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The significance and lag-time of deep throughflow: an example from a small, ephemeral catchment with contrasting soil types in the Adelaide Hills, South Australia

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Abstract

The importance of deep throughflow in a small (3.4 km²) ephemeral catchment in the Adelaide Hills of South Australia was investigated by detailed hydrochemical analysis of soil water and stream flow during autumn and early winter rains. In this Mediterranean climate with strong summer moisture deficits, several significant rainfalls are required to generate soil throughflow and stream flow (in ephemeral streams). During Autumn 2007, a large (127 mm) drought-breaking rain occurred in April followed by significant May rains; most of this precipitation occurred prior to the initiation of stream flow in late May. These early events, especially the 127 mm event, had low (depleted) stable water isotope values compared with both later rains and average winter precipitation. Thus, this large depleted early rain event provided an excellent natural tracer. During the June and July rainfall events, daily stream and soil water samples were collected and analysed. Results from major and trace elements, water isotopes ($\delta^{18}\text{O}$, δD), and dissolved organic carbon analysis clearly demonstrate that a large component of this early April and May rain was stored and later pushed out of deep soil or regolith zones. This pre-event water was identified in the stream as well as identified in deeper soil horizons due to its different isotopic signature which contrasted sharply with the June–July event water. Based on this data, the regolith and throughflow system for this catchment has been re-thought. The catchment area consists of about half sandy and half clayey soils. Regolith flow is now thought to be dominated by the sandy soil system not the clayey soil system. The clayey duplex soils had rapid response to rain events and saturation excess overland flow. The sandy soils had delayed soil throughflow and infiltration excess overland flow. A pulse of macropore throughflow was observed in the sandy soils three days after the rainfall event largely ended. The macropore water was a mixture of pre-event and event water, demonstrating the lag-time and mixing of the water masses in the sandy soil system. By contrast, the clayey soil horizons were dominated by pre-event water to a much lesser degree, demonstrating the quicker response and shallow flow through of the clayey soil system. Thus, the sandy terrain

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has a greater vadose zone storage and greater lag time of through-flow than the clayey terrain.

1 Introduction

Flow pathways through soil and regolith and their relation to streamflow and surface water chemistry have been a focus in several different types of studies. Atmospheric acid deposition and its affect on streams and lakes was an early area of investigation that combined soil hydrochemistry, atmospheric deposition rates and chemistry with surface water chemistry (Likens et al., 1977, 1996; Probst et al., 1990). Silicate weathering rates and the fluxes of weathered product including its link to carbon cycle models provided further progress in the understanding of these complex systems (Aberg et al., 1989; Edmond et al., 1995; Kump et al., 2000; Shand et al., 2007). Added to the above geochemical focused studies are hydrologic investigations in which components of stream flow are identified through utilization of techniques and methods of soil and water hydrogeochemistry (Sklash and Farvolden, 1979, 1982; Kennedy et al., 1986; Land et al., 2000). These studies have highlighted a number of befuddling complications that arise in the study of even the most simple catchments: soil and bedrock heterogeneity, groundwater or baseflow input, seasonal changes to the system in terms of hydrogeochemical (and biogeochemical) inputs, and anthropogenic disturbances such as airborne pollutants and agricultural amendments. Nonetheless, progress in comprehensively understanding the diverse range of catchments requires detailed hydrogeochemical studies of soil, regolith, groundwater, and surface water. The study presented here is based on extensive sampling and analysis of soil water, runoff, stream, and precipitation during a moderate sized precipitation event in a small ephemeral catchment in a strongly Mediterranean climate.

One complicating parameter in the catchment studies cited above is the presence of permanent groundwater and its contribution to stream flow. Thus in such catchments, groundwater input into stream and soil water needs to be separated from un-

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saturated and perched flow pathways through soil or regolith. Evaluating the ground-water component has led to assumptions about the homogeneity of groundwater as well as assumptions concerning vadose soil water being a negligible source to stream flow (Sklash and Farvolden, 1982). In the study presented here, a gauged ephemeral stream (Mackreath Creek) of 3.4 km² catchment area in the Adelaide Hills of South Australia was investigated with the aim of characterising through flow pathways and identifying their component in the resulting stream flow (Fig. 1). In humid climate settings, differentiating flow paths may be important in terms of flood response time, soil erosion, contaminant transport, and hydrogeology (Lin, 2003). These concerns are valid in the strongly Mediterranean climate of the Adelaide region. However, in the sub humid to semi-arid climatic setting of much of Australia, with its highly variable rainfalls, understanding flow paths and the amount of precipitation necessary to generate deep, sustained soil-regolith throughflow is critical to predicting landscape response to climate change. Groundwater recharge estimates also rely on assumptions regarding duration and extent of soil-regolith saturation.

2 Background

Mechanisms of stream flow generation in ephemeral streams are dominated by through flow, overland flow, and perched zones of saturated soil and regolith water. Through-flow or lateral subsurface flow has been shown to be an important flow pathway in hilly Mediterranean climate catchments (Kennedy et al., 1986). In humid settings with thick soils lateral subsurface flow has been shown to be the predominant mechanism of stream flow generation (Pearce et al., 1986; Sklash et al., 1976). In the Adelaide Hills or Mount Lofty Ranges (MLR) of South Australia, Cox et al. (2002) identified lateral subsurface flow to be the most important transport pathway for contaminants during years of average or below average rainfall. Mixing between lateral subsurface flow and overland flow on hillslopes in the MLR has been observed by Chittleborough et al. (1992) to produce similar hydrochemical signatures between flow paths.

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In settings such as the MLR, lateral subsurface flow is produced by a combination of matrix flow (diffusion through soil) and macropore flow (Smettem et al., 1991; Leaney et al., 1993; Stevens et al., 1999; Cox et al., 2002). Water flowing through the soil matrix generally obtains a signature similar to that of the exchange pool of the soil (Cox et al., 2002), while macropore flow primarily acts as a physical conduit for water to flow through and consequently the exchange pool has a lesser effect on the chemistry of water (Newman et al., 1998). Down-slope mixing of matrix flow and macropore flow can homogenise the hydrochemistry of these two pathways (Chittleborough et al., 1992).

An important aspect of tracing flow paths in catchment systems is the evaluation of pre-event water (Pinder and Jones, 1969; Genereux and Hooper, 1998; Buttle, 1998; Brown et al., 1999; Shanley et al., 2002). Such evaluation commonly entails an analysis of the groundwater input into the stream. In an ephemeral system such as Mackreath Creek where the surface water is largely disconnected from the water table (Fig. 2), an evaluation of pre-event water held in the vadose zone can be made by analysing Autumn and winter rainfall leading up to the analysed event.

3 Setting

Scott Creek and the MLR experience a Mediterranean climate with cool wet winters and warm dry summers. Temperatures range from 14–27°C in summer to 8–14°C in winter. The MLR receives strong seasonal rainfall, with 85% of rainfall between May and September (BOM, 2007). A yearly rainfall average of 804 mm/yr has been collected at the site (Scott Bottom rainfall collector) at an elevation of 210 m, which has been in operation since 1991 (James-Smith and Harrington, 2002). Evaporation of 1555 mm/yr is measured at the nearest Class A evaporation pan of Mt. Bold, resulting in evaporation exceeding rainfall from October to May.

The Mackreath Creek study site is a sub-catchment of Scott Creek Catchment (SCC) and represents ~10% of its area. Mackreath Creek and SCC are typical of MLR catchments having 100–300 m of relief, moderately steep slopes in many areas and narrow

riparian-floodplain areas. The study area, as is most of the MLR, consists of metamorphosed late Precambrian sedimentary rocks consisting of meta shales, sandstone-quartzite, and minor carbonate units (Priess, 1987). The hydrogeology of the area is that of a fractured rock aquifer with large variations in both hydraulic conductivity and groundwater salinity (Harrington, 2004a, b). Soil thicknesses of 1–2 m are typical. Weathered bedrock or regolith of several meters in thickness typically occurs beneath the soil horizons (Fig. 2). Mackreath Creek catchment is predominately comprised of native vegetation with minor human impacts such as land clearance and farm dam construction.

Mackreath Creek is ephemeral with winter flows of a few weeks duration during drought years and 4–6 months duration in average and above average precipitation years. Flows range from 0.1–0.5 ML/day for winter non-storm flows, 1.0–10 ML for typical winter storm flows, and 20–30 ML/day for 2 year peak flows.

South Australia was in a drought year in 2006, with nearly 50% less rainfall than average (BOM, 2007). In 2006 stream flows through Mackreath Creek gauging station lasted only 2 days! In 2006 there was one significant storm event of 40 mm (over 4 day) which produced the only flow in Mackreath Creek, compared to six events of greater than 40 mm in 2005 causing the creek to flow for four months.

The two main types of soils in this sub-catchment are sandy silty soils developed on quartzite bedrock (with some meta-shale) and clayey duplex soils developed on meta-shale (Fig. 1). Sites MC1 and MC2 are positioned to collect water flowing through sandy soil horizons (Fig. 2). The SB2 site represents flow through a texturally contrasting clayey duplex soil. This site is just outside Mackreath Creek sub-catchment but it is soil water and overland flow water chemistry signatures from this site will be similar to flows through the duplex soils at Mackreath Creek. Clayey duplex soils in Mackreath creek occur on slopes lacking either 0-order catchments or large areas of homogenous meta-shale and clayey duplex soil substrate.

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4 Methods

Each site indicated in Fig. 1 was instrumented with one overland flow collector and two interflow collectors. Overland flow collectors consisted of 20 m by 20 cm metal sheeting arranged into a V-shape to funnel water downhill. The metal sheets were inserted 5 cm into the ground surface and were held in place by stakes every 2 m. Polyethylene tubing was attached to the lowest point to channel water down slope and into a 25 L sample container.

To collect lateral subsurface flow, three meter deep trenches were dug at each site parallel to the hill-slope by a backhoe and access to the trenches was gained from the downhill side. Channels were dug to drain water from each trench. Trenches were covered with plastic tarpaulins to prevent direct contact of rainfall with the side walls of the trench, which could cause erosion and contaminate lateral subsurface flow samples. The face of each trench (uphill side) was instrumented with two fibreglass wick interflow collectors with 0.16 m² area of soil contact at the A/B and B/C horizons.

Interflow collectors consist of a 1 m length of fibreglass wick with 10 cm of frayed wick at one end. This was used to spread across a base plate which acted as a contact with soil water. The rest of the wick ran through PVC tubing to an outlet where a 25 L container was connected to collect soil water. Garden weed mat was used to cover the base plate to pre-filter soil water and prevent soil clogs entering the collector. Chiselling and digging tools were used to undercut a 50 by 50 cm cavern in the face of the trench so collectors could be installed. The roof of the undercut was made as flat as possible and soil from the roof of the undercut was mixed with water to create a slurry of soil, which was put on top of each collector. Each collector was propped in position using two car jacks and pieces of wood to equalise the force (one on each side of the base plate).

At A and B horizons at MC2 and A horizons at both MC1 and SB2, interflow collectors were connected to containers directly by 45 mm holes drilled through the lid of the 25 L containers. High water levels in the trenches at SB2 and MC1 required tubing to be

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connected to the PVC piping of the interflow collector and ran out of the trench downhill to a container.

Prior to filtering, samples were tested for alkalinity using a HACH titration alkalinity kit to determine the concentration of carbonates in the system. Filtering was undertaken in the laboratory a few hours after sampling using pressure packs to force sample through a pre-filter and a 0.45 µm filter. 60 ml of sample was stored in a bottle for 72 element suite analysis and acidified to a pH less than 2 using nitric acid (HNO₃). 30 ml of sample was stored in a McCartney bottle for water isotope (²H and ¹⁸O) analysis. To prevent exchange of water vapour with the air, McCartney bottles were completely filled, electrical tape was used to seal the lid of the bottle and samples were stored upside-down until analysis.

In total 75 samples were selected for 72 element suite analysis at Acme Analytical Laboratories, Canada, using Inductively Coupled Plasma Mass Spectrometry. Stable isotopes of oxygen and hydrogen were analysed at UC Davis Stable Isotope Facility, California using a Los Gatos Research Liquid Water Isotope Analyser. Standards were run every five samples to ensure correct calibration of equipment, which enabled an accuracy of 0.2‰ and 0.6‰ for ¹⁸O/¹⁶O and ²H/¹H, respectively.

5 Results

5.1 Electrical conductivity/salinity

Electrical conductivity measurements of salinity were made of Mackreath Creek, soil horizons, and overland flow before, during and after the precipitation event of late June and early July (2007) (Figs. 3 and 4). A continuous auto-logger installed in the stream provided an excellent record of EC – salinity variations. Due to low sample volume in the sandy soils during the lead-up to the precipitation event, and in fact during the first half of the event, EC measurements were not made of these samples. Thus, the EC data set in Fig. 4 is much more incomplete than time series of element concentrations

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determined from ICP analysis. The logged data from the stream was corrected with a hand-held and calibrated YSI EC meter. In addition, total dissolved solids were calculated from major and trace element analysis by ICP-AES. A very good correlation of R^2 0.970 was observed between corresponding YSI EC measurements (converted to TDS using 0.66EC) and total dissolved solids from actual analyses. This correlation allowed for the logged data to be corrected which is plotted in Fig. 4.

Clayey soil EC measurements show predictable decreases in salinity from B horizon to A horizon and to overland flow (Fig. 4a). Overall, the A horizon salinity was 10% lower than the B horizon values. Overland flow was 70% lower than B horizon values during the beginning of the event, however, dilution of soil horizon salinity during peak precipitation decreased the difference to about 15%. During the waning stage of the event, overland flow salinity reached parity with A horizon values. This compositional merging soon after peak dilution represents saturation excess overland flow and mixing of a diluted A horizon with overland flow waters. In other words, upslope from the collection point, water was flowing into and out of the A horizon mixing to form a hydrochemically homogenous water mass.

An important point to make in regard to the clayey soil water EC values is that most of the stream EC measurements (except during peak flow dilution) are higher in EC (salinity) than temporally corresponding B horizon values. Thus in this small catchment, B horizons of clayey soils, at least from the mid-slope position sampled, do not have higher salinity than the majority of the stream flow.

As stated previously, EC measurements for the sandy soil sites were incomplete due to small sample size during phase 1 and 2. Nonetheless, interesting EC values and trends were measured during phase III of the event (Fig. 4b). Overland flow salinity values are very low, the lowest of all the measurements, indicating the low exchange phase reservoir in the A horizon of these sandy soils. Sandy soil macropore flow was sampled directly in the up-slope trench site (MC2 DW) as actual macropore flow that was observed in the B horizon. During phase three of the event, water filled the two trenches at the sandy soil site. This rise in perched soil-regolith water lasted for three

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days and was a mix of observed macropore flow and matrix flow from the B horizon and was sampled as both macropore flow and “trench” water. The EC values from the perched soil-regolith water were higher than stream EC values, despite the mixing of macropore flow. EC values show dilution trends later during phase III (4B). The perched soil-regolith water was higher in EC than the B horizon macropore flow. These high EC (salinity) values will be further discussed below.

5.2 Elemental concentrations

Similar to overall EC values, major ions such as chlorine, sodium, bicarbonate, silica, calcium and magnesium, show dilution trends during and after peak flow (Fig. 5). Major elements chlorine and sodium have higher concentrations in the stream than in most of the throughflow samples (Fig. 5a, b, Table 1). Clayey soil throughflow waters are relatively high in chlorine compared to most of the sandy throughflow. Sodium and silica concentrations, however, are higher in most of the sandy throughflow than in both the clayey throughflow and stream water. For silica, higher concentrations in the sandy throughflow in the first half of the event are striking (Fig. 5c). One of the sandy system throughflow sampling horizons (site MC 2 BC, below a clayey-silt B horizon) is the exception and has elemental concentrations more like the clayey system (MC1-BC in Figs. 5 and 6).

The relationship between chlorine and sodium in throughflow and stream flow demonstrates differing water-soil interactions between the sandy and clayey systems (Fig. 6a). In addition, the low-flow stream sample (prior to the event) has the highest chlorine of any of the water samples (soil and stream); these stream concentrations of conservative chlorine indicate that there is a missing component of the system; a higher chlorine concentration has not been captured by the sampling in this study. Thus, mass balance attempts with the current data base, using elements such as silica, calcium, magnesium and potassium, which have many soil water samples with concentrations in excess of the stream values, have resulted in significant negative masses. These mass balance plots and calculations (Milgate, 2007) are not presented here.

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A few general observations can be made regarding the elemental concentrations. Stream flow chlorine and sodium concentrations have similar trends during the event to clayey soil throughflow and overland flow as would be expected for dilution during peak flow (Fig. 5a). Sandy system throughflow chlorine and sodium concentrations, for most samples, has a distinctly different trend than the clayey system: relatively lower chlorine and higher sodium (Fig. 6a). Likewise, silica is much higher in these sandy throughflow samples (Fig. 6c). As mentioned above, throughflow samples from MC1 BC (below a clayey silty B horizon) show much the same behaviour as throughflow samples from the clayey system (MC1-BC). This site has anomalous water isotope values and will be discussed below.

5.3 Dissolved organic carbon

Dissolved organic carbon analyses were obtained from 34 samples of stream water and selected throughflow and overland flow samples (Table 2, Fig. 7a). The lowest concentrations are from sandy soil overland flow (1.7, 2.8 mg/L) and the highest concentration is clayey soil A horizon from phase 1 of the event (31.2 mg/L). An interesting relationship exists in Mackreath Creek stream flow between DOC and iron and aluminium concentrations in which the concentrations rise and fall during the event hydrograph (Fig. 7a). The DOC concentration peak occurs between 2 and 3 days prior to the peak in iron and aluminium. The concentration increase of these two elements in the stream water during the event is substantial; it is 3–4 times the pre-event concentrations. DOC has a similar pattern for the event, albeit with the aforementioned earlier peak, and doubles in concentration between low, pre-event flow and early phase 2 flow. High concentrations of iron and aluminium occur in many of the sandy throughflow samples (Fig. 7a). Clayey soil throughflow, on the other hand, has concentrations of iron and aluminium below or close to those of the stream waters. These high concentrations of iron and aluminium in soil water do not correspond to high soil water DOC concentrations (Table 2), neither do they correspond to potassium concentrations (Fig. 7c). These trends will be discussed below.

5.4 Oxygen isotopes

Isotopes of oxygen ($^{18/16}\text{O}$) and deuterium ($^{2/1}\text{H}$) were sampled over the late June-early July event from Mackreath Creek, soil horizons, overland flow, and precipitation (Figs. 8 and 9). An important parameter to consider for water isotope analysis of small catchments is the antecedent moisture condition and the isotopic composition of the pre-event water in the system. In the case of a small, relatively steep ephemeral catchment in a strongly Mediterranean climate, the Autumn precipitation leading up to water flowing in the system is particularly important. In April 2007, following both a long dry summer period and a previous winter that was well below average rainfall, a large precipitation event of between 130–150 mm occurred over four days. Importantly, this large precipitation event had significantly depleted oxygen ($\delta^{18}\text{O}$ –7.43‰) and hydrogen (δD –45.5‰) isotopes when compared to more typical winter precipitation events. May 07 bulk rainfall is more typical of winter rainfall at this elevation in the MLR-Adelaide Hills with $\delta^{18}\text{O}$ –5.16‰ and δD –28.2‰ (Kaylaap, 1999). Depleted water isotope values during heavy precipitation events result from decreased fractionation between vapour and condensate as condensate fraction increases (Kendall and Doctor, 2007). June 07 bulk rainfall however is enriched compared to more typical winter values with $\delta^{18}\text{O}$ –2.43‰ and δD –5.2‰. These contrasting isotope values in the lead up to the precipitation event sampled have produced a natural tracer test. Precipitation event water was sampled at three intervals. The first two represent by far the bulk of the event and average $\delta^{18}\text{O}$ –3.36‰ and δD –10.65‰; the third sample is considerably depleted compared to the first two ($\delta^{18}\text{O}$ –4.98‰ and δD –24.6‰) and is from a few late showers.

The first thing to note from an analysis of the time series of oxygen and hydrogen isotopes (Fig. 8) is that all values are more enriched than the stream flow except one throughflow sample site, MC1-BC. This throughflow sample site is situated on the lower slope and installed below a clayey sandy-silt B horizon in the sandy landscape. AB horizon collectors from both the clayey and sandy landscapes show an enrichment

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corresponding to the influx of event water during phase I. However, during phase III, AB collectors from both sites show a depletion trend that is well below event water values. Clearly pre-event water that is depleted compared to event water mixed into the throughflow. BC horizon collectors in both the clayey and sandy systems show dilution and enrichment by event water during phase I followed by depletion during phase III, again indicating mixing of pre-event water in the throughflow system.

The lower slope BC horizon collector in the sandy system (MC1 BC) is noteworthy for the following reasons: 1) isotopic values are more depleted than the stream, 2) a depletion trend occurs from phase I to II, similar to the stream, 3) isotopic values do not show any significant enrichment trend during the event, indicating minimal mixing of event water with pre-event water. Possible flow path scenarios will be discussed below.

The differences between isotopic values of this system are well illustrated by graphing $\delta^{18}\text{O}$ and δD of the averages of the different components of the system (Fig. 9). The wide range in values of the bulked rainfall samples (April, May, and June) stand out. The depleted nature of the throughflow at MC1 BC (labelled “Deep Sandy Throughflow” in Fig. 9) and Mackreath Creek is obvious when compared to the event precipitation and most soil throughflow and overland flow averages.

6 Discussion

Despite the best efforts of our event sampling, it is clear that the sampling program at Mackreath Creek was incomplete in terms of soil-regolith flow paths. Down-slope change in soil water due to residence time within the soil due to mixing was largely undocumented. Emergent flow paths in lower slope settings as demonstrated by seasonal seeps present in the area were analysed at a reconnaissance level with field based measurements. It is clear from the range of elemental concentrations that large variations in soil water hydrochemistry are present and that many of these variations are not explained by event water dilution. Nonetheless, a number of interpretations can

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be made from the data collected.

The clayey soil system has clear dilution trends between event water and pre-event soil water. The pre-event soil water in the clayey soil horizons is closer to equilibrium with the soil exchange pool as demonstrated by higher concentrations of most elements in the clayey B horizon compared to A horizon and overland flow. Elements that show clear event dilution are magnesium, calcium, potassium, and chlorine. Conversely, concentrations of silica, iron and aluminium show a steady rise during the latter half of the event. Potassium is the notable exception in which the A horizon concentrations are higher than the clayey B horizon. Trends in potassium concentrations in these samples corresponds to DOC concentrations in terms of increases and decreases over time (Milgate, 2007) and most likely reflects release and transport of potassium as organic matter decomposes into DOC. High transient potassium concentration is a typical pattern in forest soils in which rapid release of potassium from decomposing litter commonly exceeds the capacity of the soil to retain it (Laskowski, 1995; Chang et al., 2007). Potassium may also be contained in colloidal sized plant material as was reported by Eyrolle et al. (1996).

The concentration peaks of DOC, iron and aluminium in the stream water during the event, as described above, are not in sync by two to three days. Thus, it appears that iron and aluminium are de-coupled from dissolved organic matter, contrary to long-standing work showing these elements are closely linked to DOC and organic colloids (Perdue et al., 1976; Johnson et al., 1981; Tipping, 1981). Organic complex transport of iron and aluminium is especially noted in tropical settings (Gu et al., 1995; Depré et al., 1999). Instead, due to a combination of the shift in the timing of the concentrations peaks of DOC, iron and aluminium and the lack of correlation between DOC and elevated iron and aluminium concentrations in the throughflow waters, colloidal iron oxyhydroxides and clay minerals flushed from some soil horizons may be a more likely explanation. Water samples in this study were filtered to 0.45 μm , leaving a colloidal fraction, as defined by Buffle and Van Leeuwen (1992) and Stumm (1993), in the 0.20 μm to 0.45 μm size range. It is clear that two of the sandy soil system throughflow

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5 sites showed very elevated levels of iron and aluminium during phase I when compared to clayey soil system (Fig. 7, Table 1). Thus, the elevated iron and aluminium concentrations appear to be associated with flushing of iron oxyhydroxide colloids and clay mineral colloids from sandy soil horizons. Iron colloids have been reported from cool climate systems (Pokrovski and Schott, 2002; Ranville et al., 2005). Ranville et al. (2005) reported from their study of nearby sandy loam soils in the Adelaide Hills that fine-grained colloids (0.1–0.2 μm) from throughflow samples were high in iron whereas, coarser-grained colloids (0.2–0.5 μm) contained more aluminium. Additionally, their A2 horizon samples were deficient in fine-grained colloids, due presumably to translocation of these colloids through the soil profile.

10 Most of the sandy soil system throughflow have elevated concentrations of silica and sodium, compared to the clayey soil system. Mineral weathering (silicate hydrolysis) and release of silica and sodium and to a lesser extent calcium from quartz and feldspar is most likely the dominant factor controlling the high concentrations of these elements in the sandy soil throughflow. This mineral weathering is most likely the cause of the distinct hydrochemical trends evident for the sandy throughflow when compared to the stream water and clayey soil water (Fig. 6). The highest concentrations of silica, sodium, and calcium come from flushing of sandy A and B horizons (collectors MC2-BC and MC1-AB) during the first half of the rainfall event (Fig. 5). Weathering of silicate material, both from in situ soil and from dust, in the presence of soil acids and higher moisture contents of the A horizon is probably the cause of these elevated concentrations.

25 Another factor that could explain the differing elemental concentrations in the various throughflow samples is the residence time of soil water in the soil-regolith system. Longer residence time is indicated for some of the sandy system by the dominance of pre-event water in some of these flowpaths as deduced from oxygen and hydrogen isotopes. The most ^{18}O depleted water, and therefore the water that is the most strongly influence by pre-event water (collector MC1-BC) has consistent hydrochemical trends for the seven isotopic and most elemental samples analysed. The narrow range

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of values for MC1-BC is intermediate between the high silica and sodium sandy system soil waters and the clayey soil waters in terms of most elemental concentrations (Fig. 6). Thus, although MC1-BC demonstrates the best case for longer residence time based on the presence of pre-event water, this flow path does not show elevated concentrations of silica, sodium, and calcium that would be expected from prolonged water-mineral interactions. However, MC1-BC does show very substantial increases in iron and aluminium during the second half of the event (Fig. 7), which is interpreted as a result of mixing of early (flushed) event water with pre-event water.

A deep throughflow pulse was identified in the sandy soil system based on field observations of trenches filling with water and macropore flow. Samples of this throughflow pulse (collectors MC1-AB and MC2-DW) have elevated chlorine, sodium, magnesium, and potassium concentrations but relatively lower silica, iron and aluminium concentrations (Fig. 5). Thus, a possible scenario is that this pulse flushed salts from deep in the soil-regolith profile. Why this water was not elevated in silica, from silicate mineral hydrolysis, is not known.

A possible model to explain hydrochemical data is as follows. Infiltration in the sandy soil system prior to the measured event accumulates in the regolith above the bedrock-regolith boundary. This pre-event water is depleted in ^{18}O and ^2H isotopes obtained from the large April event and to a lesser degree from May precipitation. This pre-event water is not exceeding high in dissolved constituents, when compared to later throughflow from the sandy soil system. High concentrations of silica, iron, and aluminium, and other mineral-oxide related elements appear to originate from event flushing of sandy soil A and B horizons during phase I of the event.

The clayey soil system by contrast has much less depleted ^{18}O and ^2H isotopes, especially early in the event (phase I). This demonstrates the higher saturation and shorter residence time of water in the clayey soil A and B horizons. That the B horizon shows a isotopic depletion trend as the event transpires, indicates that water, probably from deeper in the regolith, dominated by pre-event water (from April and May) was pushed out and subsequently mixed with enriched surface event water.

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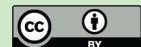
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Further support of this model of quick flow through the upper clayey soil system and delayed flow through the sandy soil system can be interpreted from DOC, iron, and aluminium concentration peaks observed in the stream during the course of the event. The DOC concentration peak occurs 2–3 days prior to iron and aluminium concentrations peaks, as has been described. The DOC peak most likely originates from clayey soil system A horizons which have both high DOC concentrations and rapid storm response. The iron and aluminium peaks are probably due to transported colloids (iron hydroxides and clay minerals) from flushing of sandy soil horizons. Why the early rains in April and May, as interpreted from water isotopes, do not show elevated concentrations of iron and aluminium, is not known. These waters infiltrated through the same sandy soil system as event waters that were much higher in iron and aluminium. Two possibilities are possible: 1) colloids from earlier flushing settled and or were filtered in the deep regolith prior to re-mobilization during the measured event. 2) Initial rain water that infiltrated the sandy soil system did not contain substantial amounts of flushed colloids; the reason for this is not known. Nonetheless, the measured event shows high concentrations of iron and aluminium coming from sandy soil horizons early in the event. These colloids were able to be transported through the porous sandy medium and into the stream. The clayey soil system, on the other hand, has much lower concentrations of iron and aluminium, probably due to filtering by matrix soil flow and by flow through disconnected macropores. Macropores would act as avenues of colloidal flushing, however, colloids could accumulate on macropore surfaces and be deposited in macropores plugging these flow paths.

7 Conclusions

The small ephemeral Mackreath Creek catchment has a complicated hydraulic and hydrochemical response to winter precipitation events. Following a long dry summer and a preceding drought year (2006), this hilly catchment did not generate stream flows until over 200 mm of precipitation fell during late Autumn rains. This Autumn drought

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breaking precipitation in April 2007 acted as a natural tracer test due to its depleted isotopic composition when compared to average winter rains and later rains in May and June. Most of this April precipitation flowed through the clayey soil system and was replaced by water from the May and June events by the time the late June-early July event occurred. By contrast, the sandy soil system apparently stored a significant portion of this water which was then displaced by event water. This displacement caused the stream water during the event to be dominated by this pre-event water, although the clayey soil system was largely dominated by event water.

Soil water flow pathways (and overland flow) before, during and after the event have distinctive hydrochemical characteristics. The clayey soil system is predictable in that it exhibits dilution by event water and increase in concentrations of most elements from overland flow to the A horizons and to the B horizon. Potassium is the exception which is highest in the A horizon, most likely due to higher amounts of organic matter and its decomposition and release of potassium. Overland flow from the sandy soil system has the lowest elemental concentrations; this is due to high infiltration rates and lack of saturation excess overland flow.

Deep throughflow is identified on the basis of both elemental concentrations and oxygen-hydrogen isotopes. Some deep flow paths in the sandy soil system are high in silica, sodium, aluminium, and iron, indicating mineral water interactions and probably transport of oxyhydroxide and clay mineral colloids.

Acknowledgements. This project was funded by Flinders University Program Grant (2006–2009), and South Australia Water Corporation grant. Access to field sites was provided by SA Water and Department of Parks and Wildlife, SA.

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Table 2. Dissolved organic carbon analyses.

MS	DOC mg/L
9:11 2 Jul 2007	13.4
9:30 3 Jul 2007	17.6
9:54 4 Jul 2007	22.3
9:27 5 Jul 2007	25.6
10:46 6 Jul 2007	25.7
12:23 6 Jul 2007	25
8:19 8 Jul 2007	21.8
12:36 11 Jul 2007	15.5
10:50 13 Jul 2007	15.2
9:39 15 Jul 2007	14.8
9:06 17 Jul 2007	24
<i>SB2 OF</i>	
11:13 4 Jul 2007	20.6
15:55 6 Jul 2007	18.1
13:03 9 Jul 2007	19.4
<i>SB2 AB</i>	
16:21 4 Jul 2007	31.2
15:55 6 Jul 2007	24.1
13:03 9 Jul 2007	22
15:58 11 Jul 2007	23.6
13:46 15 Jul 2007	14.2
<i>SB2 BC</i>	
11:01 4 Jul 2007	22.6
15:55 6 Jul 2007	16.7
13:03 9 Jul 2007	13.2
15:58 11 Jul 2007	13.1
13:46 15 Jul 2007	11.9
<i>MC1 AB</i>	
9:30 6 Jul 2007	23.1
16:00 11 Jul 2007	9.8
13:28 13 Jul 2007	10.2
13:50 15 Jul 2007	11.9
<i>MC1 BC</i>	
10:00 15 Jul 2007	19.2
<i>MC2 OF</i>	
10:31 4 Jul 2007	4.5
10:30 5 Jul 2007	2.8
11:04 6 Jul 2007	1.7
<i>MC2 DW</i>	
16:05 11 Jul 2007	11.9
13:34 13 Jul 2007	11.3

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Table 3. Stable isotopes of oxygen and hydrogen.

Site ID	Time/Date	Delta O SMOW	Delta D SMOW
MS	11:59 19 Jun 2007	-5.04	-28.1
MS	13:19 27 Jun 2007	-4.87	-27.3
MS	9:11 2 Jul 2007	-5.16	-28.4
MS	9:54 4 Jul 2007	-5.38	-25.7
MS	10:46 6 Jul 2007	-5.08	-21.5
MS	12:23 6 Jul 2007	-4.99	-21.3
MS	9:30 7 Jul 2007	-4.45	-22.2
MS	9:41 9 Jul 2007	-4.93	-25.1
MS	12:36 11 Jul 2007	-5.15	-25.4
MS	9:39 15 Jul 2007	-4.86	-23.7
MS	9:06 17 Jul 2007	-5.02	-22.8
SB2 A/B	14:16 3 Jul 2007	-3.79	-13.6
SB2 A/B	15:55 6 Jul 2007	-4.09	-17.5
SB2 A/B	10:10 7 Jul 2007	-3.59	-18.2
SB2 A/B	13:03 9 Jul 2007	-4.64	-20.6
SB2 A/B	13:46 15 Jul 2007	-4.37	-19.0
SB2 B/C	14:25 27 Jun 2007	-4.23	-18.9
SB2 B/C	9:54 2 Jul 2007	-4.18	-18.6
SB2 B/C	10:15 5 Jul 2007	-4.41	-16.4
SB2 B/C	11:29 6 Jul 2007	-3.87	-16.1
SB2 B/C	10:19 7 Jul 2007	-3.52	-17.5
SB2 B/C	10:02 10 Jul 2007	-4.42	-20.3
SB2 B/C	13:29 13 Jul 2007	-4.70	-18.5
SB2 B/C	9:52 17 Jul 2007	-4.16	-19.4
SB2 O/F	10:01 2 Jul 2007	-4.71	-22.0
SB2 O/F	11:13 4 Jul 2007	-4.55	-17.1
SB2 O/F	11:35 6 Jul 2007	-4.03	-16.5
SB2 O/F	9:20 8 Jul 2007	-4.12	-18.3
MC1 A/B	9:41 3 Jul 2007	-4.20	-18.0
MC1 A/B	11:26 6 Jul 2007	-4.22	-14.8
MC1 A/B	11:26 8 Jul 2007	-3.72	-12.8
MC1 A/B	10:41 9 Jul 2007	-4.03	-14.2
MC1 A/B	14:19 12 Jul 2007	-4.74	-20.7
MC1 A/B	13:50 15 Jul 2007	-5.03	-22.7
MC1 B/C	11:59 27 Jun 2007	-5.32	-30.5
MC1 B/C	9:41 2 Jul 2007	-5.35	-31.2
MC1 B/C	10:24 4 Jul 2007	-5.87	-30.1
MC1 B/C	11:36 06 Jul 2007	-5.75	-29.7
MC1 B/C	11:36 8 Jul 2007	-5.60	-28.7
MC1 B/C	10:30 10 Jul 2007	-5.26	-29.3
MC1 B/C	13:58 15 Jul 2007	-5.21	-24.4
MC2 B/C	11:59 27 Jun 2007	-4.04	-20.1
MC2 B/C	9:51 3 Jul 2007	-4.36	-18.6
MC2 B/C	11:46 6 Jul 2007	-4.09	-15.2
MC2 B/C	11:46 8 Jul 2007	-4.19	-15.0
MC2 O/F	9:51 03 Jul 2007	-2.72	-6.4
MC2 O/F	11:04 6 Jul 2007	-3.54	-15.7
MC2 O/F	9:45 7 Jul 2007	-5.27	-24.0
MC2 DW	17:07 10 Jul 2007	-5.14	-27.1
MC2 DW	13:34 13 Jul 2007	-5.69	-25.4
MC1 DW	10:26 17 Jul 2007	-4.85	-23.7
P	14:25 29 Jun 2007	-3.13	-13.0
P	12:34 5 Jul 2007	-3.59	-8.3
P	11:28 7 Jul 2007	-4.98	-24.6

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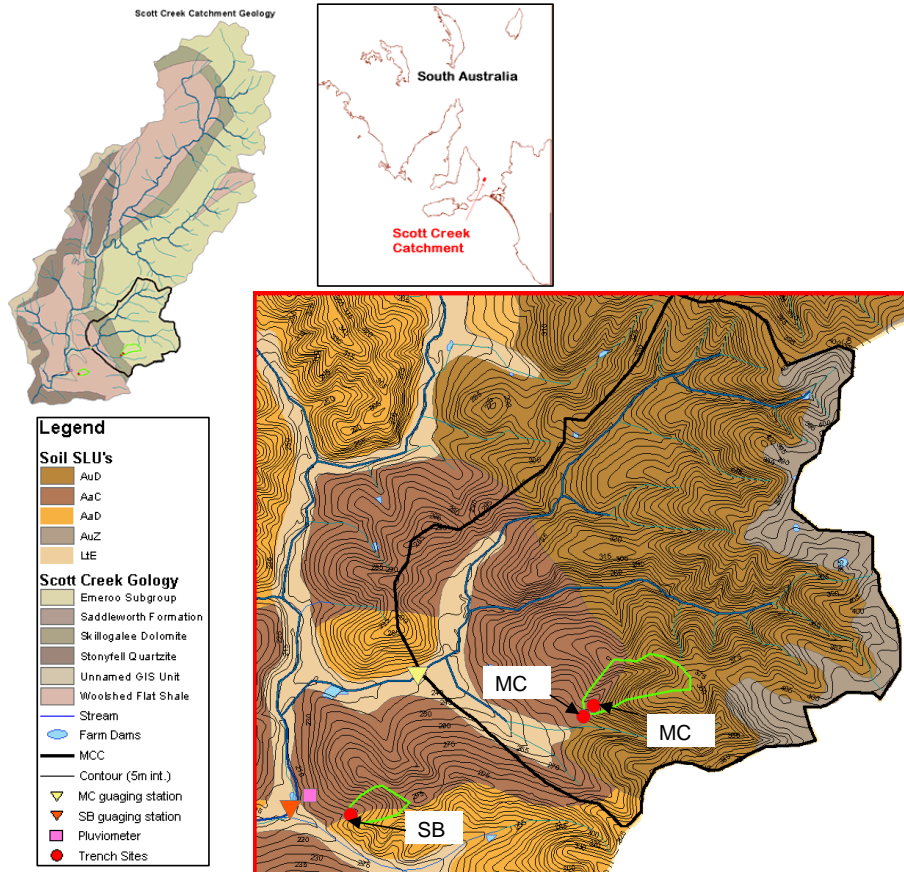


Fig. 1. Location map and maps showing the geology and soils of the MacKreath Creek catchment. Also shown are the 0-order catchments that were instrumented with soil water collectors.

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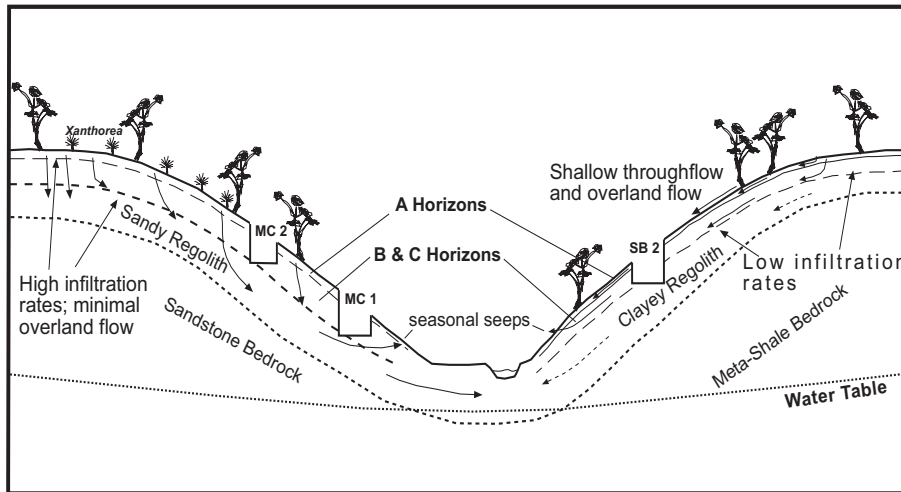


Fig. 2. Schematic cross-section of the Mackreath catchment showing sandstone and sandy soil system with high infiltration rates and clayey soil system over meta-shale with low infiltration rates. Lower in the catchment, the water table intersects the soil-regolith material as pictured.

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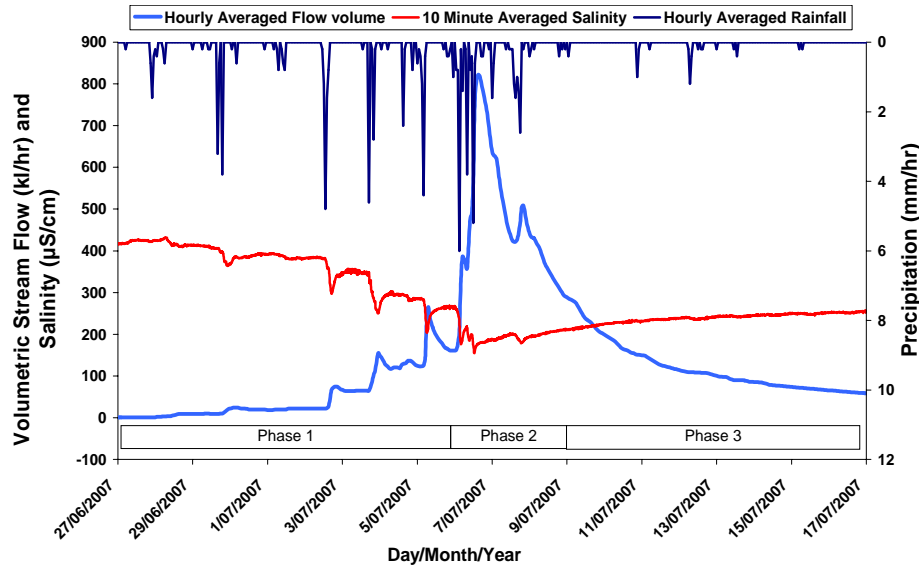


Fig. 3. Hydrograph of stream flow and rainfall of the late June–early July 2007 precipitation event.

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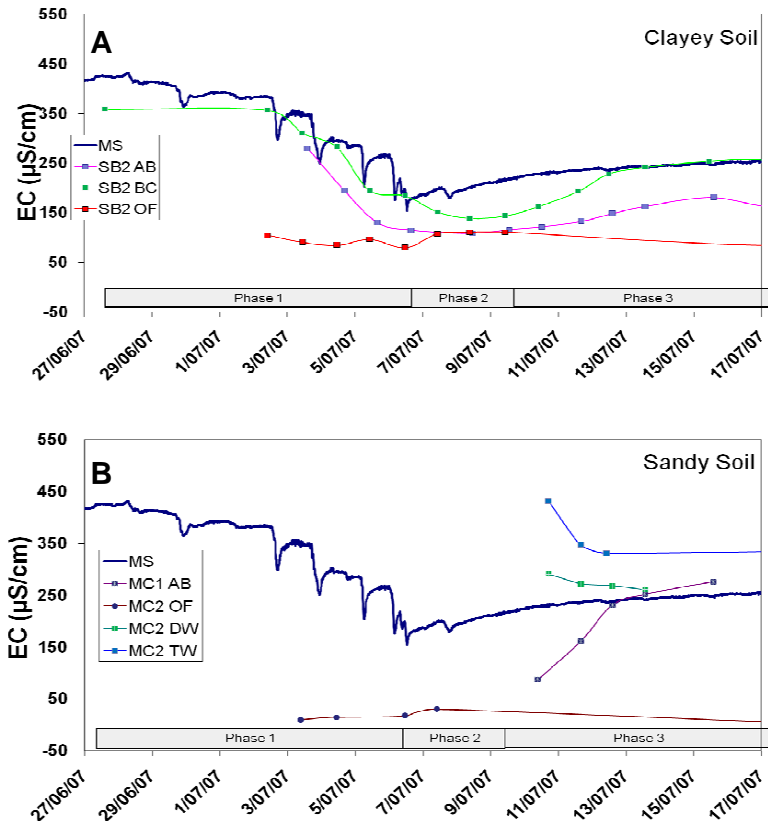


Fig. 4. Electrical conductivity of Mackreath Creek, soil A and B horizons and overland flow. **(A)** EC of clayey soil over shale bedrock and **(B)** EC of sandy soil over quartzite bedrock.

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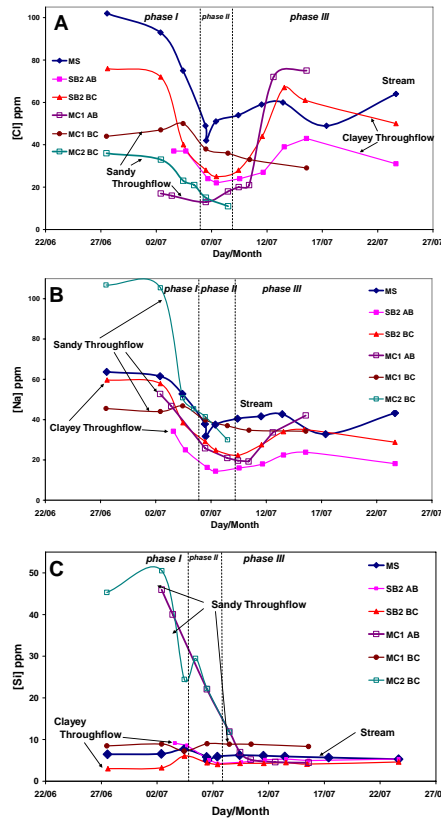


Fig. 5. Time series elemental concentration of (A) [Cl], (B) [Na], and (C) [Si] in stream waters, soil waters and overland flow during the precipitation event.

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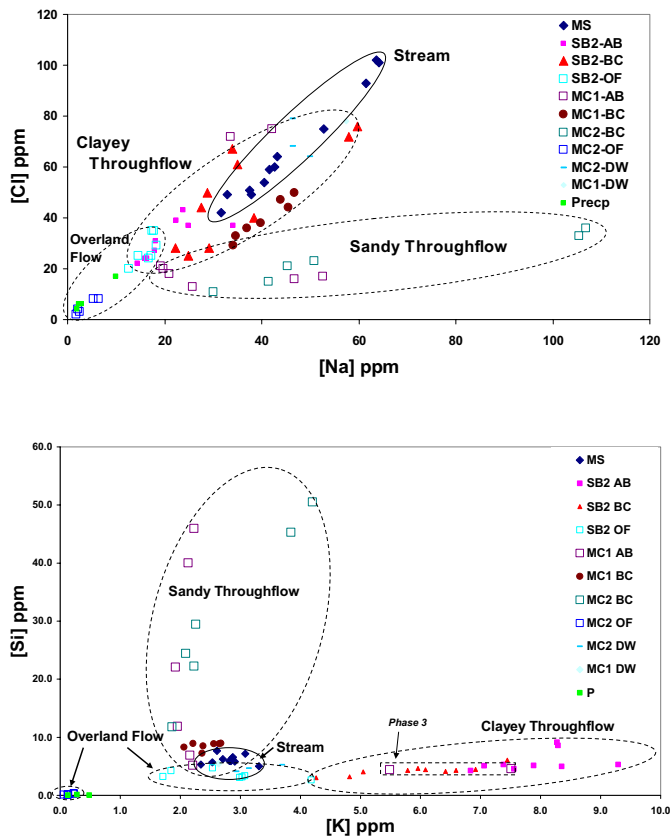


Fig. 6. Scatter plots of (A) Na and Cl and (B) Si and K in stream waters, soil waters and overland flow during the precipitation event.

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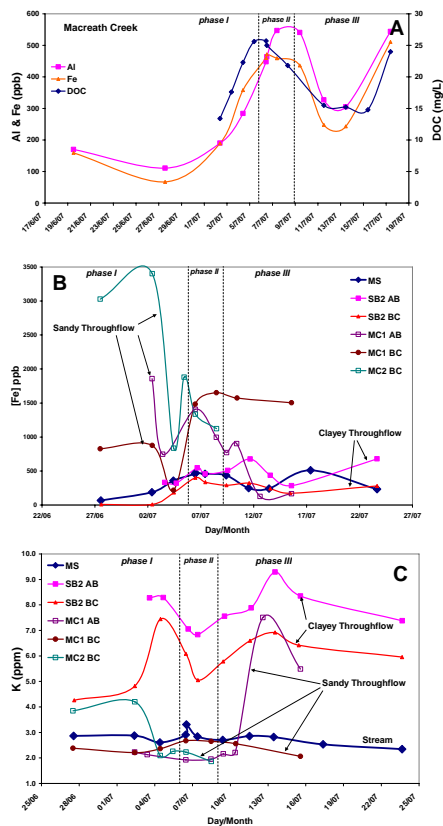


Fig. 7. Time series elemental concentrations of Fe, Al, K, and dissolved organic matter in Mackreath Stream (A), and in soil waters (B) and (C).

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Interactive Discussion



The significance and lag-time of deep throughflow

E. Bestland et al.

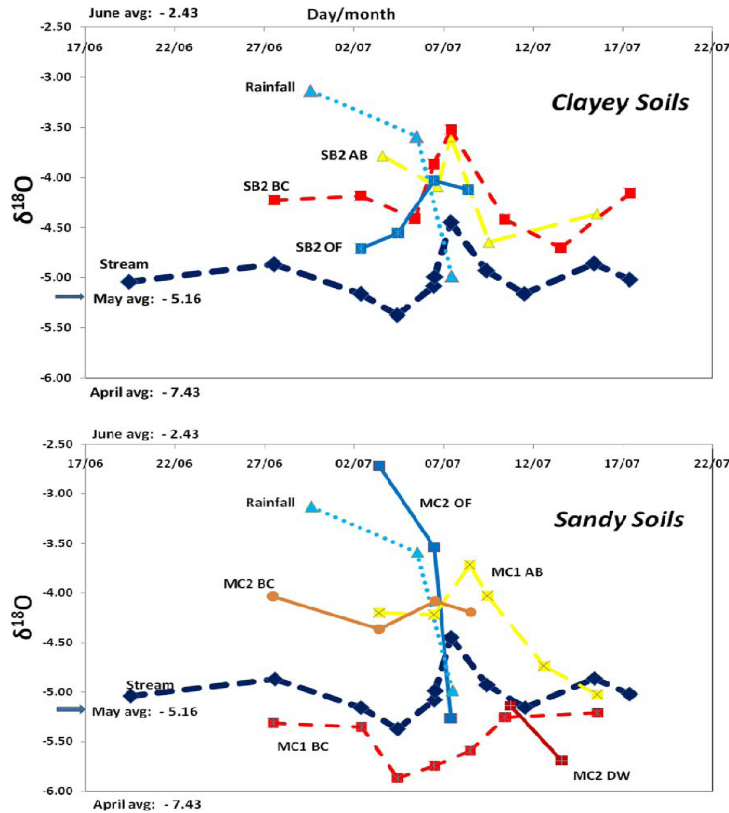


Fig. 8. Times series of oxygen isotopes from clayey soils (A) and sandy soils (B). OF – overland flow, AB – collector at A-B horizon break, BC – collector from B-C horizon transition, DW – water sampled directly from macropore flow. Analyses of bulked monthly rainfall is also given.

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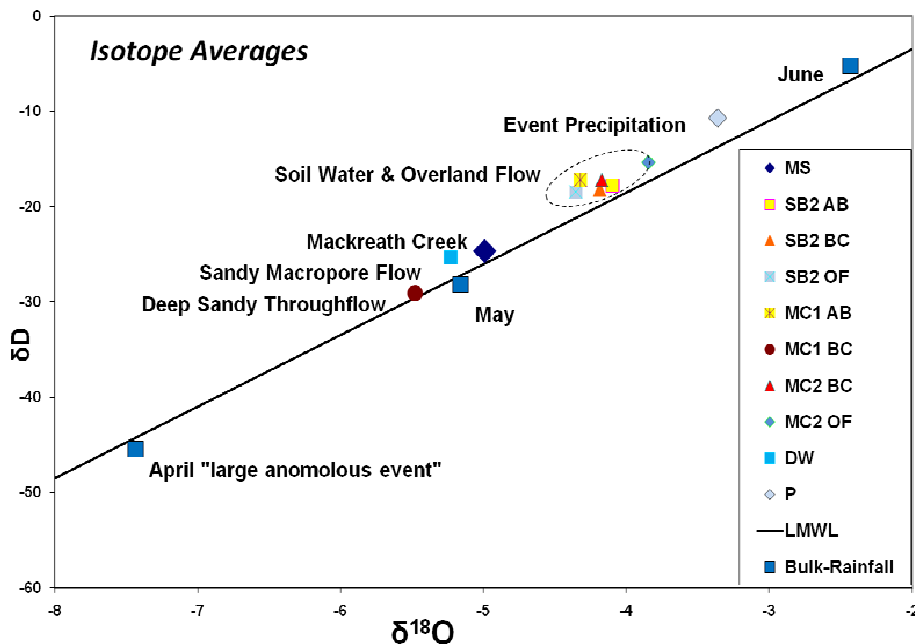


Fig. 9. Averaged isotopic composition (δD versus $\delta^{18}O$) of bulked monthly precipitation (April, May, and June, 2006), clayey soil A horizon (SB2-AB; 5 samples), clayey soil B horizon (SB2-BC; 8 samples), clayey soil overland flow (SB2-OF; 4 samples), sandy soil A horizon (MC1-AB; 6 samples), sandy soil B horizon from downslope position labelled “Deep Sandy Throughflow” (MC1-BC; 7 samples), sandy soil B horizon from up-slope position (MC2-BC; 4 samples), sandy soil overland flow (MC2-OF; 3 samples), macropore flow from sandy soils (DW; 3 samples). Local meteoric water line from Kayaalp (1999).

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