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The significance and lag-time of deep through flow: 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 soil-regolith through flow in a small ($3.4 \, \text{km}^2$) 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 through flow 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 April and May precipitation occurred prior to the initiation of stream flow in late May. These early events, especially the 127 mm April event, had low stable water isotope values compared with later rains during June and July and average winter precipitation. Thus, this large early autumn rain event with low isotopic values (δ^{18}O, δD) provided an excellent natural tracer. During later June and July rainfall events, daily stream and soil water samples were collected and analysed. Results from major and trace elements, water isotopes (δ^{18}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 and regolith zones. This pre-event water was identified in the stream as well as identified in deep soil horizons due to its different isotopic signature which contrasted sharply with the June–July event water. Based on this data, the soil-regolith hydrologic system for this catchment has been re-thought. The catchment area consists of about 60% sandy and 40% clayey soils. Regolith flow in the sandy soil system and not the clayey soil system is now thought to dominate the deep subsurface flow in this catchment. The clayey texture contrast soils had rapid response to rain events and saturation excess overland flow. The sandy soils had delayed soil through flow and infiltration excess overland flow. A pulse of macropore through flow 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 not dominated by pre-event water, demonstrating the quicker response and shallow through flow of the clayey soil system. Thus, the sandy terrain 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 stream flow 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 catchment 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
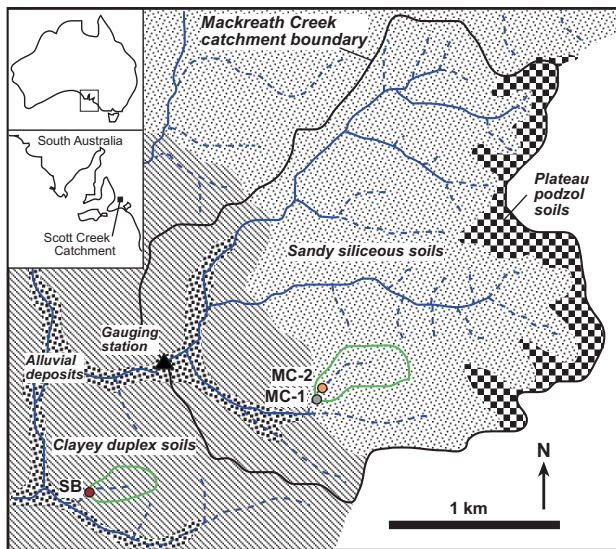
Fig. 1. Location map of the Mackreath Creek catchment showing surface drainages, the distribution of sandy and clayey soils, soil water collection sites (MC1, MC2, SB), and gauging station.

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 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. It is clear that progress toward a comprehensive understanding of the diverse range of catchments requires detailed hydrogeochemical studies of soil, regolith, groundwater, and surface water. The study presented here is based on extensive analysis of soil water, overland flow, stream water, and precipitation during a moderate sized precipitation event in a small ephemeral catchment in a strongly Mediterranean climate. In this study a catchment was selected that had minimal saturated groundwater inputs which allowed the focus to be on the unsaturated and perched soil and regolith systems.

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 unsaturated and perched flow pathways through soil and regolith. Evaluating the groundwater 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). Later studies by McDonnell et al. (1991), McGlynn et al. (2002) and others established the importance of vadose

zone water in stream flow generation, although in the very humid Maimai catchment of New Zealand that they studied, groundwater dominated over soil water.

In the study presented here, a gauged ephemeral stream (Mackreath Creek) of 3.4 km^2 catchment area in the Adelaide Hills of South Australia was investigated with the aim of characterising through flow pathways and identifying their contribution in the resulting stream flow (Fig. 1). In humid climate settings, differentiating flow paths may be important in terms of flood response, soil erosion, contaminant transport, and hydropedology (Lin, 2003). These concerns are also valid in the strongly Mediterranean climate of the Adelaide region. Important in the sub-humid to semi-arid climatic setting of much of Australia, with its highly variable rainfall, is the understanding of soil-regolith flow paths. The amount of precipitation necessary to generate deep, sustained soil-regolith through flow is critical to predicting landscape response to climate change. Groundwater recharge estimates also rely on assumptions regarding duration and extent of soil-regolith saturation.

Our original hypothesis regarding the sources and timing of stream flow generation during a precipitation event was based on assumptions of slow Darcian flow in the clayey soil-regolith system compared to more rapid subsurface flow in the sandy soil-regolith system. In this original conceptual model, macropores were thought to be important in both sandy and clayey systems; however at the hill slope scale macropores would largely be hydraulically disconnected. Thus the overall grainsize distribution of the soil-regolith and its resultant hydraulic properties would determine the rapidity of the hydraulic response to precipitation.

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 through 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 through flow to be the most important transport pathway for contaminants during years of average or below average rainfall. Mixing between through flow and overland flow on hill slopes in the MLR has been observed by Chittleborough et al. (1992) to produce similar hydrochemical signatures between flow paths.

In settings such as the MLR, soil through flow is produced by a combination of matrix flow 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, although dilute, to that of the exchange pool of the soil (Cox et al., 2002), while macropores primarily act 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 disconnected from the water table (Fig. 2), an evaluation of pre-event water held in the vadose zone can be made by an analysis of the precipitation, in this case autumn and winter rainfall leading up to the analysed event.

3 Study catchment

The Scott Creek area, which includes the Mackreath Creek study site, experiences a Mediterranean climate with cool moist winters and warm dry summers. Average daily temperatures range from 14–27°C in summer to 8–14°C in winter. The MLR receives strong seasonal rainfall, with 85% of rainfall in winter 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 at Mt. Bold; evaporation exceeds rainfall from October to May (spring, summer and autumn).

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 1.2 l/s–5.8 l/s for winter non-storm flows, 12–116 l/s for typical winter storm flows, and 232–347 l/s for two year peak flows.

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

The Mackreath Creek study site is a sub-catchment of Scott Creek Catchment and is typical of MLR catchments having 100–300 m of relief, moderately steep slopes in many areas and narrow riparian-floodplain zones. The study area, as is most of the MLR, is underlain by metamorphosed late Precambrian sedimentary rocks consisting of
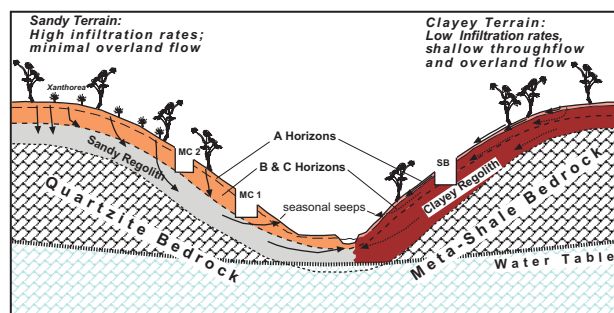

Fig. 2. Schematic cross-section of the Mackreath Creek catchment. The catchment consists of sandy soils over quartzite bedrock and clayey duplex soils over meta-shale bedrock. The sandy soils have high infiltration rates where as the clayey soil system, except for the A horizon, has low infiltration rates.

meta shales, sandstone-quartzite, and minor carbonate units (Priess, 1987). The hydrogeology of the area is that of a fractured rock aquifer (FRA) with large variations in both hydraulic conductivity and groundwater salinity (Barnett et al., 2002; Harrington, 2004a, b). The disconnection between Mackreath Creek surface water and the FRA is demonstrated by the hydraulic head of the FRA at the Mackreath Creek gauging station being lower than the stream bed by 2 to 3 m. At this gauging station there are three piezometers with depths of 16 m, 11 m and 5 m. The logs of these bores have established the fractured rock-regolith boundary at 11 m depth (Fig. 2).

The Mackreath Creek area has four landscape-soil types: 1) a narrow and shallow alluvial bottom land with sandy silty and clayey soils and deposits, 2) moderate gradient slopes underlain by meta-shale with clayey soils that have strong texture contrast between A and B horizons of the Red Brown Earth to Red Podzolic soil types (Taylor et al., 1974), 3) quartzite dominated moderate to steep slopes with Yellow Podzolic and skeletal stony and sandy soils, and 4) broad ridge tops with eroded relict and podzolized lateritic soils (Fig. 1). Of these four landscape areas, the clayey texture contrast soils and yellow podzolic soils comprise the vast majority of the catchment. Soil thickness is typically between 1–2 m. Weathered bedrock or regolith of several meters in thickness typically occurs beneath the soil horizons (Fig. 2). A number of 3–4 m deep backhoe trenches have been dug in the area and combined with drill logs has established regolith thickness and type. Where the regolith occurs over meta shale, it consists of a stony massive, heavy clay. And where the regolith occurs over quartzite, it consists of silty stony sand with some clayey zones. Small quartzite outcrops occur scattered along steep side slopes and narrow ridge tops.

Soil water collectors were installed in the two main soil types; clayey texture contrast soils and yellow podzolic soils (Fig. 1). Mackreath Creek soil water collection sites MC1
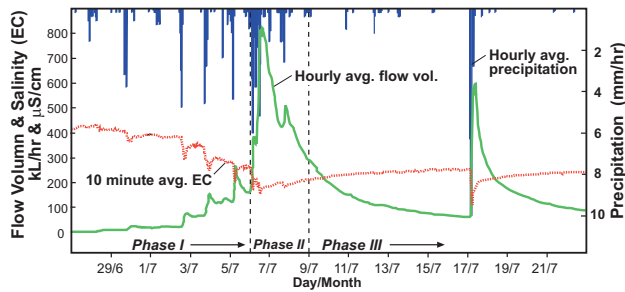
Fig. 3. Hydrograph of stream flow and rainfall of the late June-early July 2007 precipitation event. Electrical conductivity from automatic logger is also shown. Phase I refers to the rising limb of the hydrograph with a duration of about 7 days. Phase II refers to peak precipitation and stream flow with duration of 3 days. Phase III refers to the falling limb and has a duration of 8 days until the precipitation event of 17 June.

and MC2 are positioned to collect water flowing through sandy soil horizons (Fig. 2). Scott Bottom site (SB) represents flow through a texturally contrasting clayey soil. This site is just outside Mackreath Creek sub-catchment and is assumed to have soil water and overland flow hydrochemical signatures that are much the same as water flowing through the texture contrast soils at Mackreath Creek. The Scott Bottom (SB) site is underlain by the same meta shale geologic formation. Clayey texture contrast soils in Mackreath creek occur on slopes lacking either 0-order catchments or large areas of homogenous meta-shale and clayey texture contrast soil substrate.

Mackreath Creek catchment is predominately comprised of native vegetation; however, substantial human impacts have occurred and consist of land clearance on lower gradient slopes with clayey texture contrast soils, a few farm dams, and bulldozed fire tracks on most ridge tops. Native vegetation in this area consists of eucalyptus trees with lesser acacia trees. Most clayey soil sites have been cleared to some extent, and are now being replanted with native trees and shrubs. These areas are presently a mix of thick grass and large eucalyptus trees (up to 30 m) comprising a savannah landscape. Most sandy soil sites have not been cleared and consist of shorter trees (5–10 m) and an understory of shrubs, heath and scattered grasses comprising an open woodland to woodland. Deep sandy soils have areas of bracken fern. Rocky sandy soils have xanthorrhoea (grass trees) and casuarinaceae (sheoaks) in addition to eucalypts.

4 Methods

The three soil water collector sites, MC1, MC2, and SB were instrumented with one overland flow collector and two inter-flow 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 5cm 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 soil through flow, three meter deep trenches were dug at each site by a backhoe (long axis of trench was downhill) 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 through flow samples. A low levee of dirt surrounded the upper parts of the trench so that overland flow would be diverted. The face of each trench (uphill side) was instrumented with two fibreglass wick through flow collectors with 0.16 m² area of soil contact at the A/B and B/C horizons.

Soil through flow 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 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 SB, through flow 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 SB and MC1 required tubing to be connected to the PVC piping of the through flow collector and ran out of the trench downhill to a container.

An auto-logger installed in the stream provided a continuous record of electrical conductivity (EC) variations. The logged data from the stream was corrected with a hand-held and calibrated EC meter; corrected data is plotted in Figs. 3 and 4. In addition, total dissolved solids (TDS) were calculated from major and trace element analysis by ICP MS (Inductively Coupled Plasma Mass Spectrometry). A very good correlation of R^2 0.970 was observed between corresponding hand held EC measurements (converted to TDS using 0.66 EC) and total dissolved solids from ICP MS analyses.

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 (HNO_3). Water samples were transferred the same day as sampling and stored in a 30 ml McCartney bottle for water isotope ($^2H/^1H$ and $^{18}O/^{16}O$) analysis. Samples were kept cool during transport to prevent evaporation. 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 ICP MS. 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 $^{18}O/^{16}O$ and $^2H/^1H$ respectively.

5 Results

5.1 Electrical conductivity/salinity

Electrical conductivity measurements were made of Mackreath Creek at the gauging station, soil horizon through flow, and overland flow before, during and after the precipitation event of late June and early July (2007) (Figs. 3 and 4). This precipitation-stream flow event began approximately on 30 June (2007) with daily showers. These showers increased in frequency over the next 7 days culminating in a rainfall event on 6 July. This build-up of rainfall and rise in stream flow is termed phase I in this study (Fig. 3). The three day peak of stream flow following the rainfall of the 6 is termed phase II. And the falling limb of the hydrograph with a few late showers is phase III; this lasted for 8 days until the next significant precipitation event.

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; however, major and trace elemental analysis and oxygen and hydrogen isotope analyses were obtained from these low volume samples.

Clayey soil EC measurements show predictable decreases in salinity from B horizon to A horizon and to overland flow (Fig. 4). Overall, the A horizon salinity was 10% lower than the B horizon values. During the beginning of the event, overland flow was 70% lower than B horizon values. However, dilution of soil horizon EC during peak precipitation decreased the difference to about 15%. During the waning stage of the event, overland flow EC reached parity with A horizon values.

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 horizon water of clayey soils from grav-
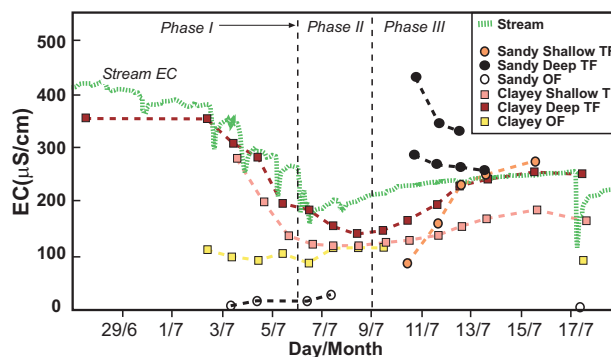

Fig. 4. Electrical conductivity of Mackreath Creek (corrected from automatic logger), deep and shallow through flow (TF) from the sandy soil system, deep and shallow through flow from the clayey soil system, and overland flow (OF) from both the clayey and sandy soil systems.

ity collectors and from the mid-slope position sampled, do not have higher EC (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 I and II of the event. Nonetheless, relatively high EC values and decreasing trends were measured for sandy deep through flow during phase III of the event (Fig. 4). Sandy shallow through flow had increasing EC during phase III reaching parity with the deep through flow, probably due to mixing of water masses during the event. Overland flow EC values were very low, the lowest of all the measurements, indicating the low exchange phase reservoir in the A horizon of these sandy soils. Low EC of sandy overland flow is also due to a lack of saturation excess overland flow in these high infiltration sandy soils.

During phase III of the event, through flow water filled the two trenches at the sandy soil site. Through flow water did not fill the clayey trench. This rise in perched soil-regolith water lasted for three days and was a mix of observed macropore flow and matrix flow from the B horizon. Sandy soil macropore flow was sampled directly in the up-slope trench site (MC2) as actual macropore flow and included in the deep sandy through flow. 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. The perched soil-regolith water was higher in EC than the B horizon macropore flow.

5.2 Elemental concentrations

Similar to overall EC values, major ion concentrations (chloride, sodium, bicarbonate, silica, calcium and magnesium) in stream flow and in most soil water show dilution trends during and after peak flow (Fig. 5, bicarbonate, calcium and magnesium not shown). Major elements chloride and sodium

Table 1. Selected elemental concentrations from ICP analysis.

		Al	Ba	Br	Ca	Cl	Fe	K	Mg	Na	S	SO4	Si	Sr
Date/Time	Site ID	ppb	ppb	ppb	ppb	ppm	ppb	ppb	ppb	ppm	ppm	ppm	ppb	ppb
19/06/2007 11:59	MS	170	65	176	9750	101	159	3084	11907	64	12	36	7166	63
27/06/2007 13:19	MS	111	48	182	11521	102	67	2866	12085	64	12	36	6450	76
02/07/2007 9:11	MS	190	41	175	8774	93	189	2876	11132	62	10	30	6564	58
04/07/2007 9:54	MS	284	142	176	6457	75	358	2609	8324	53	7	21	7655	44
06/07/2007 10:46	MS	448	141	127	4254	49	460	2907	5411	38	4	12	5823	30
06/07/2007 12:23	MS	464	59	112	3625	42	472	3311	4165	32	4	12	4996	25
07/07/2007 9:30	MS	547	85	131	3819	51	459	2841	4859	38	4	12	5915	29
09/07/2007 9:41	MS	541	36	137	3970	54	436	2707	5279	40	4	12	6232	30
11/07/2007 12:36	MS	327	32	142	4443	59	248	2855	5735	42	5	15	6128	33
13/07/2007 10:50	MS	305	44	145	4707	60	243	2819	5839	43	5	15	5956	35
17/07/2007 9:06	MS	544	52	123	4123	49	511	2532	5100	33	4	12	5687	35
23/07/2007 15:42	MS	299	39	144	4947	64	232	2344	6586	43	4	12	5293	40
03/07/2007 14:16	SB A/B	534	250	105	12875	37	331	8276	11715	34	8	24	9143	102
04/07/2007 16:21	SB A/B	407	206	118	8317	37	320	8292	7426	25	7	21	8592	73
06/07/2007 15:55	SB A/B	1004	180	95	3638	24	546	7058	3060	16	3	9	5118	32
07/07/2007 10:10	SB A/B	832	112	83	2988	22	457	6835	2590	14	3	9	4235	26
09/07/2007 13:03	SB A/B	989	51	90	3243	24	508	7554	2699	16	3	9	4558	28
11/07/2007 15:58	SB A/B	1140	51	109	3813	27	676	7887	3286	18	3	9	5151	33
13/07/2007 13:30	SB A/B	776	110	125	4979	39	437	9294	4687	22	3	9	5317	44
15/07/2007 13:46	SB A/B	727	93	117	5673	43	284	8351	5890	24	4	12	4970	52
23/07/2007 15:48	SB A/B	1014	101	108	4195	31	679	7381	3917	18	3	9	5325	44
27/06/2007 14:25	SB B/C	33	57	71	5791	76	10	4261	11656	60	17	51	3019	67
02/07/2007 9:54	SB B/C	56	70	80	6380	72	10	4821	12495	58	15	45	3220	74
04/07/2007 11:01	SB B/C	223	91	81	7036	40	184	7445	10174	38	12	36	6072	68
06/07/2007 11:29	SB B/C	724	89	82	3356	28	402	6083	5323	29	9	27	4442	36
07/07/2007 10:19	SB B/C	678	85	76	2661	25	336	5048	4239	25	8	24	4038	28
09/07/2007 10:25	SB B/C	680	44	81	2393	28	292	5787	3588	22	8	24	4306	30
11/07/2007 13:44	SB B/C	531	57	82	3656	44	323	6594	5788	28	6	18	4292	40
13/07/2007 13:29	SB B/C	295	95	86	5460	67	243	6919	9219	34	6	18	4466	66
15/07/2007 10:43	SB B/C	227	72	80	5886	61	173	6419	9816	35	6	18	4111	62
23/07/2007 15:45	SB B/C	475	71	92	4284	50	280	5958	7384	29	6	18	4617	54
27/06/2007 14:25	SB O/F	124	116	143	3380	35	71	1712	2761	18	1	3	3250	31
02/07/2007 10:01	SB O/F	220	26	142	3537	35	194	1846	2725	17	1	3	4250	33
04/07/2007 11:13	SB O/F	276	110	106	3122	25	380	2539	2916	15	1	3	4731	27
06/07/2007 11:35	SB O/F	309	30	72	2353	20	259	4181	1901	13	1	3	2663	18
07/07/2007 10:28	SB O/F	237	67	87	3370	24	228	3028	2705	17	2	6	3173	26

have higher concentrations in the stream than in most of the through flow samples (Fig. 5a, b, Table 1). Clayey soil through flow waters are relatively high in chloride compared to most of the sandy through flow. Sodium and silica concentrations, however, are higher in most of the sandy through flow than in both the clayey through flow and stream water. For silica, higher concentrations in the sandy through flow in the first half of the event are striking (Fig. 5c). These values in the sandy shallow system through flow are in contrast to much lower values in the sandy deep through flow (site MC2, BC horizon contact).

The relationship between chloride and sodium in through flow 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 chloride of any of the water samples (soil and stream); these stream concentrations of conservative chloride indicate that there is a missing component of the system. There are no known salt deposits in this area of the Mt Lofty Ranges. In order to balance high salinity pre-event stream water, a higher salinity water mass is needed but 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.

A few general observations can be made regarding the elemental concentrations. Stream flow chloride and sodium concentrations have trends during the event similar to clayey soil through flow and overland flow as would be expected for dilution during peak flow (Figs. 5a and 6a). Most sandy shallow soil system through flow samples have lower

Table 1. Continued.

Date/Time	Site ID	Al ppb	Ba ppb	Br ppb	Ca ppb	Cl ppm	Fe ppb	K ppb	Mg ppb	Na ppm	S ppm	SO4 ppm	Si ppb	Sr ppb
09/07/2007 10:29	SB O/F	231	27	90	3421	25	205	2989	2659	17	2	6	3067	25
23/07/2007 16:18	SB O/F	435	56	109	4186	29	434	3073	3260	18	2	6	3379	35
02/07/2007 9:41	MC1 A/B	5707	249	71	7427	17	1858	2229	4164	53	3	9	45964	15
03/07/2007 9:41	MC1 A/B	1498	78	78	5992	16	747	2131	3020	47	3	9	40039	13
06/07/2007 11:26	MC1 A/B	3287	101	55	3631	13	1407	1921	2616	26	2	6	22071	8
08/07/2007 11:26	MC1 A/B	2461	100	44	2241	18	995	1952	2199	21	2	6	11891	6
09/07/2007 10:41	MC1 A/B	1654	100	34	1596	20	770	2161	2028	20	2	6	6919	6
10/07/2007 9:30	MC1 A/B	1749	258	37	1625	21	902	2210	2066	19	3	9	5168	11
12/07/2007 14:19	MC1 A/B	287	73	132	2602	72	125	7508	7479	34	4	12	4591	51
15/07/2007 13:50	MC1 A/B	375	135	168	2915	75	165	5487	9684	42	5	15	4429	58
27/06/2007 11:59	MC1 B/C	2117	102	83	3613	44	826	2381	4679	46	10	30	8493	27
02/07/2007 9:51	MC1 B/C	2285	61	85	2913	47	876	2212	4427	44	10	30	8923	26
04/07/2007 10:24	MC1 B/C	390	162	90	3036	50	217	2361	4086	47	13	39	7236	27
06/07/2007 11:36	MC1 B/C	3348	140	80	2465	38	1483	2675	3746	40	10	30	8981	26
08/07/2007 11:36	MC1 B/C	3562	96	80	2028	36	1652	2647	3587	37	10	30	8889	26
10/07/2007 10:30	MC1 B/C	3735	137	79	1731	33	1574	2558	3305	35	10	30	8873	24
15/07/2007 13:58	MC1 B/C	7977	142	77	2172	29	1503	2062	3826	34	12	36	8319	25
27/06/2007 11:59	MC2 B/C	4556	153	198	17703	36	3028	3845	13622	107	5	15	45303	60
02/07/2007 9:59	MC2 B/C	6217	103	202	18872	33	3402	4202	14010	105	4	12	50517	60
04/07/2007 10:34	MC2 B/C	483	217	176	8677	23	835	2092	5616	51	7	21	24437	28
05/07/2007 10:34	MC2 B/C	3763	159	191	7893	21	1881	2258	5536	45	6	18	29471	26
06/07/2007 11:46	MC2 B/C	2790	126	164	6241	15	1335	2230	3971	41	5	15	22240	20
08/07/2007 11:46	MC2 B/C	2073	108	153	3967	11	1122	1863	2831	30	5	15	11781	15
03/07/2007 9:51	MC2 O/F	27	112	7	487	4	31	223	371	2	0.5	1.5	311	6
05/07/2007 10:34	MC2 O/F	18	189	16	766	8	12	133	508	5	0.5	1.5	206	8
06/07/2007 11:04	MC2 O/F	10	67	8	220	3	12	127	265	3	0.5	1.5	90	2
07/07/2007 9:45	MC2 O/F	61	114	23	612	8	38	227	640	6	2	6	353	6
17/07/2007 9:27	MC2 O/F	27	38	<5	223	2	16	63	134	2	0.5	1.5	131	1
10/07/2007 17:07	MC2 DW	329	173	196	2869	64	123	2938	7647	50	3	9	4133	42
11/07/2007 16:05	MC2 DW	475	158	238	2719	79	153	3698	6809	46	4	12	5246	53
13/07/2007 13:34	MC2 DW	342	107	222	2530	68	100	3142	6836	46	3	9	4690	45
17/07/2007 10:26	MC1 DW	432	272	238	3274	78	193	2640	8826	57	6	18	5430	49
29/06/2007 14:25	P	53	6	15	1815	6	44	282	491	2	<1	1.5	125	9
05/07/2007 12:34	P	17	2	16	522	6	14	483	440	3	<1	1.5	41	4
07/07/2007 11:28	P	7	2	53	473	17	<10	440	1317	10	2	6	<40	7
17/07/2007 12:26	P	27	5	11	281	4	<10	132	366	2	1	3	62	2

chloride and higher sodium than clayey system through flow (Fig. 6a). Likewise, silica is much higher in these sandy shallow through flow samples (Fig. 6b). The sandy deep through flow show much the same behaviour as clayey system through flow samples (Figs. 5 and 6), although it does not have the potassium concentration of the clayey system (Fig. 6b).

5.3 Dissolved organic carbon, aluminium and iron

Dissolved organic carbon analyses were obtained from 34 samples of stream water and selected through flow 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 from clayey soil A horizon from phase I of the event (31.2 mg/L). In Mackreath Creek, the concentrations of DOC, aluminium, and iron all rise and fall during the event hydrograph (Fig. 7a). The DOC concentration peak occurs between two and three 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 three to four 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 II flow. High concentrations of iron and aluminium occur in many of the sandy through flow samples (Fig. 7b). Clayey soil through flow, 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).

Table 2. Dissolved organic carbon analyses.

Site ID; Date & Time	DOC mg/L
MS (stream)	
02/07/2007 9:11	13.4
03/07/2007 9:30	17.6
04/07/2007 9:54	22.3
05/07/2007 9:27	25.6
06/07/2007 10:46	25.7
06/07/2007 12:23	25
08/07/2007 8:19	21.8
11/07/2007 12:36	15.5
13/07/2007 10:50	15.2
15/07/2007 9:39	14.8
17/07/2007 9:06	24
SB OF	
04/07/2007 11:13	20.6
06/07/2007 15:55	18.1
09/07/2007 13:03	19.4
SB AB	
04/07/2007 16:21	31.2
06/07/2007 15:55	24.1
09/07/2007 13:03	22
11/07/2007 15:58	23.6
15/07/2007 13:46	14.2
SB BC	
04/07/2007 11:01	22.6
06/07/2007 15:55	16.7
09/07/2007 13:03	13.2
11/07/2007 15:58	13.1
15/07/2007 13:46	11.9
MC1 AB	
6/07/2007 9:30	23.1
11/07/2007 16:00	9.8
13/07/2007 13:28	10.2
15/07/2007 13:50	11.9
MC1 BC	
15/07/2007 10:00	19.2
MC2 OF	
04/07/2007 10:31	4.5
5/07/2007 10:30	2.8
06/07/2007 11:04	1.7
MC2 DW	
11/07/2007 16:05	11.9
13/07/2007 13:34	11.3

Fig. 5. Time series elemental concentration of **(A)** chloride, **(B)** sodium, and **(C)** silicon in stream waters and soil water through flow (TF) during the measured event. Note high concentrations of sodium and silicon during phase I. Also note generally higher concentrations of chloride and sodium in stream water than in soil water.

5.4 Oxygen and hydrogen isotopes

Isotopes of oxygen ($^{18/16}$O) and hydrogen ($^{2/1}$H) were sampled over the late June-early July event from Mackreath Creek, soil horizon through flow, overland flow, and precipitation (Figs. 8 and 9). In addition, bulked rainfall samples for April, May, and June were analysed. An important parameter to consider for the analysis of isotopes of oxygen and hydrogen in small catchments is the antecedent moisture condition and the isotopic composition of the pre-event water in the system. In the case of this small, relatively steep ephemeral catchment in a strongly Mediterranean climate, the autumn precipitation leading up to water flowing in the system is particularly important. The characterisation of pre-event water
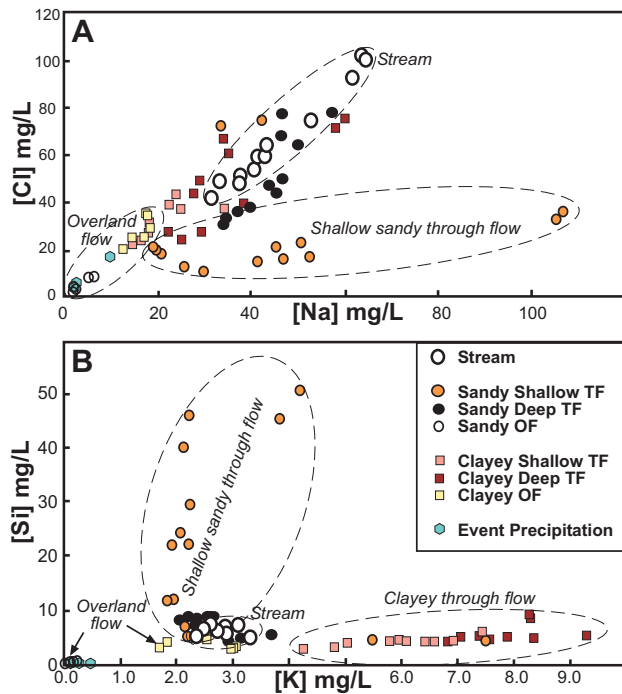
Fig. 6. Scatter plots of **(A)** sodium and chloride and **(B)** silicon and potassium in stream waters, soil water through flow (TF) and overland flow (OF) during the measured event. The sandy shallow through flow is high in silicon and sodium compared to other components of the system.

in such a system lacking baseflow is difficult. Vadose zone water prior to the event will be a mix of infiltrated rainfall that has been subjected to different degrees of evaporation. In the case studied here, the previous long dry summer and previous drought year caused a massive soil moisture deficit that is difficult to quantify. In April 2007, following this long dry summer and previous winter drought, a large precipitation event of between 130-150mm occurred over four days. Importantly, this large precipitation event had significantly lower oxygen (δ^{18}O of -7.43‰) and hydrogen (δD of -45.5‰) isotopes when compared to more typical winter precipitation events. May 2007 bulk rainfall is more typical of winter rainfall at this elevation in the MLR-Adelaide Hills with δ^{18}O of -5.16‰ and δD of -28.2‰ (Kaylaap, 1999). Low water isotope values during heavy precipitation events result from decreased fractionation between vapour and condensate as condensate fraction increases (Kendall & Doctor, 2007). June 2007 bulk rainfall however has higher isotopic values compared to more typical winter values with δ^{18}O of -2.43‰ and δD of -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 samples represent the bulk of the event and have an average isotopic composition of δ^{18}O of -3.36‰ and δD of -10.65‰. Important to
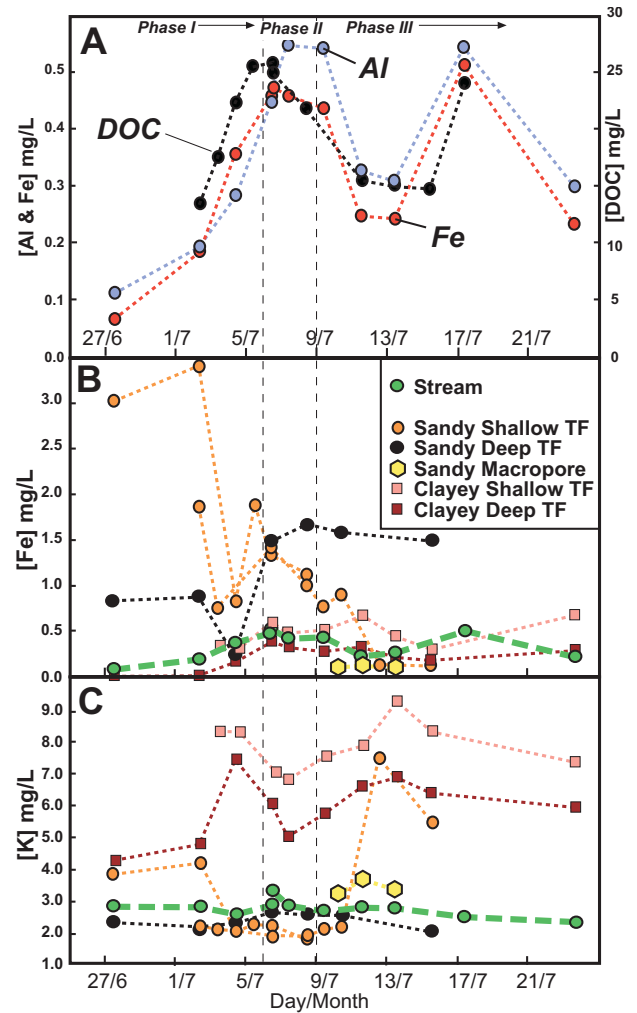

Fig. 7. Time series elemental concentrations of iron, aluminum, potassium, and dissolved organic matter in Mackreath Stream **(A)**, and in soil water through flow (TF) (**B** and **C**).

note for the time series of oxygen isotopes (Fig. 8) and hydrogen isotopes (not shown) is that the third sample is considerably lower compared to the first two (δ^{18}O of -4.98 and δD of -24.6‰) and is from a few late small showers.

Important to note from the plot of the time series of oxygen and hydrogen isotopes (Fig. 8, hydrogen isotopes not shown) is that all values are higher than the stream flow except for the sandy deep through flow samples (MC1-BC). This through flow sample site is situated lower on the hill slope and with the collector installed below a clayey sandy-silt B horizon. There is a natural seasonal seep a few meters from this site that became active during the wet season. This sandy deep through flow becomes lower in isotopic value during the transition between phase I and II of the event, similar to the stream (Fig. 8b). Shallow soil horizon collectors (from A/B horizon contact) from both the clayey and sandy landscapes show an increase in isotopic values corresponding
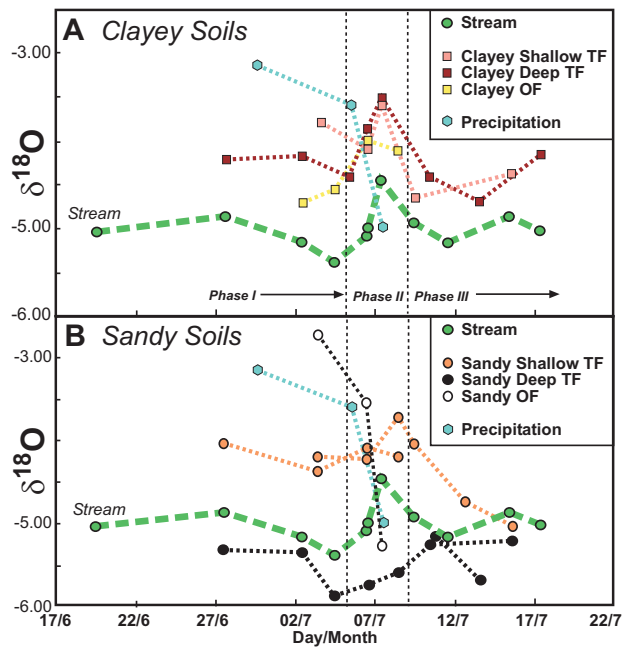
Fig. 8. Times series of oxygen isotopes from clayey soils (**A**) and sandy soils (**B**) compared to stream water (TF – through flow; OF – overland flow). Sandy deep through flow has lower δ^{18}O and δD values. The first two precipitation samples record the vast majority of the event; last sample was of late showers.

Fig. 9. Averaged isotopic composition (δD versus δ^{18}O) of bulked monthly precipitation (April, May, and June, 2007), clayey soil through flow (TF) from both A and B horizons horizon (12 samples), shallow sandy through flow (9 samples), and deep sand through flow (7 samples). Volume averaged event precipitation is also shown. Local meteoric water line (LMWL) from Kayaalp (1999).

to the influx of higher isotopic values of the event water during phase I. However, during phase III, shallow soil water collectors from both sandy and clayey sites show a decrease in isotopic values that is well below the first two event precipitation sample values. Clearly pre-event water that is lower in isotopic value compared to event water mixed into the through flow. Deep through flow collectors in both the clayey and sandy systems show dilution and an increase in isotopic values by event water during phase I followed by a decrease in isotopic values during phase III, again indicating mixing of pre-event water in the through flow system. This decrease in isotopic values in the through flow during phase III is most likely not due to the small volume of water from the late showers which have relatively low isotopic values.

The sandy deep through flow waters are noteworthy for the following reasons: 1) isotopic values are lower 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 increase in isotopic value during the event, indicating minimal mixing of event water with pre-event water.

The isotopic values of the various components of this system (sandy deep through flow, sandy shallow through flow, clayey through flow, event precipitation, and monthly bulked rainfall) are well illustrated by graphing δ^{18}O and δD of both the averages of the different components of the system and individual data points (Fig. 9). The bulked rainfall samples of April, May, and June 2007 have a large range of values as has
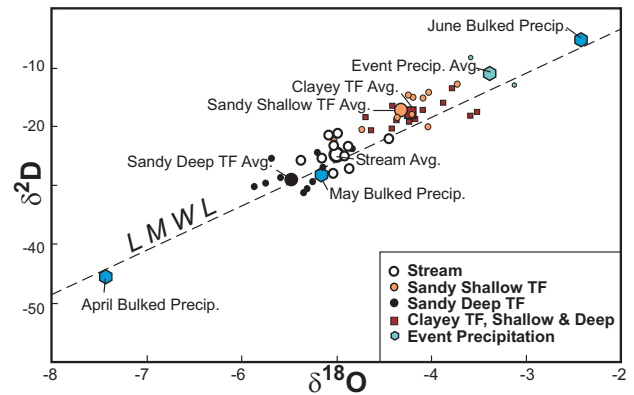
been described above. The low isotopic value of the sandy deep through flow and Mackreath Creek are obvious when compared to the event precipitation and other soil through flow samples and averages.

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 capturing all significant soil-regolith flow paths. There are important findings from the present study that are directing on-going research. Down-slope change in soil water due to increased residence time within the soil was largely undocumented in the present study but which is presently being investigated. 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 some of these variations are not explained by event water dilution. Nonetheless, a number of interpretations can be made from the data collected.

The overland flow from the clayey soil system reaches parity in its EC and in other elements (Milgate, 2007) with the shallow soil through flow (Fig. 4). 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. Soon after peak rainfall, the compositions diverge with A horizon concentrations increasing and overland flow remaining the same.

Table 3. Stable isotopes of oxygen and hydrogen.

Site ID	Date/Time	Delta O SMOW	Delta D SMOW
MS	19/06/2007 11:59	−5.04	−28.1
MS	27/06/2007 13:19	−4.87	−27.3
MS	02/07/2007 9:11	−5.16	−28.4
MS	04/07/2007 9:54	−5.38	−25.7
MS	06/07/2007 10:46	−5.08	−21.5
MS	06/07/2007 12:23	−4.99	−21.3
MS	07/07/2007 9:30	−4.45	−22.2
MS	09/07/2007 9:41	−4.93	−25.1
MS	11/07/2007 12:36	−5.15	−25.4
MS	15/07/2007 9:39	−4.86	−23.7
MS	17/07/2007 9:06	−5.02	−22.8
SB A/B	03/07/2007 14:16	−3.79	−13.6
SB A/B	06/07/2007 15:55	−4.09	−17.5
SB A/B	07/07/2007 10:10	−3.59	−18.2
SB A/B	09/07/2007 13:03	−4.64	−20.6
SB A/B	15/07/2007 13:46	−4.37	−19.0
SB B/C	27/06/2007 14:25	−4.23	−18.9
SB B/C	02/07/2007 9:54	−4.18	−18.6
SB B/C	05/07/2007 10:15	−4.41	−16.4
SB B/C	06/07/2007 11:29	−3.87	−16.1
SB B/C	07/07/2007 10:19	−3.52	−17.5
SB B/C	10/07/2007 10:02	−4.42	−20.3
SB B/C	13/07/2007 13:29	−4.70	−18.5
SB B/C	17/07/2007 9:52	−4.16	−19.4
SB O/F	02/07/2007 10:01	−4.71	−22.0
SB O/F	04/07/2007 11:13	−4.55	−17.1
SB O/F	06/07/2007 11:35	−4.03	−16.5
SB O/F	08/07/2007 9:20	−4.12	−18.3

Table 3. Continued.

Site ID	Date/Time	Delta O SMOW	Delta D SMOW
MC1 A/B	03/07/2007 9:41	−4.20	−18.0
MC1 A/B	06/07/2007 11:26	−4.22	−14.8
MC1 A/B	08/07/2007 11:26	−3.72	−12.8
MC1 A/B	09/07/2007 10:41	−4.03	−14.2
MC1 A/B	12/07/2007 14:19	−4.74	−20.7
MC1 A/B	15/07/2007 13:50	−5.03	−22.7
MC1 B/C	27/06/2007 11:59	−5.32	−30.5
MC1 B/C	02/07/2007 9:41	−5.35	−31.2
MC1 B/C	04/07/2007 10:24	−5.87	−30.1
MC1 B/C	06/07/2007 11:36	−5.75	−29.7
MC1 B/C	08/07/2007 11:36	−5.60	−28.7
MC1 B/C	10/07/2007 10:30	−5.26	−29.3
MC1 B/C	15/07/2007 13:58	−5.21	−24.4
MC2 B/C	27/06/2007 11:59	−4.04	−20.1
MC2 B/C	03/07/2007 9:51	−4.36	−18.6
MC2 B/C	06/07/2007 11:46	−4.09	−15.2
MC2 B/C	08/07/2007 11:46	−4.19	−15.0
MC2 O/F	03/07/2007 9:51	−2.72	−6.4
MC2 O/F	06/07/2007 11:04	−3.54	−15.7
MC2 O/F	07/07/2007 9:45	−5.27	−24.0
MC2 DW	10/07/2007 17:07	−5.14	−27.1
MC2 DW	13/07/2007 13:34	−5.69	−25.4
MC1 DW	17/07/2007 10:26	−4.85	−23.7
P	29/06/2007 14:25	−3.13	−13.0
P	05/07/2007 12:34	−3.59	−8.3
P	07/07/2007 11:28	−4.98	−24.6

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. 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 et al., 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 through flow waters, colloidal iron oxyhydroxides and clay minerals flushed from some soil horizons may be a more likely explanation. Another possible source of colloids could be remobilised sediment from creek beds; however, in 2007 the previous flow of similar volume occurred two years prior, thus remobilisation is unlikely.

Water samples in this study were filtered to $0.45\,\mu$m, leaving a colloidal fraction, as defined by Buffle and Van Leeuwan (1992) and Stumm (1993), in the $0.20\,\mu$m to $0.45\,\mu$m size range. It is clear that the sandy shallow through flow sites showed very elevated levels of iron and aluminium during phase I when compared to stream and 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 shallow 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–$0.2\,\mu$m) from through flow samples were high in iron whereas, coarser-grained colloids (0.2–$0.5\,\mu$m) contained more aluminium. Additionally, their A2

horizon samples were deficient in fine-grained colloids, presumably due to translocation of these colloids through the soil profile.

The sandy shallow soil system through flow has elevated concentrations of silica and sodium, compared to the stream and 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 through flow. This mineral weathering is most likely the cause of the distinct hydrochemical trends evident for the sandy shallow through flow 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 during phase I of the event (Fig. 5). Weathering of silicate material, both from in situ soil and from dust, in the presence of soil acids and higher moister contents of the A horizon is probably the cause of these elevated concentrations.

Another factor that could explain the differing elemental concentrations in the various through flow samples is the residence time of soil water in the soil-regolith system. Longer residence time is indicated for the sandy deep through flow system by the dominance of pre-event water in this flow path as deduced from oxygen and hydrogen isotopes. The lowest $\delta^{18}O$ and δD water, and therefore the water that is the most strongly influence by pre-event water (sandy deep through flow; MC1-BC) has consistent hydrochemical trends for the seven isotopic and most elemental samples analysed. The narrow range of values for MC1-BC is intermediate between the high silica and sodium sandy shallow through flow waters and the clayey through flow 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 through flow pulse of macropore water was identified in the sandy soil system based on field observations of trenches filling with water and active macropore flow. Samples of this through flow pulse have elevated chloride, sodium, magnesium, and potassium concentrations but relatively lower silica, iron and aluminium concentrations (Figs. 5 and 7, Mg and Al not shown). Thus, a possible scenario is that this pulse flushed dissolved solids from deep in the soil-regolith profile. Why this water was not elevated in silica, from silicate mineral hydrolysis, is not known. One possibility is that the pre-event water from the April event may have infiltrated the soil without extensive flushing of exchangeable constituents due to the very dry nature of the landscape prior to this precipitation event.

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 has low values of ^{18}O and ^{2}H isotopes obtained from the large April event and to a lesser degree from May precipitation. When compared to later through flow from the sandy soil system, this pre-event water is not exceedingly high in dissolved constituents. 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.

The clayey soil system by contrast has lower concentrations of ^{18}O and ^{2}H 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 has a lowering of isotopic values as the event progresses, indicating that water, probably from deeper in the regolith and dominated by pre-event water (from April and May), was pushed out and subsequently mixed with higher isotopic ratio surface event water.

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 two to three 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. Pre event water in the sandy soil system from early rains in April and May do not show elevated concentrations of iron and aluminium. These waters infiltrated through the same sandy soil system as event waters that were much higher in iron and aluminium. Two possibilities are: 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 but could be due to the severe dryness of the landscape prior to this initial April event. Nonetheless, the measured event shows high concentrations of iron and aluminium coming from sandy soil horizons early in the event. These colloids were probably 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 breaking precipitation in April 2007 acted as a natural tracer test due to its low $\delta^{18}O$ and δD 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 through flow in the sandy system was identified mainly on the basis of oxygen and hydrogen isotopes. Strongly contrasting oxygen and hydrogen isotopes of autumn and early winter precipitation combined with a severe soil moisture deficit prior to detailed measurement created a natural tracer experiment.

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