-aquifer groundwater flows.

26 Many studies have used surface- and groundwater compositions (i.e. isotopes, and
27 major and minor ions) to report on the connection between streams and alluvial groundwater
28 (e.g. Soulsby, 2007; Barrett et al., 1999; Kirchner et al., 2010; Mandal et al., 2011;
29 Morgenstern et al., 2010; Siwek et al., 2011; Négrel and Petelet-Giraud, 2005). However,
30 studies that use isotopes and hydrochemistry to assess the connectivity between alluvial
31 aquifers and intermittent or ephemeral streams (e.g. Kumar et al., 2009; Vanderzalm et al.,
32 2011), or report specifically on the effects of episodic groundwater recharge from flooding
33 (e.g. Cartwright et al., 2010b; Cendón et al., 2010; Simpson et al., 2013) are less common.
34 This study uses groundwater stable isotopes together with a detailed assessment of $\delta^2\text{H}$ and
35 $\delta^{18}\text{O}$ in rainfall to assess episodic recharge. Rainfall isotope time-series data are commonly

1 used to assess long-term trends in groundwater recharge (e.g. Zhu, et al. 2007, Praamsma et
2 al. 2009); however, they are rarely applied to assess event recharge of shallow aquifers (e.g.
3 Scholl et al. 2004; Gleeson et al. 2009). The value of considering time-series data of rainfall
4 stable isotopes in hydrogeological investigations is clearly demonstrated by this study, and
5 the outcomes will be important for the management of the alluvial groundwater resources of
6 the study area and for understanding flood-related processes in similar alluvial settings.

7 **2 Hydrogeological setting**

8 The Cressbrook Creek catchment covers an area of approximately 200 km² in southeast
9 Queensland, Australia. The area considered for this study extends from the Cressbrook Dam
10 in the headwaters to the confluence with the Brisbane River in the northeast; it excludes the
11 area up-gradient of Cressbrook Dam, which is a drinking water supply dam for the
12 Toowoomba City Council (Fig. 1). The topographically elevated areas in the southwest of the
13 catchment (ranging from 220 to 520 m Australian Height Datum, AHD) are forested and
14 mostly undeveloped, whereas alluvial plains along the drainage system host rich farm land
15 (>90% of the total alluvium by area), particularly in the lower part of the catchment to the
16 northeast (approximately 70 to 150 m AHD). In this part of the catchment, irrigators use up
17 to 3 GL of alluvial groundwater annually (DNRM, 2012), but groundwater abstraction is
18 often restricted due to low groundwater levels. With the construction of Cressbrook Dam in
19 1983, flow in Cressbrook Creek was further reduced, resulting in lower groundwater levels.
20 While water was initially released from the dam to recharge the alluvium, releases were
21 controversially phased out in the late 1990s due to drought-induced water shortages.

22 In this study, the catchment has been arbitrarily divided into four regions for ease of
23 discussion: the Catchment Headwaters, the Upper Catchment, the Mid Catchment and the
24 Lower Catchment (Fig. 2).

25 **2.1 Climate and surface water drainage**

26 Southeast Queensland is a subtropical region with hot, humid summers and dry, mild
27 winters. The average annual rainfall at Toogoolawah in the lower part of the catchment (Fig.
28 3) is 847 mm, although total annual rainfall can be highly variable, ranging from 366 to 1418
29 mm between 1909 and 2011 (Station number 040205; BOM, 2012). However, even in wet
30 years the diffuse recharge is limited by high evapotranspiration rates, with mean annual pan
31 evaporation rates of 1809 mm measured at Gatton (Fig. 1), located about 25 km to the south
32 of the study area (Harms and Pointon, 1999).

1 This climatic variability has been particularly evident in recent years, when below
2 average rainfall from 2000 to 2009 resulted in very low creek flow, especially from mid-
3 2006 until early 2008 when flow in the creek ceased completely (Fig. 4b). Due to that
4 extended drought, water levels at Cressbrook Dam in the headwaters of the catchment (Fig.
5 2) did not reach the overflow in the period between 1999 and early 2011, and there was no
6 flow from the dam to the creek. Despite the lack of outflow from the dam, intermittent flow
7 was recorded in Cressbrook Creek during this period of time (Fig. 4b), indicating that the
8 creek was recharged by both overland and groundwater contributions along its course. The
9 period of drought was then followed by two wet years (2010 and 2011), culminating in
10 significant flooding in January 2011 (Fig. 4b), approximately five months prior to the
11 sampling conducted during this study. As a result of this flooding, Cressbrook Dam reached
12 the overflow and discharged to Cressbrook Creek until 24 June 2011, with peak flows of
13 approximately $330 \text{ m}^3 \text{ s}^{-1}$. During the surface water sampling campaign (7–8 June 2011),
14 approximately $0.5 \text{ m}^3 \text{ s}^{-1}$ was discharging from Cressbrook Dam (Toowoomba Regional
15 Council, 2012) and Cressbrook Creek was flowing at approximately $0.7 \text{ m}^3 \text{ s}^{-1}$ at CC3 (Fig.
16 3; DNRM, 2013), indicating that the majority of flow in Cressbrook Creek was probably
17 derived from the dam during this period.

18 Groundwater hydrographs show that during the peak of the drought in 2008,
19 groundwater levels had dropped to approximately 4 to 5 m below the base of the creek in the
20 Lower Catchment. Additionally, the groundwater gradient in the Lower Catchment indicated
21 that the creek was losing during this drought period. However, groundwater levels recovered
22 following the flooding and heavy rain in 2010 to 2011. Subsequent to the flood, the
23 groundwater gradient reversed and Cressbrook Creek became a gaining stream in the Mid to
24 Lower Catchment (Fig. 3), suggesting that groundwater gradients between the alluvial
25 aquifer and stream are dynamic and dependent on the antecedent rainfall conditions.
26 However, it is apparent that the alluvium receives substantial recharge from Cressbrook
27 Creek in the Mid to Lower Catchment (King et al., 2014).

28 **2.2 Geology**

29 **2.2.1 Bedrock**

30 The alluvial aquifer system of Cressbrook Creek overlies bedrock of variable geology, with
31 volcanic rocks, metamorphic rocks and granodiorite prominent in the upper part of the
32 catchment (Fig. 2 and 3). Basaltic rocks are particularly prominent in the Upper Catchment,
33 whereas the bedrock in the Mid to Lower Catchment is composed mainly of the Mesozoic
34 sedimentary rocks of the Esk Formation. Primary porosities of these bedrock units are

1 generally low, but permeabilities are enhanced in some regions by weathering of
2 granodiorites and fracturing in other rocks (GSQ & IWSC, 1973).

3 The Esk Formation underlies many of the alluvial sampling sites in the Mid to
4 Lower Catchment (Fig. 3), and has a broad range of sedimentary strata and grain sizes
5 (Cranfield et al., 2001). Geological borehole logs (DNRM, 2012) confirm that this formation
6 is very heterogeneous, with clayey sandstones, feldspathic sandstones, shale and basalt, all
7 recorded at shallow depths within the Mid to Lower Catchment.

8 **2.2.2 Alluvium**

9 The alluvial system at Cressbrook Creek is characterised by fining-upwards sequences,
10 which typically consist of basal sands and gravels, overlain by silts and clays. Minor
11 carbonate veins have been identified within granodiorites (Zahawi, 1972). However, their
12 contribution to the alluvium, if any, has not been detected in X-ray diffraction (XRD)
13 analyses of sediments collected from Lake Wivenhoe, which is located downstream of the
14 confluence with the Cressbrook Creek and the Brisbane River (Fig. 1). In addition, no
15 carbonate was detected in the weathered granodiorite profile (Douglas et al., 2007) as any
16 potential carbonate particles are likely to dissolve. This apparent lack of carbonates implies
17 that radiocarbon dating of alluvial groundwaters is unlikely to be significantly affected by
18 interactions with carbonate minerals.

19 King et al. (2014) describe this complex, multi-layered alluvial system as a two-layer
20 system based on sediment grain size assessment. The basal coarse-grained layer consists
21 mostly of sands and gravels, whereas the upper low permeability layer is primarily
22 composed of fine-grained sediments such as silts and clays. This fining upwards sequence is
23 characteristic of many alluvial systems in eastern Australia (e.g. Cendón et al., 2010; Cox et
24 al., 2013), largely due to diminishing surface water flows in the late Quaternary (Knighton
25 and Nanson, 2000; Maroulis et al., 2007; Nanson et al., 2008). The thickness of the low
26 permeability layer increases with distance downstream, whereas the thickness of the basal
27 high permeability layer decreases down-gradient; these variations suggest that there is
28 probably less recharge in the lower parts of the catchment compared to the upper parts.

29 **3 Water sampling and analytical methods**

30 Surface and groundwater samples were collected in June and September 2011 from eight
31 surface water sites, 18 bores screened in the alluvial aquifer and eight bedrock bores. In
32 addition, two samples were collected from bores where the screened intervals (slotted section
33 of casing) encompass both the lower 1 – 2 m of the alluvium and the top 1 – 2 m of the

1 bedrock (B92 and B158); these sites are categorised as “bedrock sites” (Fig. 3). Alluvial
2 boreholes are less than 20 m deep and they usually have a 3 m long screened section at the
3 base of the alluvium, whereas bedrock boreholes are generally deep, except for three shallow
4 bores screened in the Esk Formation (Table 1).

5 Prior to sampling, three well volumes were pumped from the boreholes and the
6 specific (electrical) conductance (SC), temperature, redox potential (Eh) and pH were
7 monitored using a flow cell to ensure that these parameters had stabilised prior to sampling.
8 Field measurements were taken with a TPS 90 FL field meter, which was calibrated in
9 accordance with the manufacturer’s specifications prior to use.

10 **3.1 Major and minor ions**

11 Samples for major and minor cations (Na, K, Ca, Mg, Fe, Mn, Al and Sr) were collected in
12 acid-cleaned 125 mL HDPE (High Density Polyethylene) bottles and acidified to
13 approximately pH 2 using HNO₃. Cations were analysed at Queensland University of
14 Technology (QUT) by inductively coupled plasma optical emission spectroscopy (ICP-
15 OES). Samples for major anion analyses (Cl, NO₃, SO₄ and HCO₃) were collected in pre-
16 rinsed 250 mL HDPE bottles, with no further treatment until analysis, which was performed
17 at QUT using an automated discrete analyser (Seal AQ2), ion chromatography (Dionex ICS-
18 2100) and by manual titration for alkalinity.

19 **3.2 Isotopes**

20 Stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of groundwater and surface water samples collected during
21 this study were analysed using a Los Gatos Liquid Water Isotope Analyzer at the University
22 of New South Wales (after Lis et al., 2008). The $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC)
23 was analysed at GNS Science (New Zealand). Strontium isotopes were analysed using multi
24 collector-inductively coupled plasma mass spectrometry (MC-ICP-MS) at the University of
25 Melbourne following the methods described by Hagedorn et al. (2011). The internal
26 precision (2se) and external precision (2sd) for the MC-ICP-MS procedure is $\sim\pm 0.000020$
27 and ± 0.000040 , respectively. Tritium and radiocarbon were analysed at the Australian
28 Nuclear Science and Technology Organisation (ANSTO). For ^{14}C analysis, the total DIC was
29 converted to CO₂ using a custom built extraction line. The CO₂ sample was then graphitised,
30 graphite targets were analysed by AMS at ANSTO’s STAR accelerator following procedures
31 of Fink et al. (2004). Conventional radiocarbon ages were reported as percentage Modern
32 Carbon (pMC) with 1 σ errors of less than 0.37 pMC (Stuiver and Polach, 1977). Samples for
33 ^3H analysis were distilled and electrolytically enriched, and subsequently analysed using a
34 liquid scintillation counter. Results are reported in tritium units (TU) with an uncertainty of
35 ± 0.04 to 0.08 TU and quantification limits of 0.13 TU.

1 Rainfall from Brisbane Airport was collected as a monthly composite of daily rain
2 gauge samples, following the technical procedure recommended for GNIP
3 sampling (<http://www-naweb.iaea.org/napc/ih/documents/userupdate/sampling.pdf>).
4 Samples from June to October 2010 were analysed by Isotope Ratio Mass Spectrometry at
5 the CSIRO Land and Water Isotope Lab (Adelaide) (reported accuracy of ± 1.0 and $\pm 0.15\%$
6 for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively) or Alberta Innovates Technology Futures Isotope Hydrology
7 and Geochemistry Lab (reported accuracy of ± 1.0 , $\pm 0.2\%$ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively).
8 Samples from November 2010 to June 2011 were analysed at the ANSTO Institute for
9 Environmental Research using a Cavity Ring-Down Spectroscopy method on a Picarro
10 L2120-I Water Analyser (reported accuracy of ± 1.0 and $\pm 0.2\%$ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$,
11 respectively).

12 **3.3 Geochemical calculations**

13 Evaporation curves and saturation state calculations were performed using PHREEQC
14 (Parkhurst and Appelo, 1999). Evaporation curves were calculated under the assumption that
15 calcite, dolomite and gypsum precipitate when they reach saturation and are not re-dissolved.
16 Mineral stability diagrams were calculated after Drever (1997), using groundwater analyses
17 collected as part of this study.

18 **4 Aquifer testing methodology**

19 Rising/falling head tests were conducted in order to estimate the hydraulic conductivity of
20 the aquifer at each site. This information was consequently used to estimate recharge, as
21 described later in the study. Rising head tests were conducted using a bailer, or, for the more
22 permeable sites, two bailers joined end-to-end. Falling head tests were performed by pouring
23 water into the bore, and the response was measured using a pressure transducer that recorded
24 the water level at 1 second intervals. The hydraulic conductivity was then calculated using
25 the Hvorslev method (Hvorslev 1951).

26

27 **5 Results**

28 **5.1 Aquifer testing**

29 Hydraulic conductivity generally decreases with distance downstream, based on
30 falling/rising head tests that were conducted as part of this study (Table 2). Also, the more
31 permeable alluvium is generally located close to Cressbrook Creek.

1 **5.2 Hydrochemistry**

2 Surface waters are generally fresh ($SC < 850 \mu S \text{ cm}^{-1}$; Table 2) with similar proportions of
3 major cations (Na, Ca and Mg; Fig. 5). The major anions are Cl and HCO_3 and the Cl/ HCO_3
4 molar ratio of water from Cressbrook Creek ranges from 0.92 to 1.35, with ratios generally
5 increasing with distance downstream. Alluvial groundwaters are fresh to brackish (SC
6 369 to $5930 \mu S \text{ cm}^{-1}$) with no clear dominant major cations and low SO_4 concentrations, with
7 SO_4/Cl molar ratio ranges from 0.001 to 0.21. The Cl/ HCO_3 molar ratio ranges from 2.9 to
8 33.9, with ratios increasing with salinity. The hydrochemistry of the bedrock groundwaters is
9 highly variable, although the Na/Cl ratio is generally higher than in alluvial waters (Fig. 6).

10 **5.3 Mineralogy and geochemical interactions with groundwater**

11 To assess the interaction of groundwater with minerals in the soil zone and the aquifer
12 matrix, groundwater hydrochemical data was incorporated into silicate stability diagrams
13 (Fig. 7) to determine the relative stability of common silicate minerals in equilibrium with
14 groundwater collected from major bedrock aquifers (Esk Formation and the Eskdale Igneous
15 Complex) and the alluvium (Fig. 7). The silicate stability diagrams show that kaolinite is
16 usually in equilibrium with groundwaters from the Cressbrook Creek catchment, except for
17 Ca-rich minerals, which are generally in equilibrium with smectite.

18 **5.4 Stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$)**

19 Isotopic signatures for groundwater and surface water are compared to rainfall data collected
20 from Brisbane Airport and Toowoomba (Fig. 8) between May 2008 and May 2010 (Crosbie
21 et al., 2012), and new data collected by ANSTO between June 2010 and June 2011 (Table
22 4). Rainfall collected from the Brisbane Airport (Fig. 1), located approximately 60 km east
23 of the study site, is isotopically similar to rainfall collected from Toowoomba, which is
24 located approximately 20 km to the southwest (Fig. 8a; Crosbie et al., 2012). This suggests
25 that there is limited spatial variation in the study region, and that data from Brisbane and
26 Toowoomba are representative of the Cressbrook Creek catchment. The Brisbane Meteoric
27 Water Line (MWL) has a slope of 7.9 (Hughes and Crawford, 2012), which is close to the
28 global average of 8.2 (Rozanski et al., 1993). However, the deuterium excess (d) of 13.1‰ is
29 higher than the global average of about 10‰, as observed in other coastal eastern Australian
30 sites (Cendón et al., 2014), probably due to the influence of convective rainfall (Liu et al.,
31 2010).

32 During the 12 months prior to the June 2011 sampling campaign, rainfall stable isotope
33 signatures were depleted compared to previous rainfall events, particularly during, and
34 immediately prior to, the flooding in January 2011. Rainfall from December 2010 and

1 January 2011 (316 and 424 mm respectively; BOM, 2012) was particularly depleted in δ 2H
2 (-30.2 and -27.8, respectively) and δ 18O (-5.34 and -5.13, respectively; Table 4) compared
3 to the weighted average for rainfall, which was -3.4 and -12.7 for δ 2H and δ 18O
4 respectively (Crosbie et al. 2012). This confirms observations by Hughes and Crawford
5 (2013), who also noted that high precipitation rainfall events associated with east coast
6 pressure systems in Australia can be significantly depleted. The slope of the groundwater
7 evaporation line is approximately 3.1 (Fig. 8a).

8 **5.5 Strontium isotopes**

9 Strontium isotope ratios of surface and groundwaters in the Cressbrook Creek catchment
10 range from 0.7042 to 0.7119 (Fig. 9), although most samples are within a narrower range of
11 0.7051 to 0.7078. No measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rainwater were conducted for
12 the study area, and as a consequence, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rainfall used in this study (Fig.
13 9a) are based on data from elsewhere in Australia. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rainfall are
14 typically similar to modern seawater (0.7092; Dia et al., 1992) near the coast, but they
15 become progressively more radiogenic inland due to the addition of atmospheric dust.
16 Strontium isotope measurements of rainfall from Hamilton, Casterton and Willaura in
17 Victoria (south-eastern Australia), which are located approximately 60, 70 and 100 km from
18 the coast respectively, were 0.7094, 0.7097 and 0.7107 (Raiber et al., 2009). In comparison,
19 the rainfall $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured at Woodlawoolana located approximately 500-600 km
20 inland in South Australia is 0.71314 (Ullman and Collerson, 1994). The Cressbrook Creek
21 catchment is approximately 70 km from the eastern coast of Australia (Fig. 1). Assuming a
22 similar increase of the strontium isotope ratios of rainfall with increasing distance from the
23 coast, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Cressbrook Creek catchment may be in a similar range to
24 those reported by Raiber et al. (2009), although it is acknowledged that local factors and
25 temporal variability can have a substantial influence. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of
26 rainfall at Cressbrook Creek should not be significantly different to the range presented in
27 Fig. 9a, and any local variations would not affect the hydrological interpretation.

28 **5.6 Groundwater residence times**

29 Tritium and ^{14}C activities have been used to qualitatively assess groundwater residence times
30 in the alluvium and in the surface water of Cressbrook Creek. Tritium is particularly useful
31 for groundwater studies in the Southern Hemisphere, where ^3H activities of rainfall have
32 been about 2-3 TU for over 20 years (Morgenstern et al., 2010; Tadros et al., 2014). In
33 southeast Queensland, the ^3H activities of rainfall have been estimated to be in the range
34 of 1.6-2 TU for the period from 2005 to 2011 (Tadros et al., 2014). The ^3H activity of
35 rainfall is no longer affected by interference from bomb tritium, but is instead controlled by

1 natural cosmogenic production, allowing for a more accurate interpretation of groundwater
2 residence times using a single ^3H measurement (Morgenstern and Daughney, 2012).

3 The ^{14}C activities of DIC can also provide insight into groundwater residence times
4 and recharge processes. However, the interpretation of ^{14}C ages is often difficult, because ^{14}C
5 activities can be altered by geochemical processes that occur in the unsaturated- and
6 saturated zone (Plummer and Glynn, 2013). Nuclear weapons testing further complicated
7 interpretation of ^{14}C ages in modern samples by increasing atmospheric ^{14}C activities in the
8 1950s. The radiocarbon activity of alluvial groundwater in Cressbrook Creek catchment
9 ranges from 81.12 to 104.22 pMC (Table 3). Conventional radiocarbon ages calculated from
10 these data range from modern to 1,650 years BP. Two samples (B37 and B83) have modern
11 uncorrected ^{14}C ages, which correlate well with their relatively high ^3H activities of 1.08 and
12 1.15 tritium units (TU), respectively. This confirms that there is a substantial modern
13 groundwater component contained in these groundwaters.

14 The uncorrected ^{14}C ages of the samples collected from B57, B36, B18 and B51 are
15 55, 345, 1025 and 1680 years BP, respectively. However, it should be noted that the ^{14}C ages
16 have not been corrected for interactions with carbonate minerals. Tritium analyses of the
17 same samples (B57, B36, B18 and B51) indicate that they contain a modern component (i.e.
18 less approximately 70 years old), with values of 1.02, 0.70, 0.50 and 0.13 TU, respectively.

19 **6 Discussion**

20 **6.1 Origin of solutes and hydrochemical evolution**

21 **6.1.1 Hydrochemical facies**

22 Surface and groundwaters in the upper part of the catchment are generally fresh, with SC
23 values of $<700 \mu\text{S cm}^{-1}$ (Table 2; Fig. 3), whereas salinities are moderately higher in the
24 lower catchment. Five hydrochemical facies have been identified based on a visual analysis
25 of major ions proportions (Fig. 5). These hydrochemical facies differ slightly from those
26 presented by King et al. (2014), which were determined by hierarchical cluster analysis
27 (HCA) using major and minor ions and pH. Despite these differences, there are similarities
28 between the hydrochemical facies identified in this paper and the clusters derived using
29 HCA. For example, Hydrochemical Facies 5 of the current paper correlates well with
30 subclusters B2 and B3 of King et al. (2014) and Hydrochemical Facies 3 shares similarities
31 with subclusters A3 and 1.

32 Hydrochemical Facies 1 to 3 contain fresh water samples ($\text{SC} < 1150 \mu\text{S cm}^{-1}$; Table
33 5) and samples assigned to these facies have similar concentrations of Ca, Mg and Na (no

1 dominant cation), and low SO₄ concentrations (2.5 to 62.9 mg/L); therefore, these three
2 groups are mainly distinguished by the relative proportions of Cl to HCO₃. Hydrochemical
3 Facies 1 is mostly composed of fresh bedrock groundwater samples, but interestingly, it also
4 includes one surface water sample (Ock). This group is characterised by HCO₃-dominated
5 waters with molar HCO₃:Cl ratios of ≤5. Si concentrations are relatively high (median SiO₂
6 concentration of 43 mg/L) and low nitrate concentrations (median NO₃ concentration of 0.15
7 mg/L; Table 5). Hydrochemical Facies 2 and 3 are composed of fresh water samples with
8 slightly higher Cl concentrations than samples assigned to Hydrochemical Facies 1 (49 to
9 297 mg/L). Hydrochemical Facies 4 and 5 both contain brackish groundwaters (SC ranges
10 from 1145 to 13,750 μS cm⁻¹) with Cl as the dominant anion, but the samples in
11 Hydrochemical Facies 5 have a median NO₃ concentration of 4.0 mg/L, compared to those in
12 Facies 4 which have a median NO₃ concentration of just 0.19 mg/L (Fig. 5 and 6 and Table
13 5).

14 **6.1.2 Bedrock groundwater**

15 Bedrock groundwater samples have diverse hydrochemical compositions (Facies 1, 2 and 5;
16 Table 2) and ⁸⁷Sr/⁸⁶Sr ratios (Fig. 9), reflecting the wide range of bedrock types in the study
17 area including granodiorite, basalt, sandstone and shale. Hydrochemical end-members are
18 highly variable due to superimposed processes such as evaporation of water from the
19 unsaturated zone prior to groundwater recharge, transpiration, and mixing from multiple
20 sources. The dominance of HCO₃ for bedrock samples in the Upper Catchment
21 (Hydrochemical Facies 1) suggests that there are several potential processes that contribute
22 towards the observed patterns of major ion concentrations, including carbonate dissolution,
23 oxidation of organic matter, and silicate weathering. The latter can be assessed using
24 ⁸⁷Sr/⁸⁶Sr ratios and silicate stability diagrams.

25 Groundwaters from the Esk Formation (B229, B103 and B92; Fig. 3) typically have
26 low ⁸⁷Sr/⁸⁶Sr ratios (0.7042 to 0.7062), even though the weathered soils from this formation
27 are comparatively radiogenic (Fig. 9a) with values ranging from 0.7070 to 0.7115 and a
28 mean of 0.7090 (Douglas et al., 2007). This suggests that ⁸⁷Sr/⁸⁶Sr ratios of groundwaters
29 from the Esk Formation do not reflect the weathered whole-rock signature, but are instead
30 probably controlled by weathering of plagioclase. Weathering of anorthite (Ca-rich
31 plagioclase) releases ⁸⁶Sr (substituted for Ca) into groundwater, but very little ⁸⁷Sr is released
32 (McNutt, 2000), resulting in groundwaters with low ⁸⁷Sr/⁸⁶Sr ratios. Many other studies have
33 also reported similar observations where groundwater ⁸⁷Sr/⁸⁶Sr ratios are lower than the
34 whole rock ⁸⁷Sr/⁸⁶Sr ratios, attributed to the dominant influence of plagioclase dissolution
35 (e.g. Fritz et al., 1992; Richards et al., 1992; Made and Fritz, 1989). This plagioclase

1 dissolution process is supported by geochemical evidence, which shows that Esk Formation
2 soils are rich in smectite (Douglas et al., 2007), and that Ca-rich minerals of the Esk
3 Formation, such as anorthite, are likely to weather to smectite (Fig. 7), whereas minerals that
4 are rich in K, Na and Mg are likely to weather to kaolinite. Therefore, it appears as though
5 silicate weathering is a significant process affecting the major ion concentration of the
6 bedrock groundwaters, particularly in the Esk Formation.

7 **6.1.3 Alluvial groundwaters**

8 Alluvial groundwater evolution is marked by an increase in salinity (Fig. 5), longer
9 groundwater residence times, a decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Fig. 9b) and higher Cl/HCO_3 ratios
10 (Fig. 5). The more evolved groundwaters in Hydrochemical Facies 4 and 5 have probably
11 been subjected to higher degrees of evapotranspiration. Evaporation processes are evident
12 from stable isotopes measurements, which show that most samples collected during this
13 study are displaced significantly to the right of the Brisbane and Toowoomba MWL (Fig.
14 8a). This is in agreement with pan evaporation rates that far exceed the average annual
15 rainfall in the catchment (Section 2.1).

16 In addition to evaporation, transpiration also appears to be an important control of
17 groundwater salinity in some areas, as documented by elevated Cl and stable isotope
18 signatures that do not show any substantial influence of evaporation (Fig. 8b). However, Mg
19 and Ca concentrations of the samples from Hydrochemical Facies 4 are higher than would be
20 expected from evaporation, based on modelled evaporation curves from fresh water samples
21 from the Upper and Lower Catchment (Fig. 6).

22 Similarly, the Na concentrations are lower than expected from the evaporation curve,
23 suggesting that the groundwater composition of samples assigned to Hydrochemical Facies 4
24 have been influenced by interactions with aquifer materials. As carbonate rocks are absent in
25 the alluvium of this catchment, weathering of silicate minerals appears to be the most likely
26 source of dissolved ions. This is also supported by a moderate correlation between ^3H and
27 the saturation indices (SI) of albite ($R^2 = 0.45$; Fig. 9d), compared to the weak correlation
28 between ^3H and calcite SI ($R^2 = 0.24$; Fig. 9e). Furthermore, many of these more evolved
29 waters have Ca/HCO_3 ratios (and Mg/HCO_3 ratios) that are higher than the 1:2 molar ratio
30 that could be expected from the dissolution of carbonates alone (Fig. 6; Appelo and Postma,
31 2005).

32 It is likely that this increase in Ca and Mg is augmented by dissolution of mafic
33 minerals such as olivine, pyroxene and anorthite, which are commonly present in basaltic
34 rocks such as those in the Mid to Upper Catchment (Palaeozoic rocks; Fig. 3). Alluvial
35 sediments probably contain detrital material that was eroded off these basalts, providing a

1 source of Ca and Mg for alluvial groundwaters and surface waters in the lower part of the
2 catchment. This is supported by XRD analyses, which show that there are significant
3 amounts of smectite in weathered sediments sampled from Lake Wivenhoe (Fig. 1; Douglas
4 et al., 2007), and silicate stability diagrams (Fig. 7) demonstrate that the smectite is probably
5 the result of the weathering of Ca-rich minerals such as anorthite.

6 In contrast to Hydrochemical Facies 4, the samples from Hydrochemical Facies 5
7 have followed a different evolutionary pathway (Fig. 5): groundwaters that are members of
8 Hydrochemical Facies 5 generally have longer residence times (Table 5), higher Na
9 concentrations (Fig. 5) and its groundwater evolution more closely follows an evaporative
10 trend (Fig. 6). Nevertheless, the evaporation curve (Fig. 6) indicates that Ca and Mg
11 concentrations are still higher than expected if evaporation alone was the controlling factor,
12 suggesting that the dissolution of silicates is also an important process influencing the
13 chemistry of these waters.

14 **6.2 Radiocarbon groundwater residence times**

15 The uncorrected ^{14}C ages of the samples collected from B18 and B51 are 1025 and 1680
16 years BP, respectively; however, tritium analyses indicate that this groundwater has a
17 modern component. This discrepancy between the apparent tritium ages and the ^{14}C ages
18 indicates that the ^{14}C activity may have been altered by carbonate dissolution, or
19 alternatively, that there has been mixing between an older water component and a younger
20 water component that contains tritium.

21 The Ca:Na ratio of the alluvial groundwaters ranges from 0.19 to 1.00, with an
22 average of 0.54 and the Ca/Na ratio of the samples from B18 and B51 are 0.19 and 0.24.
23 This indicates that significant calcite dissolution is unlikely, as groundwaters that have
24 experienced significant calcite dissolution generally have Ca/Na ratios >1 (Mast et al., 1990;
25 Leybourne et al., 2006).

26 Calcite dissolution can also be assessed using the $\delta^{13}\text{C}_{\text{DIC}}$ composition, which is
27 affected by interactions with organic materials and the aquifer substrate. The $\delta^{13}\text{C}_{\text{DIC}}$
28 composition of recharging groundwater is largely controlled by the composition of the
29 decomposing plant matter. For plants that use the C_3 photosynthesis, the $\delta^{13}\text{C}_{\text{DIC}}$ composition
30 of the soil is usually around -23% , whereas it is likely to be approximately -9% in areas
31 with C_4 plants (Clark & Fritz, 1997). The study catchment is located in a water-poor area and
32 plant productivity is often limited by the lack of water. Therefore, landholders commonly
33 cultivate plants that use water efficiently, such as those that use the C_4 carbon fixation
34 pathway (e.g. corn and sorghum). However, some drought resistant plants that use the C_3
35 carbon fixation pathway (e.g. Lucerne) are also cultivated. Similarly, approximately 74% of

1 grass species in the Cressbrook Creek region use the C₄ carbon fixation pathway (Hattersley,
2 1983).

3 Assuming that approximately 60% to 90% of the ¹³C is derived from plants
4 that use the C₄ carbon fixation pathway, soil CO_{2(g)} δ¹³C_{DIC} values would be
5 approximately -15‰ to -10‰. The δ¹³C_{DIC} value will typically increase by around
6 7.9‰ as soil CO_{2(g)} dissociates to HCO₃⁻ (at 25⁰ C; Clark & Fritz, 1997), which will
7 result in groundwater with δ¹³C_{DIC} values between around -7‰ and -2‰. The
8 δ¹³C_{DIC} values at B18 and B51 are -4.4 and -4.9, indicating that there has probably
9 been no significant dissolution of old calcite, and that the uncorrected ¹⁴C ages are
10 valid. This is not unexpected, as the alluvium is composed primarily of components
11 derived from erosion of silicate rocks, and it is unlikely to contain significant
12 amounts of carbonate.

13 **6.3 Hydrological processes, recharge and the impact of flooding**

14 **6.3.1 Cressbrook Creek and Cressbrook Dam**

15 Surface water samples from Cressbrook Creek follow an evaporative trend line that
16 intersects the meteoric waterline near the flood-generating rainfall (Fig. 8a). Cressbrook
17 Dam was overflowing into Cressbrook Creek at the time of sampling (Toowoomba Regional
18 Council, 2012), and water from the dam appears to be dominated by depleted heavy rainfall
19 from December 2010 and January 2011. This is not surprising, as the storage volume of
20 Cressbrook Dam was at record low levels (7.5% of total capacity) in February 2010
21 (Toowoomba Regional Council, 2014). In addition, rainfall in the Catchment Headwaters
22 and at Cressbrook Dam may be further depleted due to the altitude effect, as the dam is
23 approximately 250 m AHD and the surrounding hills reach elevations of more than 500 m
24 AHD.

25 Stable isotopes were a valuable tool for the identification of episodic recharge in this
26 study. Previous studies have used stable isotopes to link groundwater recharge with high
27 precipitation rainfall events. For example, Cendon et al. (2010), compared alluvial
28 groundwater isotope signatures with the weighted average isotopic signatures of rainfall
29 events that were greater than 95 mm. However, it is rare to use stable isotopes to assess
30 groundwater recharge from an individual flood event.

31 **6.3.2 Upper Catchment**

32 In the Upper Catchment, recharge to the alluvium is dominated by diffuse infiltration of
33 rainfall rather than channel leakage (Fig.10a and 10b). This is supported by evidence that

1 indicates that the stream is gaining in this part of the catchment, including field observations
2 of groundwater discharge into the stream in the Upper Catchment, the sustained flow in
3 Cressbrook Creek during years when there was no discharge from Cressbrook Dam and the
4 increase in discharge volume between Cressbrook Dam and CC3 (Fig. 3) at the time of
5 sampling (Section 2.1). Groundwater is recharged rapidly in this part of the catchment, based
6 on the low salinity (Fig. 3). In addition, the comparison of the high groundwater ^3H activities
7 (Table 3) with the rainfall ^3H activities presented by Tadros et al. (2014) for the period from
8 2005-2011 for southeast Queensland and stream waters analysed during this study confirms
9 that a high component of groundwater consists of very recent recharge. This documents the
10 usefulness of ^3H to assess recharge processes to alluvial aquifers, as previously highlighted
11 by other studies elsewhere (e.g. Cartwright and Morgenstern, 2012; Baudron et al. 2014).

12 Groundwater major ions and stable isotopes from samples collected near the
13 confluence of Cressbrook Creek and Kipper Creek are similar to the surface water sample
14 collected from Kipper Creek (KC1; Fig. 3), suggesting that Kipper Creek receives baseflow
15 from the alluvium in the vicinity of KC1. As there was no flow in Kipper Creek in the
16 Catchment Headwaters at the time of sampling, the creek must have received groundwater
17 baseflow in the Upper Catchment (i.e. near KC1). The stable isotope signature of
18 groundwaters collected from the Upper Catchment and surface water from Kipper Creek is
19 intermediate to the evaporation trends that originate from the flood-generating rainfall and
20 the longer-term weighted average rainfall value. This suggests that recharge is sourced from
21 the flood and from smaller rainfall events that occurred subsequent to the flood. However,
22 the sample collected from Cressbrook Creek in the Upper Catchment has a more depleted
23 stable isotope signature than other surface waters or groundwater samples from the Upper
24 Catchment, probably because water in Cressbrook Creek has a high proportion of
25 isotopically depleted flood runoff and quick flow from Cressbrook Dam (Section 5.3.1).

26 The sample collected from Oaky Creek (Ock; Fig. 3) is grouped in a different
27 hydrochemical facies to other surface water samples. This sample has been assigned to
28 Hydrochemical Facies 1, together with bedrock samples collected from the Upper
29 Catchment, including a sample collected from the granodiorite foothills in the Oaky Creek
30 sub-catchment (B104; Fig. 3). The bedrock appears to have a major impact on the chemical
31 composition of the water in Oaky Creek, probably because the alluvial aquifer is thin and
32 narrow in the Oaky Creek sub-catchment and because the upper layers of granodiorite are
33 highly weathered, and therefore comparatively permeable. This permeable weathered
34 granodiorite probably provides baseflow to Oaky Creek.

6.3.3 Mid to Lower Catchment

Most groundwaters from the lower part of the catchment also follow the evaporative trend that intersects the meteoric water line near the flood-generating rainfall of December 2010 and January 2011, indicating that groundwater was recharged rapidly by channel leakage and/or that the flood generated substantially more recharge than other smaller rainfall events. Heavy rainfall events often have depleted stable isotope signatures, as suggested by the depleted signatures of rainfall in December 2010 and January 2011 (Table 5), and observations elsewhere (e.g. Hughes and Crawford, 2013). In addition, the most devastating flood to affect southeast Queensland occurred in 1974, and the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of rainfall during this event were -64.2‰ and -9.5‰, respectively (IAEA/WMO, 2014).

In the Lower Catchment, fresh groundwaters with short residence times, such as those contained in Hydrochemical Facies 2 and 3, are probably recharged rapidly by surface waters (Fig. 10c and 10d). These sites are generally located close to the creek and it appears as though groundwater quality is significantly improved due to interactions with surface water in this part of the catchment, confirming the observation from King et al. (2014). These groundwater-surface water interactions also appear to affect surface water compositions, as is evident from observed changes in the chemical composition of Cressbrook Creek with distance downstream. This includes an: 1) an increase in total dissolved salts (Fig. 3); 2) an increase in the apparent water age, as indicated by the ^3H activities at CC1 (Upper Catchment; 1.60 TU) and CC6 (Lower Catchment; 1.44 TU; Table 3); 3) enrichment of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$; Fig. 8b); and 4) a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 9a).

Groundwater-surface water interactions are subjected to a large degree of temporal and spatial variations due to the losing/gaining nature of the stream. Cressbrook Creek is generally losing after high flow events, such as the flood of January 2011, but turns into a gaining stream after this event (Fig. 4). Similarly, the losing/gaining condition of the stream is likely to vary spatially as a result of changes in the streambed elevation (riffles and pools) and groundwater levels (Winter et al. 1998).

The more evolved groundwater samples from the Mid and Lower Catchment (Hydrochemical Facies 4 and 5) were generally collected from alluvial wells that are located further away from the creeks (Fig. 3) and/or where the unsaturated zone is thick (e.g. >10 m). These sites are also located in areas where the alluvium is less permeable, suggesting that infiltrating rainfall from small rainfall events is subjected to a significant degree of evapotranspiration processes during infiltration through the unsaturated zone, and large rainfall events are probably required to generate groundwater recharge. Therefore, it is likely

1 that these more evolved waters are predominately recharged during high rainfall events, such
2 as those associated with the flooding in January 2011.

3 **6.4 Hydraulic connectivity between bedrock and alluvium**

4 Tritium data show that alluvial groundwaters assigned to Hydrochemical Facies 5 have
5 relatively long residence times (B90, B18 and B51, Table 5). In particular, the low ^3H
6 activities from B18 and B51 (0.50 and 0.13 TU, respectively) indicate that older bedrock
7 groundwater could be interacting with the alluvium at these sites. Furthermore, the sample
8 collected from B158, which is screened in both the alluvium and the bedrock, is also
9 included in Hydrochemical Facies 5.

10 The sample from B90 has a stable isotope signature that indicates a substantial
11 degree of evaporation (Fig. 8), whereas other alluvial samples assigned to Hydrochemical
12 Facies 5 (B51 and B18) are isotopically more depleted. As previously mentioned, alluvial
13 groundwaters assigned to Hydrochemical Facies 5 were probably subjected to significant
14 amounts of evaporation. However, groundwater samples from sites B18 and B51 (Fig. 3)
15 have a relatively depleted stable isotope signature considering their high Cl concentrations
16 (Fig. 8), which suggests that these sites may have received seepage from depleted bedrock
17 groundwater.

18 This was independantly confirmed by the use of strontium isotopes, which are
19 ideally suited for the assessment of seepage from basalts and granitic rocks to the alluvium
20 due to their distinguishable signatures resulting from their contrasting mineralogy and the
21 very different ages of the rocks. This study builds on work by Raiber et al. (2009), who used
22 strontium isotopes to investigate interaction of groundwater with basalts and granitic rocks in
23 south-western Victoria, Australia. The groundwater sample from B18 has a radiogenic
24 $^{87}\text{Sr}/^{86}\text{Sr}$ signature similar to groundwater sampled from the granodiorite, which forms the
25 bedrock at this site, and sample B51 has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio similar to the Esk Formation
26 samples (Fig. 9a). Also, the ^{14}C groundwater ages of samples from B18 and B51 are greater
27 than 1,000 years BP, but there is detectable tritium in these samples, indicating that the water
28 is less than approximately 100 years old. This discrepancy is consistant with mixing of old
29 bedrock groundwater with younger alluvial groundwater.

30 Overall, the isotopic evidence (groundwater ^{14}C , $\delta^{13}\text{C}$, stable isotopes and $^{87}\text{Sr}/^{86}\text{Sr}$
31 ratios) confirms that the aquifer at sites B18 and B51 receives seepage from the underlying
32 bedrock. Interestingly, the only other two samples with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios below the 99%
33 confidence interval (Fig. 9a) are the samples from B36 and B57, which were also collected
34 from monitoring bores overlying the Esk Formation. Furthermore, apart from B18 and B51,
35 they are the only other two samples with non-modern uncorrected ^{14}C ages, and they have

1 relatively depleted stable isotope signatures, suggesting that the alluvial aquifer at these sites
2 has probably also received seepage from the underlying bedrock aquifer. Moreover, there is
3 a strong correlation ($R^2 = 0.94$) between ^3H and ^{14}C activities (Fig. 9c), which suggests that
4 the samples from B57 and B36 have been affected by similar hydrological processes (i.e.
5 bedrock seepage) as the samples from B51 and B18.

6

7 **7 Conclusions**

8 This study outlines the benefits of the simultaneous application of multiple environmental
9 isotopes (^2H , ^{18}O , $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H and ^{14}C) in rainfall, groundwater and surface water in
10 combination with a comprehensive hydrochemical assessment. The aim was to study the
11 influence of a flood on groundwater recharge and to assess the hydrological connectivity of
12 an alluvial aquifer system with associated streams and underlying highly diverse bedrock
13 aquifers.

14 Groundwater evolution is largely controlled by silicate dissolution and
15 evapotranspiration processes, as demonstrated by the silicate stability diagrams, theoretical
16 evaporation curves and saturation indices. In the Upper Catchment, rainfall is quickly
17 recharged through relatively coarse-grained alluvial sediments. Conversely, rainwater
18 infiltrates more slowly in the Mid and Lower Catchment, particularly in the flood-plain distal
19 to Cressbrook Creek, as indicated by the lower tritium and ^{14}C values and the elevated
20 salinity. In contrast, surface water leakage to the alluvial aquifer is an important mechanism
21 for maintaining groundwater quality and for the generation of recharge in the lower part of
22 the catchment.

23 The flood-generating rainfall in 2011 was isotopically more depleted ($\delta^2\text{H}$ and $\delta^{18}\text{O}$)
24 than the long-term weighted average, and groundwater from the lower part of the catchment
25 plots along an evaporative trend line that intersects the meteoric water line near this depleted,
26 flood-generating rainfall of December 2010 and January 2011. This confirmed that the flood
27 events of January 2011 generated significant recharge, whereas infiltrating water from
28 smaller rainfall events is subject to evapotranspiration, especially in the lower part of the
29 catchment where the unsaturated zone is relatively thick and the permeability is low.
30 Recharge from episodic flooding is probably important in other similar settings where low
31 permeability sediments are incised by stream channels. Groundwater in the Upper
32 Catchment follows an evaporative trend initiated from rainfall that is intermediate to the
33 long-term weighted average rainfall and the “flood rainfall”. The floods of 2011 also
34 generated significant recharge in this part of the catchment. However, as the evaporative

1 trend is initiated from a more enriched rainfall signature (i.e. closer to the long-term
2 weighted average), it appears likely that smaller rainfall events also generate groundwater
3 recharge here, probably due to the more permeable and thinner soil material in this part of
4 the catchment. The study clearly demonstrated the value of time-series rainfall stable isotope
5 data for the identification of hydrological processes such as aquifer recharge and the
6 generation of baseflow resulting from flooding.

7 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were used to identify bedrock seepage to the alluvium at several
8 locations. This conclusion was supported by the ^3H and ^{14}C data, which show that the
9 alluvium contains a mixture of older, bedrock derived groundwater and more recently
10 recharged groundwater. The connectivity between the alluvium and the bedrock is likely to
11 be spatially and temporally variable.

12 The complementary use of multiple isotopes and hydrochemistry of rainfall,
13 groundwater and surface water enabled an effective assessment of hydrological processes
14 throughout the catchment, including recharge of the alluvial deposits from surface water
15 flows and variable bedrock aquifers, recharge specifically from flood events and an
16 understanding of isotopic and hydrochemical parameters in the context of variable climatic
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Table 1. Geological description of bedrock hydrochemical sampling sites (DNRM, 2012).

ID	DNRM Aquifer Description	DNRM Aquifer Interpretation	Inferred Aquifer	Depth of well (m below ground level)
B16	Conglomerate	Esk Fm	Esk Fm	10.0
B92	Alluvium (0.4 m)	Alluvium	Both alluvium and the	14.2
	Sandstone (2.6 m)	Esk Fm	Esk Fm	
B158	Alluvium (2.0 m)	Alluvium	Both alluvium and the	13.6
	Sandstone (1.0 m)	Esk Fm	Esk Fm	
B103	Sandstone	Esk Fm	Esk Fm	24.7
B229	No Record	No Record	Esk Fm	>50.0
B256	Basalt and shale	No Record	Pinecliff Fm	40.5
B546	Basalt	No Record	Pinecliff Fm	68.6
B104	Granite	No Record	Eskdale Igneous Complex	64.0
B251	Shale	No Record	Maronghi Creek Beds	49.5

Note: The screened (slotted) section is 3 m long at B92 and B158. The values in parentheses in column 2 represent the length of the screened section that is encompassed by each geological material.

Table 2. Hydraulic conductivities from falling/rising head tests in the alluvium of the Cressbrook Creek catchment..

Well	Hydraulic conductivity (m/day)	Catchment area	Distance from surface water (m)
B74	17	Upper	310
B18	0.02	Mid	440
B21	14	Mid	120
B90	50	Mid	310
B89	30	Mid	120
B158	22	Lower	210
B36	9.5	Lower	540
B33	2	Lower	20
B37	0.015	Lower	530
B93	25	Lower	50
B82	7.5	Lower	130
B83	2.2	Lower	80
B51	0.005	Lower	50
B44	0.001	Lower	260
B57	4	Lower	180

1 Table 3. Hydrochemical data for surface and groundwater samples from Cressbrook Creek catchment.

Sampling Site	Date	Geology	Sub-catchment	Depth to base of casing (m)	HF facies	pH	SC ($\mu\text{S cm}^{-1}$)	Eh (mV)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)	Sr (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	NO ₃ -N (mg/L)	SiO ₂ (mg/L)	%CBE
B157	15/06/2011	Alluvium	Lower	7.2	4	6.4	1145	80	57	11.1	28	67	0.58	7.00	0.38	284	41.4	59.2	0.01	1.26	38.7	-8.6
B18	14/06/2011	Alluvium	Mid	9.5	5	6.7	4140	-55	460	2.1	141	194	1.20	5.30	1.11	1122	19.1	310.6	0.14	0.19	39.1	5.3
B21	14/06/2011	Alluvium	Mid	13	2	6.7	720	-180	51	1.2	27	49	1.10	1.40	0.25	106	42.0	206.0	0.07	0.17	35.3	-2.9
B33	14/06/2011	Alluvium	Lower	10.4	2	6.7	492	-21	40	1.3	15	27	0.81	0.45	0.16	86	10.8	140.3	0.05	0.10	27.2	-6.2
B36	14/06/2011	Alluvium	Lower	15.2	3	6.3	651	42	39	1.8	20	42	0.23	0.53	0.34	152	4.5	100.8	0.01	0.09	43.8	-4.7
B37	22/06/2011	Alluvium	Lower	9.4	4	7.2	4750	-330	360	22.0	321	630	0.31	0.20	4.22	2663	17.4	182.1	0.26	11.68	37.4	-3.4
B44	19/09/2011	Alluvium	Lower	12.8	3	7.0	708	35	51	0.6	29	55	0.02	0.32	0.38	183	13.0	145.3	0.09	3.07	49.4	-4.2
B51	8/06/2011	Alluvium	Lower	13.7	5	6.7	5930	-60	690	1.6	228	231	0.05	8.80	3.71	1711	43.9	699.0	0.32	0.98	42.6	-0.3
B57	19/09/2011	Alluvium	Lower	14.7	4	6.8	1251	-160	73	0.8	55	110	0.06	2.20	0.8	384	18.9	122.6	0.06	3.01	48.1	-1.2
B74	7/06/2011	Alluvium	Upper	7.9	2	6.6	587	45	44	1.9	26	35	0.04	0.00	0.25	82	46.4	158.8	0.04	2.99	26.3	-2.4
B76	21/06/2011	Alluvium	Upper	8.0	2	6.6	369	-60	36	1.3	19	28	0.04	0.00	0.19	83	13.8	157.9	0.04	0.29	30.8	-7.4
B82	15/06/2011	Alluvium	Lower	14	3	6.7	1110	170	70	1.1	38	66	0.55	0.00	0.44	297	36.4	177.1	0.06	0.89	34.0	-12.0
B83	15/06/2011	Alluvium	Lower	9.5	4	6.3	1422	180	74	1.0	49	90	0.16	0.00	0.68	344	3.9	125.2	0.02	4.96	49.8	-2.0
B89	8/06/2011	Alluvium	Mid	12.3	3	6.4	938	-25	50	1.3	41	66	0.61	2.10	0.37	203	40.8	173.9	0.03	0.03	31.7	-3.0
B90	14/06/2011	Alluvium	Mid	9.4	5	6.5	1880	130	150	1.2	68	100	0.00	0.00	0.83	491	30.5	169.6	0.04	3.68	48.8	-1.2
B91	21/06/2011	Alluvium	Mid	11.5	2	6.8	468	-60	47	1.8	22	35	0.89	11.00	0.21	111	27.9	136.3	0.05	0.42	29.7	-3.3
B93	8/06/2011	Alluvium	Lower	16.5	3	6.4	1082	-5	65	1.9	42	67	2.10	3.70	0.43	266	20.8	131.8	0.02	0.10	35.9	-2.3
B837	21/06/2011	Alluvium	Upper	15.8	3	6.5	454	26	37	0.9	26	40	0.00	0.00	0.25	92	41.4	103.6	0.02	2.78	35.1	3.5
B158	14/06/2011	Both Alluvium & Bedrock	Lower	13.6	5	6.4	2770	110	260	1.1	79	150	0.04	0.00	1.15	785	12.3	250.0	0.05	0.17	40.9	-2.3
B92	15/06/2011	Both Alluvium & Bedrock	Lower	14.2	1	6.4	403	-47	29	1.5	10	18	0.36	22.00	0.16	40	5.0	133.9	0.02	0.03	44.3	-5.9
B103	15/06/2011	Bedrock	Lower	24.7	5	6.5	13750	-60	1350	3.4	555	650	0.58	0.00	10.3	4415	193.9	679.6	0.30	0.02	29.9	-1.0
B104	19/09/2011	Bedrock	Upper	64	1	7.3	437	210	42	1.5	17	43	0.00	0.05	0.12	34	2.5	287.7	0.38	0.38	64.8	-3.3
B16	15/06/2011	Bedrock	Upper	10	2	7.0	614	-61	38	1.9	21	37	0.41	0.94	0.23	99	14.8	143.5	0.08	0.24	37.9	-1.7
B229	21/06/2011	Bedrock	Lower	>50	1	7.4	787	-15	120	0.5	20	59	0.05	0.00	0.84	190	4.1	279.3	0.46	0.11	42.3	-1.2
B251	16/06/2011	Bedrock	Mid	49.5	1	7.3	898	150	67	0.7	43	120	0.02	0.00	0.34	127	37.7	516.8	0.63	0.42	30.4	-1.8
B256	21/06/2011	Bedrock	Upper	40.5	1	7.0	501	115	79	5.4	18	31	0.00	0.00	0.18	90	2.9	320.3	0.18	0.19	58.8	-8.5
B546	21/06/2011	Bedrock	Upper	68.6	2	6.4	497	25	49	3.1	20	49	0.17	0.00	0.35	104	62.9	158.4	0.03	1.33	29.7	-4.8
CC1	7/06/2011	Surface Water	Upper	N/A	2	7.0	295	75	22	2.7	13	18	0.03	0.32	0.11	49	12.4	86.6	0.05	0.16	15.8	-1.6
CC2	7/06/2011	Surface Water	Mid	N/A	2	7.5	356	110	25	2.3	15	20	0.02	0.32	0.12	59	10.0	110.3	0.20	0.17	17.8	-4.9
CC4	8/06/2011	Surface Water	Mid	N/A	2	7.6	415	120	29	2.1	18	24	0.03	0.14	0.28	71	10.7	133.1	0.32	0.04	19.2	-5.2
CC5	8/06/2011	Surface Water	Lower	N/A	2	7.6	572	38	38	2.4	24	35	0.16	0.27	0.21	107	11.8	140.8	0.34	0.06	20.1	-1.0
CC6	7/06/2011	Surface Water	Lower	N/A	2	7.5	602	140	39	2.4	25	36	0.10	0.13	0.23	113	17.6	144.3	0.25	0.15	20.7	-2.6
KC1	7/06/2011	Surface Water	Upper	N/A	3	6.8	540	73	33	1.8	26	28	0.01	0.00	0.09	103	27.9	79.2	0.03	0.18	18.8	2.0
Ock	8/06/2011	Surface Water	Mid	N/A	1	7.2	543	110	39	0.9	22	43	0.02	0.00	0.13	73	16.4	234.8	0.23	0.02	34.2	-4.8
BR1	8/06/2011	Surface Water	Lower	N/A	2	7.0	829	110	65	2.6	37	54	0.06	0.00	0.45	162	12.6	199.9	0.13	0.19	21.6	2.9

2 Note: %CBE = percentage charge balance error.
 3 Sub-catchment boundaries are shown in Fig. 3..
 4
 5

6 Table 4. Water isotopic and hydrochemical data for surface and groundwater samples from the Cressbrook Creek catchment. Saturation indices (SI) for calcite and albite were calculated using PHREEQC (Parkhurst and Appelo, 1999).

Sampling Site	Geology	Sub-catchment	Water type	$\delta^{18}\text{O}$	$\delta^2\text{H}$	Deuterium excess (<i>d</i>)	Tritium (TU)	$\delta^{13}\text{C}$ (‰)	^{14}C (pMC)	^{14}C Uncorrected Age (yrs BP)	$^{87}\text{Sr}/^{86}\text{Sr}$	Calcite (SI)	Albite (SI)
B157	Alluvium	Lower	Ca-Na-Mg-Cl	-3.6	-23.8	4.82					0.70638	-1.68	1.24
B18	Alluvium	Mid	Na-Mg-Ca-Cl	-3.7	-22.6	6.83	0.50	-4.4	88.02	1025	0.70702	-0.27	-0.47
B21	Alluvium	Mid	Ca-Mg-Na-HCO3-Cl	-2.8	-17.4	4.81	1.17				0.70705	-0.82	-1.48
B33	Alluvium	Lower	Na-Ca-Mg-Cl-HCO3	-4.0	-24.8	6.91					0.70677	-1.16	-0.59
B36	Alluvium	Lower	Ca-Na-Mg-Cl-HCO3	-3.8	-23.8	6.49	0.70		95.81	345	0.70580	-1.52	-0.15
B37	Alluvium	Lower	Ca-Mg-Na-Cl	-2.5	-16.1	4.33	1.08		104.22	Modern	0.70628	0.34	1.64
B44	Alluvium	Lower	Ca-Mg-Na-Cl-HCO3	-4.5	-28.8	7.09	0.88				0.70629	-0.66	-0.98
B51	Alluvium	Lower	Na-Mg-Cl	-3.6	-21.2	7.30	0.13	-4.9	81.12	1680	0.70509	0.07	1.62
B57	Alluvium	Lower	Ca-Mg-Na-Cl	-4.7	-29.4	8.33	1.02		99.32	55	0.70571	-0.62	-0.89
B74	Alluvium	Upper	Mg-Na-Ca-HCO3-Cl	-3.4	-19.6	7.43					0.70664	-1.12	-1.96
B76	Alluvium	Upper	Na-Mg-Ca-HCO3-Cl	-3.0	-18.2	5.70	1.40				0.70667	-1.22	-0.63
B82	Alluvium	Lower	Ca-Mg-Na-Cl-HCO3	-3.7	-22.1	7.12	1.14				0.70660	-0.83	0.20
B83	Alluvium	Lower	Ca-Mg-Na-Cl	-4.0	-22.9	8.96	1.15		100.38	Modern	0.70607	-1.28	0.42
B89	Alluvium	Mid	Mg-Ca-Na-Cl-HCO3	-3.2	-22.2	3.57	1.66				0.70705	-1.08	-1.83
B90	Alluvium	Mid	Na-Mg-Ca-Cl	-2.1	-14.6	2.49	1.23				0.70631	-0.88	-0.73
B91	Alluvium	Mid	Na-Mg-Ca-Cl-HCO3	-3.3	-21.2	5.61					0.70687	-1.07	-1.72
B93	Alluvium	Lower	Mg-Ca-Na-Cl-HCO3	-4.2	-25.2	8.24					0.70687	-1.21	0.69
B837	Alluvium	Upper	Mg-Ca-Na-Cl-HCO3	-3.7	-21.1	8.44	1.46				0.70688	-1.14	-1.76
B158	Both Alluvium & Bedrock	Lower	Na-Ca-Mg-Cl	-3.4	-22.0	5.51					0.70617	-0.72	0.90
B92	Both Alluvium & Bedrock	Lower	Na-Ca-Mg-Fe-HCO3-Cl	-2.1	-15.1	2.00					0.70573	-1.67	-1.55
B103	Bedrock	Lower	Na-Mg-Ca-Cl	-3.4	-22.2	4.66					0.70555	0.18	1.61
B104	Bedrock	Upper	Ca-Na-Mg-HCO3	-5.4	-31.8	11.10					0.71186	-0.06	-0.66
B16	Bedrock	Upper	Ca-Mg-Na-Cl-HCO3	-2.4	-15.9	3.30					0.70615	-0.81	-0.01
B229	Bedrock	Lower	Na-Ca-Cl-HCO3	-4.1	-25.5	7.52					0.70422	0.08	0.75
B251	Bedrock	Mid	Ca-Mg-Na-HCO3-Cl	-2.0	-14.2	1.94					0.70781	0.47	0.19
B256	Bedrock	Upper	Na-Ca-Mg-HCO3-Cl	-4.1	-24.8	7.95					0.70582	-0.61	1.17
B546	Bedrock	Upper	Ca-Na-Mg-Cl-HCO3	-3.5	-19.8	8.16					0.70609	-1.21	-0.58
CC1	Surface Water	Upper	Mg-Na-Ca-HCO3-Cl	-3.9	-25.2	6.10	1.60				0.70756	-1.37	-2.41
CC2	Surface Water	Mid	Mg-Na-Ca-HCO3-Cl	-3.8	-24.7	5.38						-0.70	-2.21
CC4	Surface Water	Mid	Mg-Na-Ca-HCO3-Cl	-3.8	-24.9	5.60						-0.44	-2.03
CC5	Surface Water	Lower	Mg-Ca-Na-Cl-HCO3	-3.6	-23.8	5.27						-0.28	-1.90
CC6	Surface Water	Lower	Mg-Ca-Na-Cl-HCO3	-3.6	-23.2	5.77	1.44				0.70685	-0.41	-1.82
KC1	Surface Water	Upper	Mg-Na-Ca-Cl-HCO3	-3.7	-21.8	7.52					0.70774	-1.33	-2.29
Ock	Surface Water	Mid	Ca-Mg-Na-HCO3-Cl	-4.3	-24.8	9.20					0.70779	-0.35	-1.33
BR1	Surface Water	Lower	Mg-Na-Ca-Cl-HCO3	-3.9	-24.6	6.99					0.70596	-0.57	-1.61

7 Note: Sub-catchment boundaries are shown in Fig. 3.

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Table 5. Rainfall stable isotopes collected from the Brisbane Airport between June 2010 and June 2011.

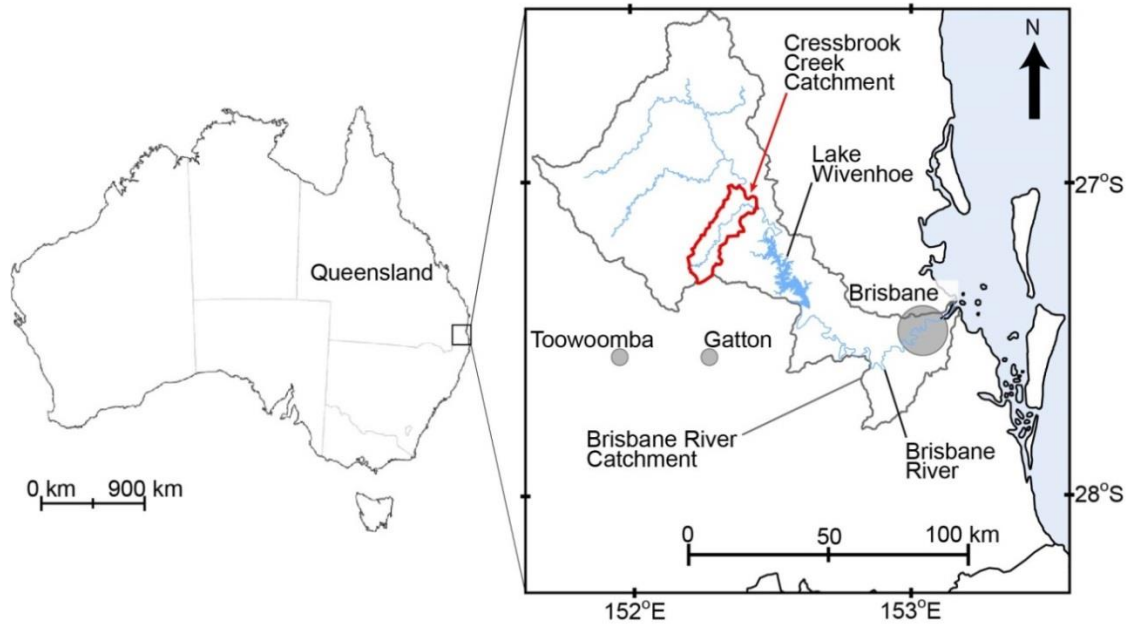
Sample Month	$\delta^2\text{H}$ (‰ VSMOW)	$\delta^{18}\text{O}$ (‰ VSMOW)	Monthly Precipitation (mm)
June 2010	9.0	-1.49	12.8
July 2010	-1.8	-2.58	36.0
August 2010	-4.4	-1.90	108.2
September 2010	-24.6	-4.44	77.0
October 2010	-11.9	-3.45	337.3
November 2010	-1.6	-2.14	53.2
December 2010	-30.2	-5.34	499.4
January 2011	-27.8	-5.13	346.8
February 2011	-15.3	-3.22	79.8
March 2011	-13.5	-3.58	188.6
April 2011	0.1	-2.62	94.8
June 2011	-2.8	-2.12	7.4

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Table 6. Main features of the five hydrochemical facies (median values).

Hydrochemical facies	pH	SC ($\mu\text{S}/\text{cm}$)	Eh	SiO_2 (mg/L)	$\text{NO}_3\text{-N}$ (mg/L)	^3H (TU)
1	7.2	522	113	43	0.15	N/A
2	7.0	497	38	26	0.17	1.42
3	6.5	708	35	35	0.18	1.14
4	6.6	1337	-40	43	4.0	1.08
5	6.5	4140	-55	41	0.19	0.50

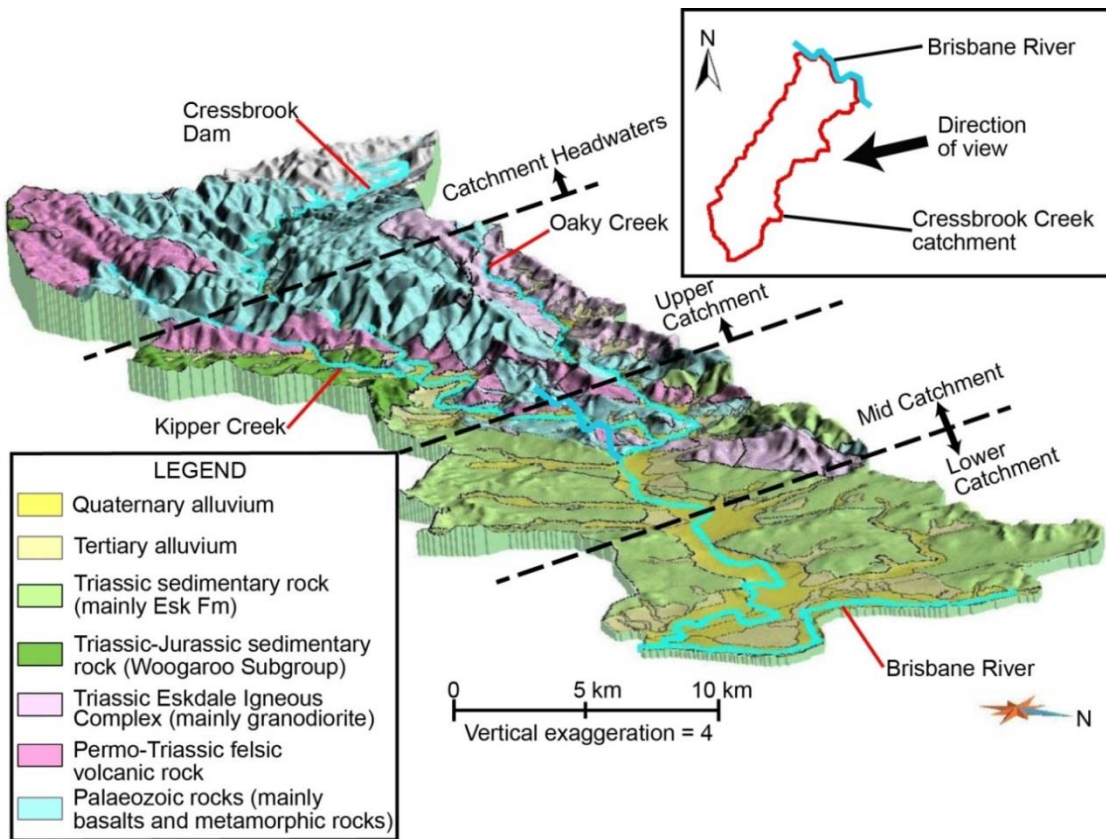
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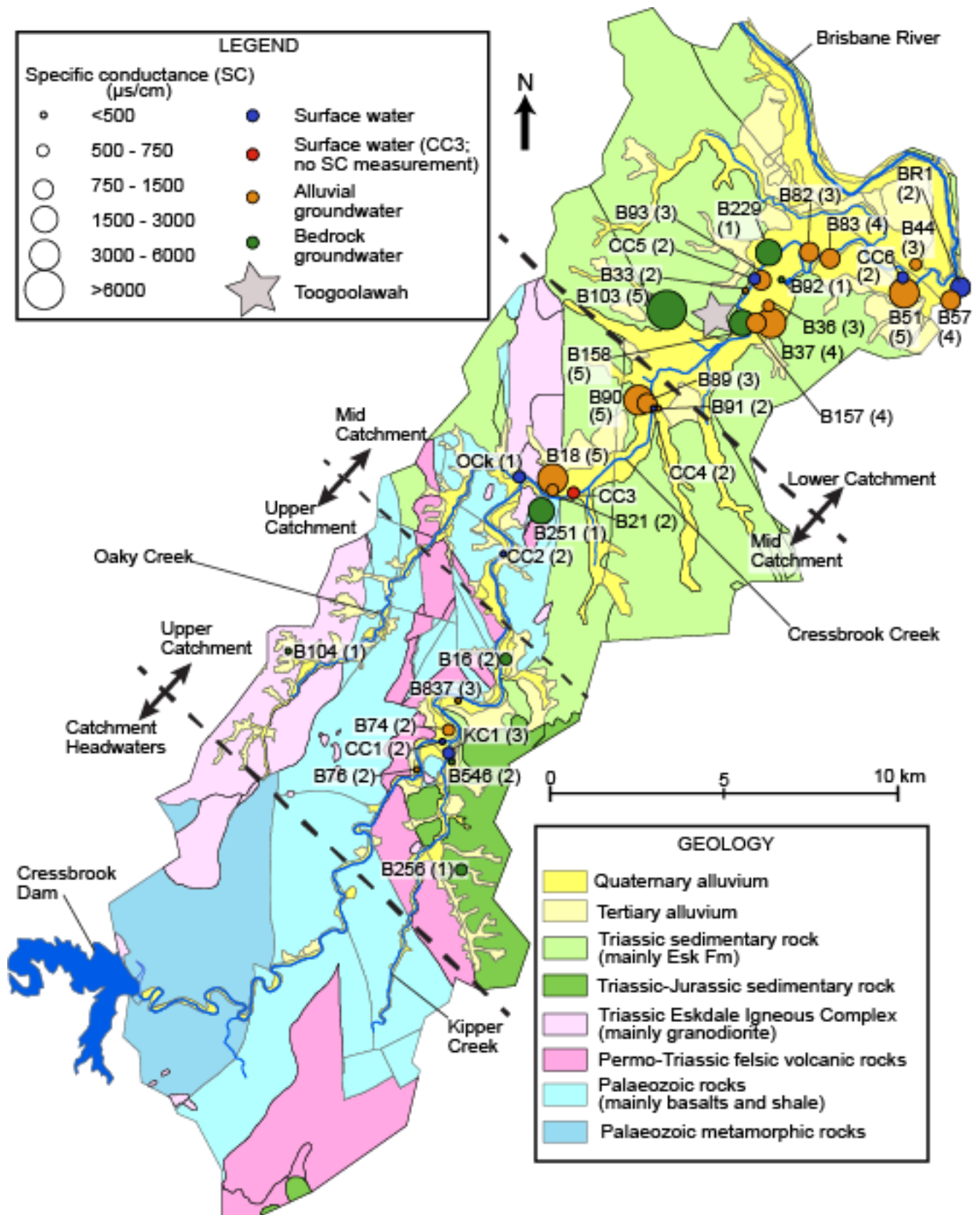
19 Fig. 1. Cressbrook Creek catchment in southeast Queensland, located approximately 80 km northwest
 20 of Brisbane and within the upper Brisbane River catchment.

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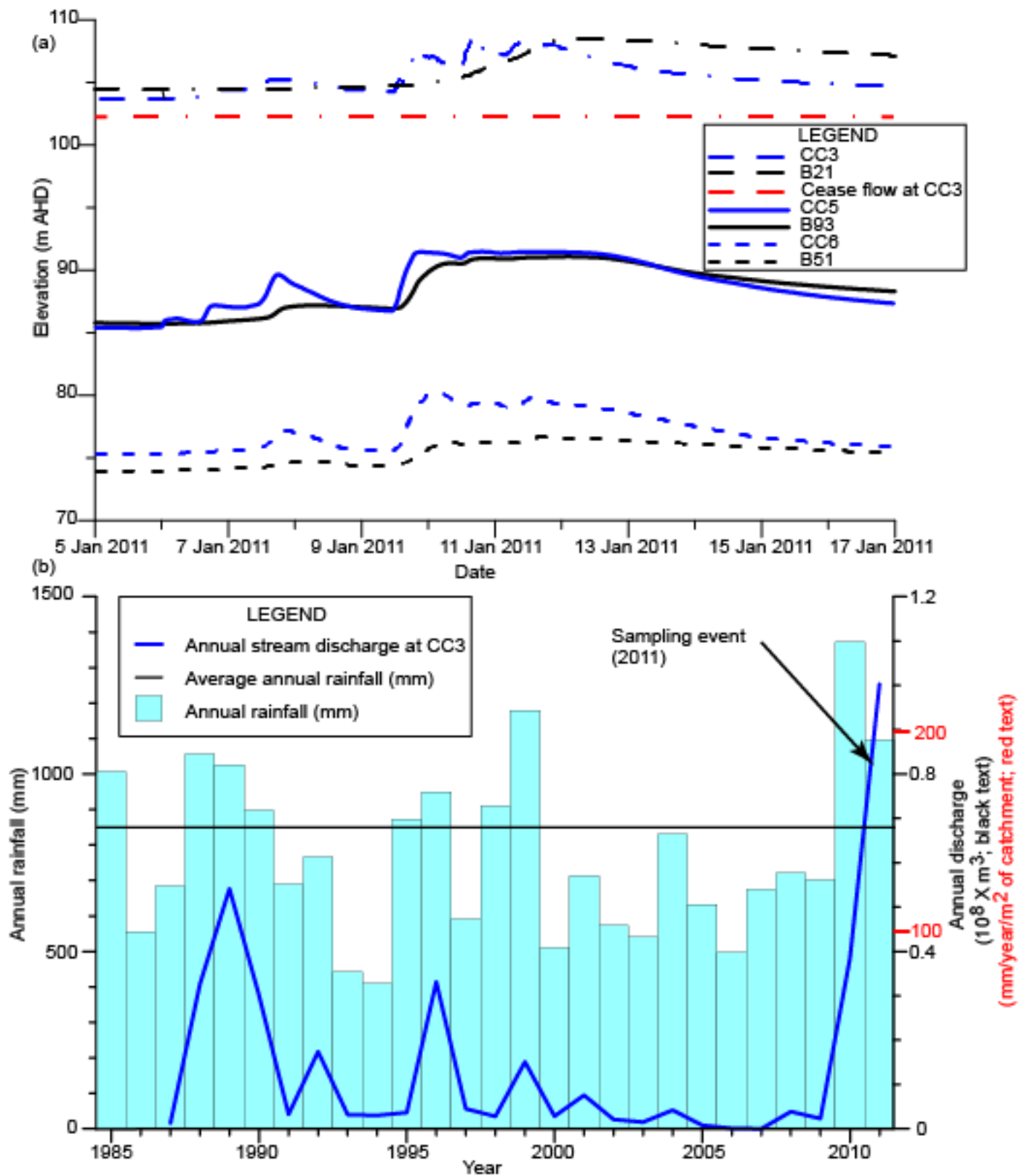
23 Fig. 2. Geology, topography and surface drainages of the Cressbrook Creek catchment (viewed from
 24 the east; adapted from King et al., 2014).



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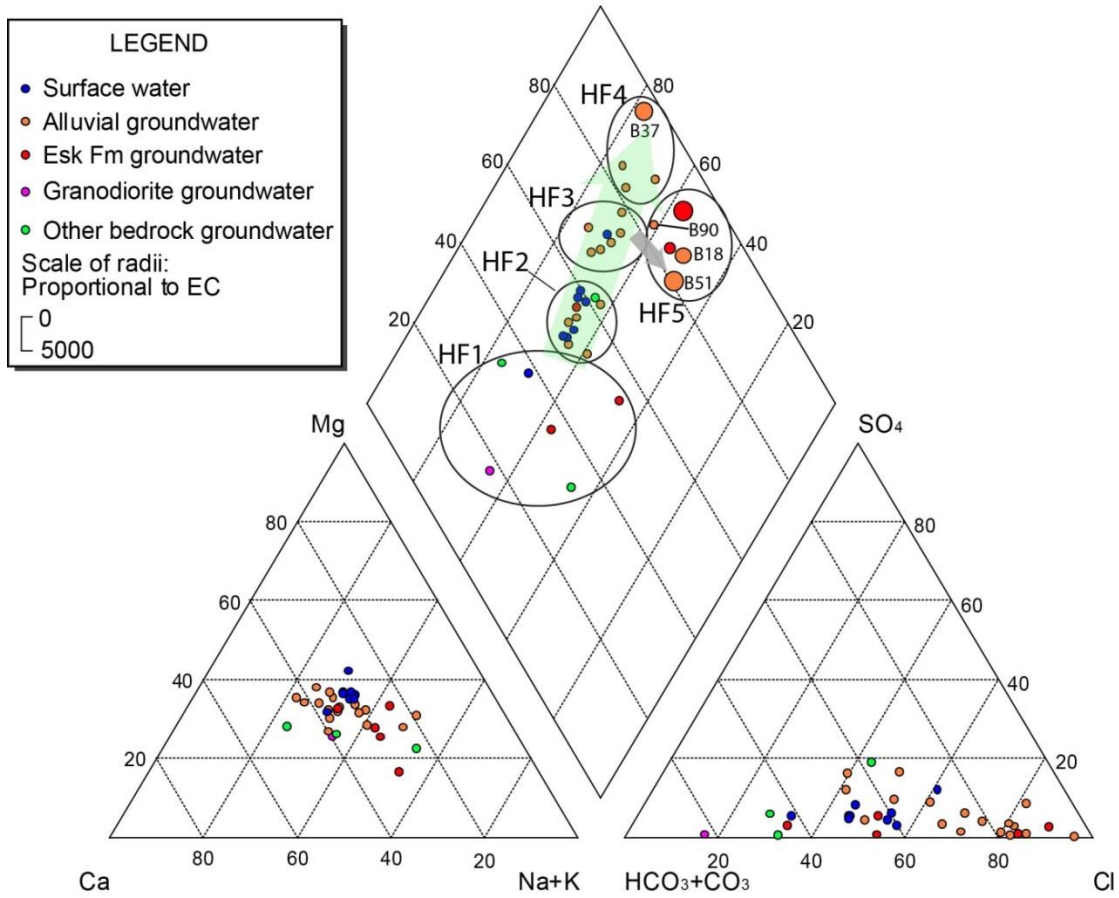
26 Fig. 3. Location of sampling sites, and catchment-wide distribution of specific conductance (SC) and
 27 hydrochemical facies distribution (in parentheses; Section 5.1.1) in the Cressbrook Creek catchment.

28 The samples were collected in June 2011 (see Table 3 for exact dates).



29

30 Fig. 4. a) Groundwater and stream hydrographs from the flood period; b) Annual rainfall (BOM 2012)
 31 for the Cressbrook Creek catchment and annual stream discharge at CC3 (Stream gauge 143921A;
 32 DNRM 2012). Stream discharge is displayed in units of m³/year and mm/year/m² of catchment,
 33 assuming that the catchment area is 447 km². Also shown is time of sampling.



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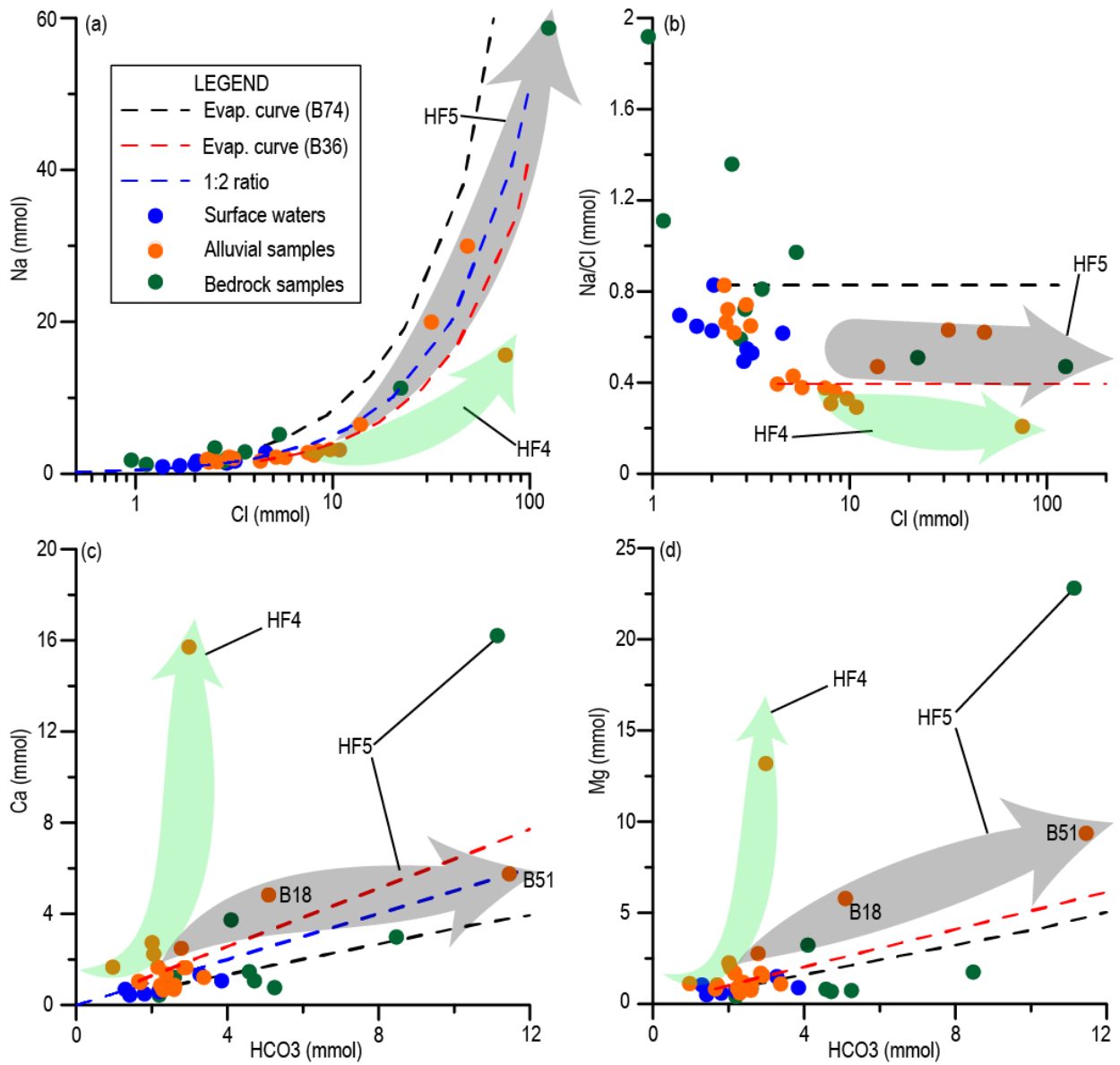
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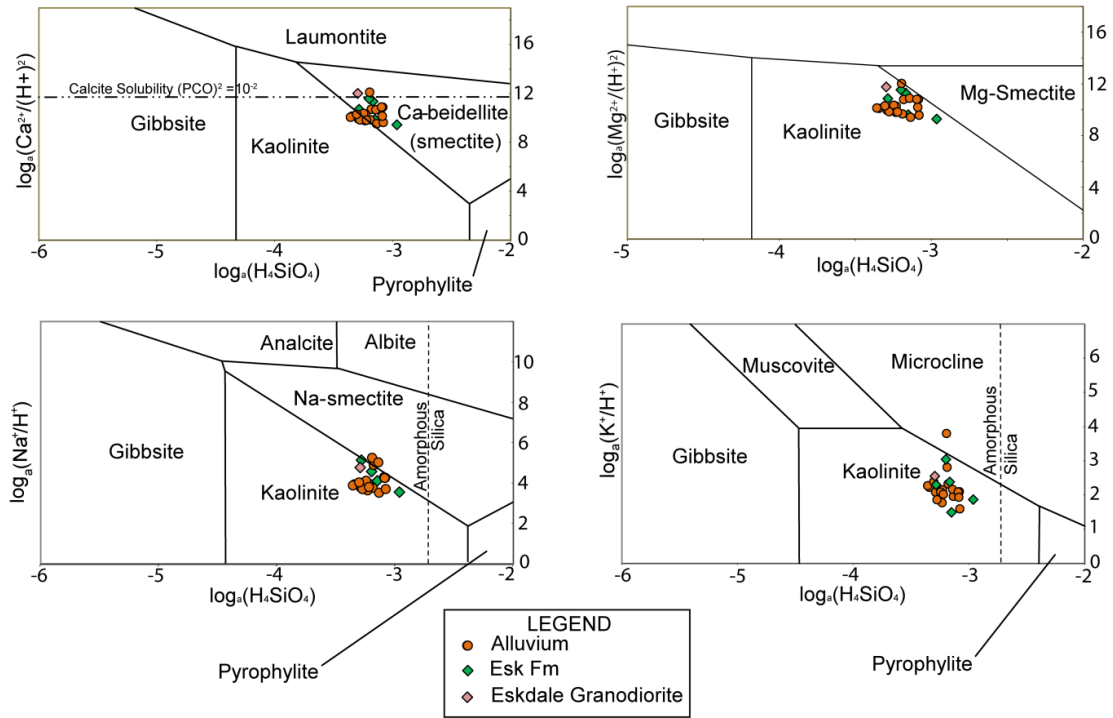
Fig. 5. Piper diagram showing hydrochemical facies (HF) for surface and groundwater samples collected in the Cressbrook Creek catchment. The green and grey arrows show divergent evolutionary pathways.



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41 Fig. 6. Major and minor ions plotted against the theoretical evaporation curves for fresh groundwater
 42 from the Upper Catchment (B74) and the Lower Catchment (B36). Evaporation curves were
 43 calculated using PHREEQC (Parkhurst and Appelo, 1999).

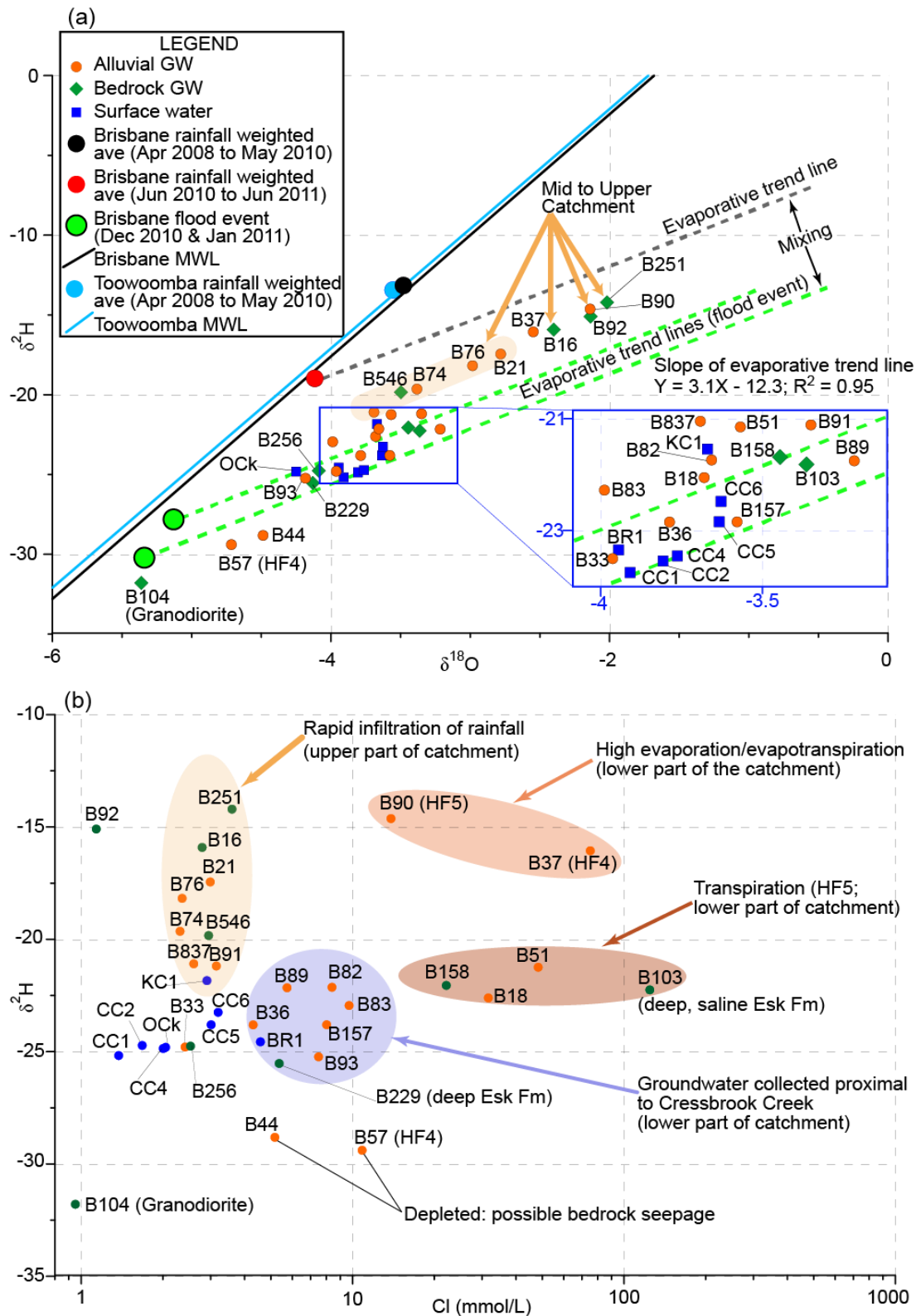
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46 Fig. 7. Groundwater silicate stability diagrams based on groundwater samples collected from the
 47 study site in 2011 for the: a) CaO-Al₂O₃-SiO₂-H₂O system; b) MgO-Al₂O₃-SiO₂-H₂O system; c)
 48 Na₂O-Al₂O₃-SiO₂-H₂O system, including albite; and d) K₂O-Al₂O₃-SiO₂-H₂O system, including
 49 microcline.

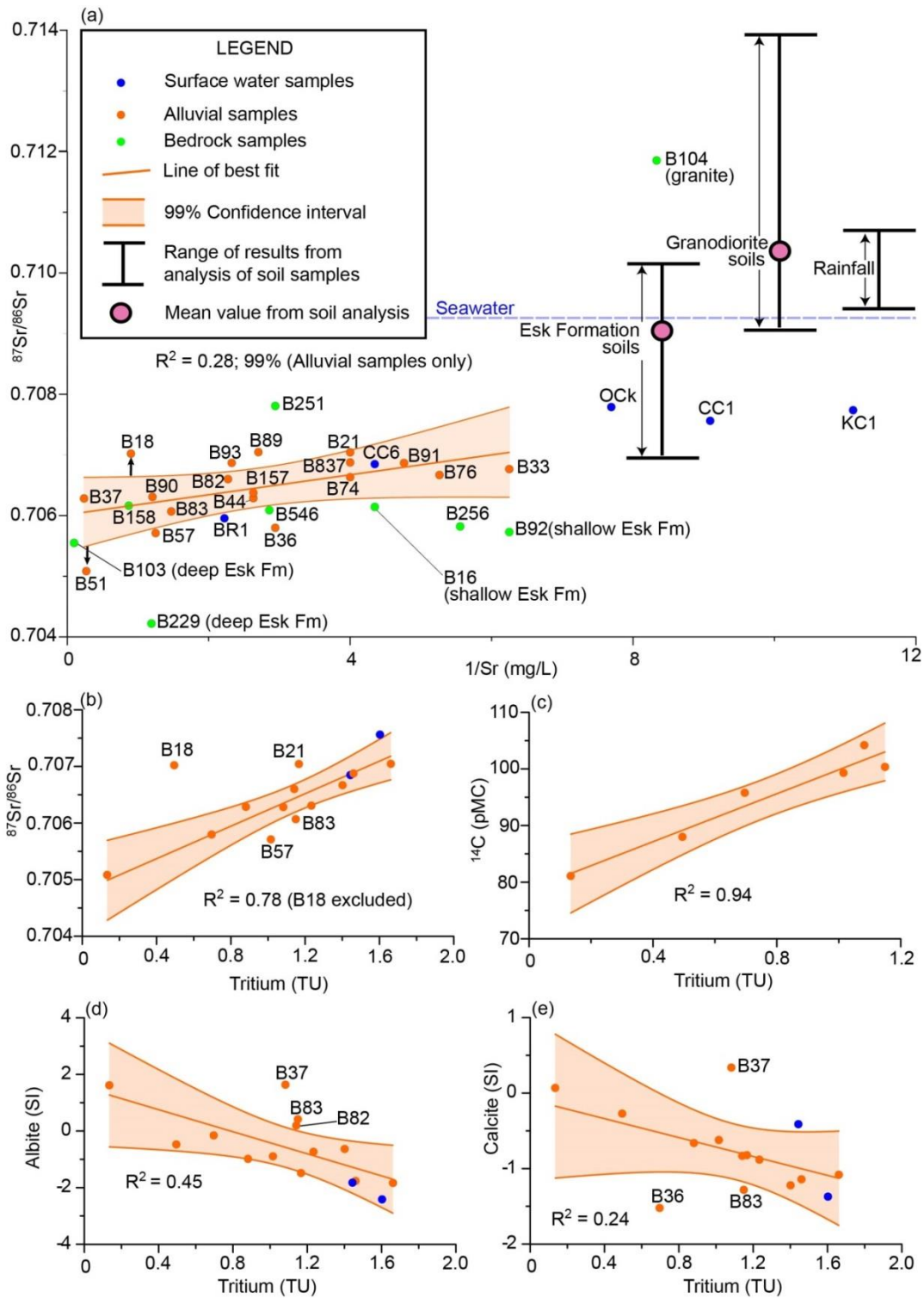
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52 Fig. 8. a) $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ values (‰ Vienna Standard Mean Ocean Water, VSMOW) compared to
 53 flood rainfall (ANSTO) and the meteoric water line for Brisbane and Toowoomba (Crosbie et al.,
 54 2012); and b) semi-log plot of $\delta^2\text{H}$ (‰ VSMOW) versus Cl.

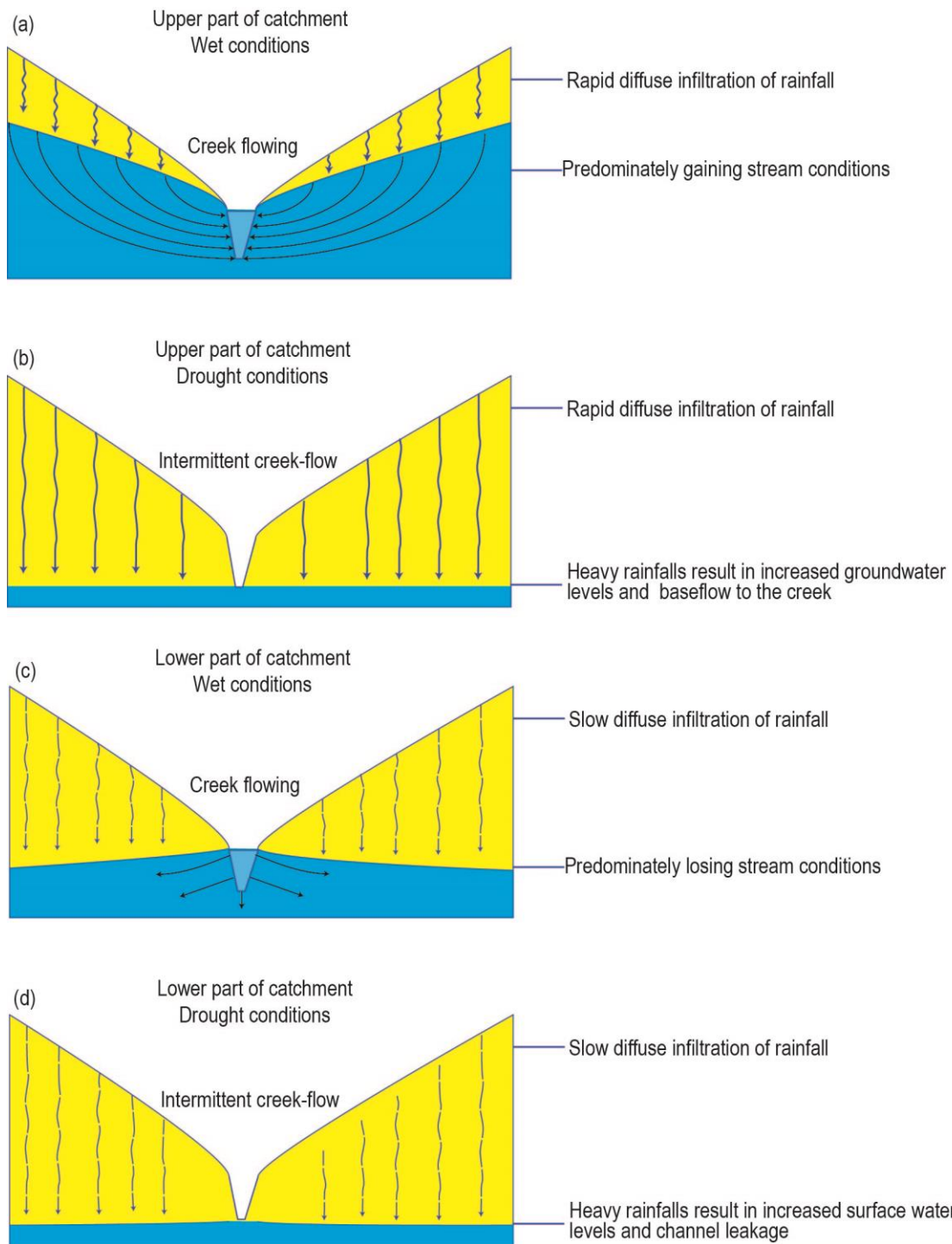
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57 Fig. 9. a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$; b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus tritium; c) ^{14}C (pMC) versus tritium; d) saturation
 58 index (SI) for albite versus tritium; and e) SI for calcite versus tritium. Soil analyses were performed
 59 by Douglas et al. (2007), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for seawater was sourced from Dia et al. (1992), and the
 60 rainfall data is from Raiber et al. (2009).

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63 Fig. 10. Conceptual model of recharge processes in the: a) upper part of catchment during wet
 64 conditions; b) upper part of catchment during drought conditions; c) lower part of catchment during
 65 wet conditions; and d) lower part of catchment during drought conditions.

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