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Biomass uptake and fire as controls on groundwater solute evolution on a southeast Australian granite: aboriginal land management hypothesis

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Abstract

The chemical composition of groundwater and surface water is often considered to be dominated by water–rock interactions, particularly weathering; however, it has been increasingly realised that plant uptake can deplete groundwater and surface water of nutrient elements. Here we show, using geochemical mass balance techniques that at our study site in Southwest Victoria, Australia, water–rock interactions do not control the hydrochemistry. Instead the chemical species provided by rainfall are depleted by plant biomass uptake and exported, predominantly through fire. Regular landscape burning by Aboriginal land users is hypothesized to have caused the depletion of chemical species in groundwater for at least the past 20 000 yr by accelerating the export of elements that would otherwise have been stored within the local biomass. These findings are likely to be representative of southeast Australia, as well as similar climatic regions elsewhere in the globe, and contrast with Northern Hemisphere studies of groundwater and surface water chemistry, where water–rock interactions are the dominant hydrochemical control.

1 Introduction

The geochemistry of groundwater has been generally considered to be dominated by water–rock interactions (Garrels and Mackenzie, 1967; Moulton et al., 2000; Pogge von Strandmann et al., 2008; Taylor and Velbel, 1991; Turner et al., 2010; Velbel, 1985; Velbel and Price, 2007; White et al., 2002). However, despite often being in contact with the aquifer rock for long periods of time, groundwater in southeast Australia does not always show strong water–rock interaction signatures (e.g. Bennetts et al., 2006; Edwards and Webb, 2009; Raiber et al., 2009).

Furthermore, it has been increasingly recognised that vegetation can influence the composition of groundwater in two ways. Firstly, through increased weathering rates resulting from low pH microenvironments around the roots, accelerating the release

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of elements from rock and soil minerals and encouraging cation exchange. Secondly, through biomass acting as a nutrient sink, exporting chemical species in organic matter that is removed from the system through flooding and fire (Calmels et al., 2011; Cleaves et al., 1970; Edwards and Webb, 2009; Feikema et al., 2012; Moulton et al., 2000;

5 Taylor and Velbel, 1991; Velbel and Price, 2007; White et al., 2002).

Ca^{2+} , K^+ , HCO_3^- , Mg^{2+} , and S (macronutrients), and Na^+ and Si (micronutrients) are all utilised by plants and are sourced from the regolith and water infiltrating through it (Atwell et al., 1999; Marschner, 1989). As a result the infiltrating water can become depleted in these elements, potentially overwriting any water–rock signature in the

10 groundwater and surface water (Edwards and Webb, 2009). To what extent vegetation removes these elements from the system and temporarily locks them up in biomass depends on the vegetation type, whether uptake is consistent year-round, the underlying geology, and the amount of water moving through the system (Moulton et al., 2000; Velbel and Price, 2007).

15 To assess the relative importance of different processes on the evolution of groundwater and surface water composition as they travel through a hydrological system, geochemical mass balances are commonly used (Bricker et al., 2004; Garrels and Mackenzie, 1967; Locsey et al., 2012; Rasmussen et al., 2011; Velbel and Price, 2007; Wood and Low, 1986). Most geochemical mass balance studies have focused on surface water, looking at the export of chemical species from a system via stream baseflow (e.g. Turner et al., 2010). These present-day (short term) studies look at a snapshot of weathering, extrapolating to consider the broader impacts of silicate weathering on CO_2 dynamics over longer timescales (Velbel and Price, 2007). The same mass balance approach can be used to investigate the longer term evolution of groundwater,

20 taking into account the entire chemical evolution that has taken place while the water was beneath the surface (Chapelle, 2010; Locsey et al., 2012; Plummer and Back, 1980; Wood and Low, 1986).

Previous studies on the role of plant uptake in groundwater and surface water chemistry are dominated by high rainfall, Northern Hemisphere settings. In contrast, the

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present study is in the much drier southeast of Australia where the vegetation was native Eucalypt forest for the relevant timescales of this study. This study aims to determine the geochemical evolution of groundwater at the study site over the time scales that the groundwater represents (~20 000 yr BP), and to investigate the role of vegetation uptake within this process.

2 Background

2.1 Wider project

This study is part of a larger paired-catchment investigation into the impacts of tree plantations on the quality and quantity of groundwater and surface water resources in Victoria, Australia (Adelana et al., 2014; Camporese et al., 2013; Dresel et al., 2012). Due to the age of the groundwater (generally 1000–7000 yr old, with a maximum age of ~20 000 yr; see later discussion) it was not possible to use the hydrochemistry to determine the effect of the new plantation on the water composition, as the trees were planted in June 2008.

2.2 Study site

The study area is a pair of small, adjacent catchments, 1.33 km² in total, in Southwest Victoria, situated on the Devonian-aged Dwyer Granite, ~390–395 Ma old (Fig. 1; Hergt et al., 2007; VandenBerg, 2009). The mineralogy of the Dwyer Granite is dominated by potassium-rich alkali-feldspar, quartz and plagioclase (An_{18-30} , with phenocryst cores generally $\sim An_{25-30}$), along with minor biotite, calcic hornblende and accessory phases, the latter including opaque oxides, apatite, allanite, titanite and zircon (Hergt et al., 2007). The upper ~20 m of the granite is well weathered, porous and permeable saprolite; below this is relatively fresh, fractured bedrock. The fractured granite aquifer extends no deeper than 150 m, as below this depth the fracture conductivity is negligible due to the high lithostatic pressure (Cook, 2003; Boutt et al., 2010; Dept.

Sustainability and Environment, 2012). The topography of the site, a series of hills in the middle of a broad valley (Fig. 1), means both catchments are local ground water systems, and there are no regional groundwater inputs.

The climate is maritime/temperate, Cfb in the Köppen classification; the average annual rainfall for the area is 672 mm ($\pm 125 \sigma$), while pan evaporation is 1350 mm annually, exceeding rainfall for the majority of the year, excepting the winter months of May through September (data from Bureau of Meteorology, Hamilton, Australia; Fig. 2).

The pre-European vegetation of the area was mostly open Eucalypt woodland (Department of Sustainability and Environment, Victoria; Fig. 3). Following European settlement there was extensive land clearance, and the catchments were entirely converted to pasture by 1869 (White et al., 2003); a *Eucalyptus globulus* plantation, planted in July 2008, now covers the majority of the northern catchment (Fig. 1). Eucalypt forests are evergreen and transpire and grow throughout the year, but tend to have slower growth and transpiration periods over winter due to decreased sunlight hours.

15 3 Materials and methods

3.1 Water sampling

All 23 groundwater bores across the entire site, along with weirs on the streams draining the two catchments, Lambing Hut and Dwyer's Creeks, were sampled once each over a period of a year, August 2010 to August 2011 (Table 1, Fig. 1 – note six are nested bore sites, and are represented by only a single dot). Seasonal variability in groundwater composition is considered negligible due to the older age of the groundwater at the study site (see Table 1), and repeat sampling produced virtually identical field parameters. For example bore 2278 was sampled twice within the year-long sampling campaign, three months apart, and showed no significant compositional changes over this time, which included a shift from drought to wetter conditions. Six other bores (2285, 2289, 2290, 2291, 2292 and 2294) were also sampled twice, 10 months apart.

for field parameters only, and showed no significant change either. Groundwater bores were sampled after first removing three holding volumes to ensure representative water samples were obtained (USEPA, 1999). Temperature, pH, dissolved oxygen and electrical conductivity were all measured in the field, at the time of sampling.

- 5 The focus of this study is on the long term groundwater evolution, with no intention of reporting a “present-day” weathering mass balance which would require a much higher resolution sampling of the surface water (Velbel and Price, 2007).

3.1.1 Chemical analysis

Sub-samples for cations were filtered through 0.45 µm filter paper, acidified using

- 10 HNO_3 . Na^+ and K^+ were analysed on a flame photometer, and Ca^{2+} and Mg^{2+} were analysed using Atomic Absorption Spectroscopy. Subsamples for anions were filtered with 0.45 µm filter paper, but not acidified. HCO_3^- was manually repeat-titrated to a pH of 4.5 using HCl standardised to NaCO_3 . Si was analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy, Cl^- was analysed using Ion Chromatography, and SO_4^{2-} was analysed using both these methods. Each of these analyses was completed at La Trobe University, Melbourne. All charge balance errors were within ±10 %, except for one sample in Group B (−19 %, most likely due to an underestimation of Ca^{2+}), which is very dilute (Table 1), and so this level of accuracy is acceptable (Hem, 1985).

20 3.1.2 ^{14}C analysis

Radiocarbon dating was carried out at the Australian Nuclear Science and Technology Organisation (ANSTO) in Sydney, where dissolved inorganic carbon was extracted from the water samples by addition of phosphoric acid and sparging with He. CO_2 was collected cryogenically then converted to graphite by reduction with hydrogen over an iron catalyst at 600 °C (Hua et al., 2001). The graphite target was measured on the STAR or ANTARES accelerator, with all measurements normalised against the oxalic

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acid (HOXI) international standard. For each sample ^{14}C concentration and/or radio-carbon age was determined after corrections for AMS machine background, procedural blank and isotopic fractionation using the $\delta^{13}\text{C}$ of the graphite which was obtained by analysis using EA-IRMS (Fink et al., 2004). Radiocarbon ages are uncalibrated ages (Table 2). Samples with pMC values > 100 are considered modern; those samples with pMC > 95 are designated “young” as they all contain measurable tritium, i.e. younger than 1950 (Clark and Fritz, 1997). A correction for dead carbon was not required due to the absence of carbonates in the granite and overlying regolith (based on XRD analyses), and the limited effects of other processes potentially affecting the ^{14}C activity in this region (Cartwright, 2010).

3.1.3 Tritium analysis

Samples were analysed for tritium at ANSTO by distillation, electrolytic enrichment and finally counting using the Liquid Scintillation Counting technique. Samples containing measurable tritium values are taken as “modern,” i.e. recharged in the past 50 yr, (Clark and Fritz, 1997). Using data from Adelaide, Cape Grim and Melbourne for atmospheric tritium present in rainfall and the decay curve of tritium (half life of 12.32 yr), sample ages can be estimated, e.g. sample 2297 is most likely to have received some recharge in 1960 or earlier (Fig. 4). However, the age of most samples is poorly constrained, e.g. sample 2281 has a much broader age window, from 1975–1995 or during 1960 and earlier (Fig. 4).

3.2 Geochemical mass balance

Geochemical mass balances are a popular method for determining the source of solutes in groundwater and surface water, particularly the contribution from weathering (Garrels and Mackenzie, 1967; Velbel and Price, 2007). In a typical geochemical mass balance, the local rainfall composition is subtracted from the groundwater composition,

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3.2.1 Isocon diagram and element mobility

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- During granite weathering, feldspars and mafic minerals are altered to clays with a concomitant loss of soluble ions into groundwater. The overall chemical change can be quantified by comparing the unaltered granite composition with that of the in situ overlying weathered granite regolith using an isocon plot (Grant, 1986). In this method, the changes in element concentrations as fresh rock is weathered to regolith are determined by plotting the weight percents of all elements in both materials against each other. Immobile elements plot along a straight line (the isocon), those that are lost as the fresh rock weathers plot below the isocon, and those that become enriched, or more concentrated during weathering, plot above the isocon (Grant, 1986). Zr is generally immobile during weathering so isocons are typically defined using this element (Grant, 1986; Webb and Golding, 1998).

The slope of the isocon defines the mass change during alteration; the relative enrichment or depletion of mobile elements can then be calculated from:

$$15 \quad \% \text{ change in composition} = \frac{C_x[\text{weathered regolith}] - A \cdot C_x[\text{fresh rock}]}{A \cdot C_x[\text{fresh rock}]} \cdot 100 \quad (1)$$

where A is the slope of the isocon ($Zr_{[\text{weathered regolith}]} / Zr_{[\text{fresh rock}]}$; Zr is the concentration of Zirconium), and C_x is the concentration in wt% of element x in either the weathered regolith or the fresh rock (Grant, 1986). The change in composition calculated from

- 20 Eq. (1) is exactly equivalent to the mass transfer coefficient of Brimhall et al. (1991), and is the negative of the chemical depletion fractions (CDF) as defined by Riebe et al. (2003):

$$\text{CDF}_x = \left(1 - \frac{C_x[\text{weathered regolith}]}{C_x[\text{fresh rock}]} \frac{Zr[\text{fresh rock}]}{Zr[\text{weathered regolith}]} \right) \quad (2)$$

- 25 Those elements that have been lost from the system during the weathering of the fresh rock to regolith can be clearly identified, and are assumed to enrich the groundwater

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and surface water as they are exported (Garrels and Mackenzie, 1967). In the present study, the isocon was calculated using the composition of the fresh granite taken from Hergt et al. (2007), and the composition of the weathered granite in the overlying regolith obtained from XRF analyses (Table 4; Fig. 6).

5 3.2.2 X-ray fluorescence (XRF) and X-ray diffraction (XRD)

The bulk chemical composition of weathered granite samples from bore 2281 at depths of 6 m, 18 m and 38 m was determined by XRF using 0.7500 ± 0.0001 g of sample mixed with 6.7500 ± 0.0001 g of 66 : 34 lithium tetraborate : lithium metaborate flux (oven-dried at 400°C for 2 h) and fused at 1050°C into a glass button using an automated fusion machine. Glass buttons were analysed using a Siemens SRS 303 AS Wavelength Dispersive XRF spectrometer. Elements were reported as wt% oxides (Table 4).

XRD analysis was performed on the same samples (dried and milled to $\sim 60\,\mu\text{m}$) from $4\text{--}70^\circ$ for 90 min, using a Siemens D5000 X-ray Diffractometer.

15 4 Results and discussion

4.1 Geochemical mass balance I – Group A groundwater and surface water samples

For the majority of groundwater samples (20), once the rainfall had been subtracted from the normalised concentrations, the remaining concentrations of all the major 20 chemical species were negative (Table 5); these samples are termed Group A. These negative values mean that there are no remaining element concentrations to assign to water–mineral interactions once rainfall inputs have been taken into account, and therefore the mass balance cannot be taken past this step.

The groundwater samples show a wide variety of ages, from modern to 20 000 yr old, but there is no clear relationship between aquifer residence time and cation concentra-

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tions (Fig. 7a and b). The varying times for groundwater to interact with the aquifer rock have not resulted in an increase in cation concentrations with groundwater age; most of the modern groundwater (containing tritium: 0.035–0.399 Bq kg⁻¹) shows a similar range of cation depletion to much older samples. There is also no relationship between 5 groundwater sampling depth and cation concentrations (Fig. 7c).

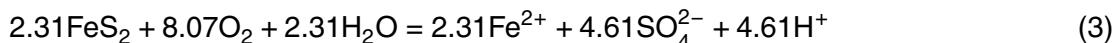
Surface water in both creeks in the study area, like the Group A groundwater, is depleted in all species with respect to rainfall (Table 6), but because we don't know the rate of elemental uptake by biomass, and the surface water was not regularly sampled, the stream compositions cannot be used for weathering rate estimations as in some 10 other geochemical mass balance studies (e.g. Turner et al., 2010).

4.2 Geochemical mass balance II – Group B groundwater samples

For three of the samples, Na⁺, SO₄²⁻ and H₄SiO₄ concentrations were still positive after subtracting rainfall inputs (Table 5); these samples are termed Group B. The strong SO₄²⁻ excess after normalisation and rainfall subtraction is attributed to pyrite oxidation.

15 Pyrite is present in small amounts in the granite (Atkinson, 1976), but pyrite oxidation is evident in only a few of the groundwater samples in this study. This is because pyrite distribution in the granite is very heterogeneous and/or because the resulting SO₄²⁻ addition is small relative to the effect of evapotranspiration. Acidity released by pyrite oxidation (Eq. 3) has attacked plagioclase in the Dwyer Granite (Eq. 4); biotite and K-feldspar are present in much smaller amounts than plagioclase and so do not contribute significantly to the water composition (Hergt et al., 2007).

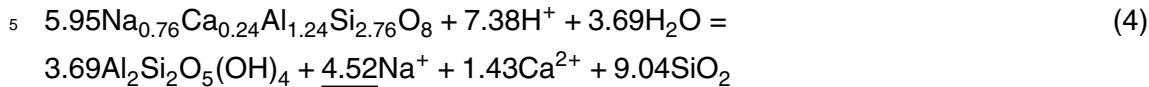
20 The pyrite oxidation reaction (Eq. 3) is balanced using the median input SO₄²⁻ levels (underlined) from the Group B groundwater analyses (Table 5):



The plagioclase weathering reaction (Eq. 4) results in the formation of kaolinite (the only clay mineral identified in the soil using XRD), and is balanced using the average composition of plagioclase in the Dwyer Granite (An_{18–30}; Hergt et al., 2007) and the

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excess Na⁺ levels present in Group B samples (underlined). The H⁺ released by pyrite oxidation is less than that consumed by plagioclase weathering, indicating an additional source of acidity, probably carbonic acid from CO₂-rich soil water (Garrels and Mackenzie, 1967):



Once the ions released by these two weathering reactions are accounted for, the Group B samples are depleted in all chemical species, preventing the use of additional mineral weathering reactions in the mass balance (Table 7).

Two of the Group B samples are modern (tritium concentrations of 0.304 and 0.339 Bq kg⁻¹; Fig. 7b) and are very dilute, showing minimal influence of evapotranspiration (150–220 µScm⁻¹; Table 1). This suggests that they were recharged rapidly, despite their sampling depths, along preferential pathways, most likely open fractures in surface outcrops of the granite (Fig. 7c). This is clearly visible in the groundwater potentiometric surface from late 2012, where preferential flow paths through these two bores are evident compared to the surrounding bores (Fig. 8). They show evidence of pyrite oxidation, probably facilitated by the rapid influx of oxygenated waters. This reaction releases relatively large amounts of acidity quickly, so it has caused rapid alteration of weatherable minerals in the granite, accounting for the evidence of plagioclase weathering in these samples (Table 5).

The third sample in Group B (2281) represents mixing between modern dilute water with a rock-weathering signature and detectable levels of tritium, and older water containing datable radiocarbon (see Sect. 3.1.3; Figs. 4 and 7a). As a result some rock-weathering input is evident in this sample, but it is not as obvious as in the other two samples of Group B.

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4.2.1 Predicted groundwater inputs from granite weathering

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TiO₂, FeO and SiO₂ all plot along the Zr isocon suggesting they have not moved significantly during weathering (within the uncertainty due to compositional variations; Fig. 6; Grant, 1986; Webb and Golding, 1998). The small gain in Al is not believed to be significant. CaO, K₂O, MgO, MnO and Na₂O are all strongly depleted in the weathered granite saprolite (by 52–96 %; Table 4). These elements are lost into the groundwater, and so the groundwater should therefore be enriched in these species with respect to rainfall. However, for the majority of groundwater samples, the geochemical mass balance shows that all species are depleted (Table 5). This has been observed in a nearby catchment where Ca²⁺, HCO₃⁻, K⁺, Mg²⁺ and Na⁺ are all depleted in the groundwater (Edwards and Webb, 2009). Even the Group B groundwater samples in this study are enriched in only two species (Na⁺ and SO₄²⁻; Table 7).

4.3 Depletion of chemical species

It is evident that one or more processes overwrite the influence of rock weathering on the hydrochemistry, causing depletion of all species in the groundwater. This depletion could be due to mineral precipitation (Adams et al., 2001; Bennetts et al., 2006; Bullen et al., 1996), cation exchange (Adams et al., 2001; Bennetts et al., 2007), or plant uptake (Edwards and Webb, 2009).

Mineral precipitation can cause species depletion, but PHREEQC equilibrium modelling (to determine saturation indices) shows that groundwater and surface water saturation indices in the study area for all likely minerals (calcite, gypsum, aragonite and halite), are all strongly negative (Table 8). XRD analyses of the soil profile in the study area and nearby areas found that none of these or other minerals are present, and only kaolinite is being formed by the weathering process, which is already accounted for in geochemical mass balance II (see Sect. 4.2; Edwards and Webb, 2009).

Cation exchange on clays cannot be causing the depletion in the Group A samples because there is no evidence of cation enrichment in the water compositions to balance

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2007; White and Blum, 1995; White et al., 2002). In contrast, water–rock interactions have only localised effects in this study, observed as excess Na^+ and SO_4^{2-} due to plagioclase weathering and pyrite oxidation (see Sect. 4.2), with the vast majority of samples having a signature of element depletion due to the overriding impact of plant uptake.
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4.4 Export of chemical species

Depletion of elements in the soil and the groundwater and surface water over the Dwyer Granite indicates that the vegetation is mining the hydrological system, removing more nutrients than are being introduced through precipitation and rock weathering. However, important nutrient species utilised by the vegetation are recycled; in Eucalypt species like those growing in the study area, leaf litter, bark shedding, and dead wood re-introduce large amounts of nutrient species back into the system (Attiwill, 1978; Feikema et al., 2012). Continued input through precipitation and rock weathering, together with recycling by vegetation, should result in a buildup of elements in the system, but there is no evidence of this occurring in the isocon plot (Fig. 6), or the groundwater and surface water mass balance calculations (Tables 5–7), so export of elements must be taking place. The erosion of particulate organic matter is a potential export process, but because of generally low flows in southeast Australian rivers, large scale removal of organic matter occurs only during infrequent flood events and is therefore unlikely to be the major process responsible for export of nutrients from the system (Edwards and Webb, 2009; McMahon et al., 1987).
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A much more effective process of nutrient removal is through fire. Burning clears away the forest understory and fallen bark, branches and leaf litter (Atwell et al., 1999; Gammage, 2011); nutrients are exported in smoke and rapidly leached out of the ash, causing nutrient pulses in surface water following bush fires (Chessman, 1986; Lane et al., 2008).
25

Recharge of the majority of groundwater samples (15) collected in this study occurred prior to European settlement, during the Late Pleistocene and Holocene

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(Fig. 6a). Fire has been a feature of the Australian landscape during this time, as shown by charcoal distribution in sediment cores throughout Australia, and has been attributed to anthropogenic promotion of fire across most of Australia for the last ~45 000 yr (Bowman, 1998; Edney et al., 1990; Head, 1988, 1989; Kershaw, 1986; Kershaw et al., 1991; 5 Lynch et al., 2007; Mooney et al., 2011). Controlled fire was used regularly by Aboriginal land users in Australia to increase the productivity of the land, burning areas as often as once every two to four years, to the extent that the pre-European settlement forests were generally very open and mostly devoid of understory (Gammage, 2011). Fire encourages seed release, seed germination and the stimulation of budding and 10 flowering, with many Australian plant species dependent on fire for seed propagation and fruit production (Bowman, 1998; Gammage, 2011; Gott, 2005). Newly germinated bulbs, seeds and grasses promoted by burning the land can soon attract animals, expose their tracks and increase their visibility for hunting, improving the availability of 15 this food source for Aboriginal land users (Attiwill et al., 1978; Bowman, 1998).

Comparing the rainfall deficit from Table 5 with the leaf biomass element concentrations for *Eucalyptus camaldulensis*, a common tree species at the study site prior to European clearance, shows that a burning frequency in the order of every one to ten years would account for the species depletion observed (Table 10; Briggs and Maher, 1983; values for *E. camaldulensis* hybrids were used for Na content and to compare 20 biomass concentrations; Fekeima et al., 2012). The leaf biomass values are calculated from the average composition of Eucalypt foliage (Fekeima et al., 2012), and median values of yearly leaf litter ($163\,000\,\text{kg}\,\text{ha}^{-1}$) in an *E. camaldulensis* swamp in NSW, approximately 450 km northeast of the study site ($33^{\circ}51'\,\text{S}, 144^{\circ}50'\,\text{E}$; Briggs and Maher, 1983); the tree density is believed to be similar to that of the pre-European forest in the 25 study area.

The calculated fire frequencies are probably too high, as they underestimate the biomass lost in fires, because although leaf mass represents the bulk of the tree material removed during fire, other biomass such as bark and smaller limbs are also consumed. Gammage (2011) estimated that Aboriginal burning occurred in landscapes

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like that of the study area as frequently as every two to four years. This broadly matches the calculated fire frequencies from Table 10, where, for example, the vegetation foliage would need to be burned every eight years to account for the observed depletion of K in the groundwater based on average rainfall K compositions.

Many Australian plant species are fire adapted, recovering rapidly after fire, especially when competition species are eliminated, as the ash is a rich source of plant nutrients (Atwell et al., 1999; Gammage, 2011). Fire was common in southwest Victoria throughout the time that most of the older groundwater samples at the study site were being recharged, providing a strong link between Aboriginal land management practices and groundwater composition.

Hydrochemical studies in higher rainfall, Northern Hemisphere areas have not shown a significant influence of plant uptake and nutrient export on the water composition; rock-weathering processes dominate (Garrels and Mackenzie, 1967; Moulton et al., 2000; Taylor and Velbel, 1991; Turner et al., 2010; Velbel and Price, 2007; White et al., 2002). This is due either to reduced uptake by the vegetation species compared to Australian Eucalypts, and/or the lack of large, regular export events. The larger input from rock-weathering is not due solely to greater element availability in rocks freshly exposed by recent glacial processes either, as some of the study areas are beyond the limit of the Pleistocene glaciations (Garrels and Mackenzie, 1967; Taylor and Velbel, 1991; Velbel and Price, 2007; White et al., 2002).

Some of the groundwater samples in this study (9 including mixed samples, Fig. 6b) are young enough to have been recharged following European settlement in the area, but show the same depletion pattern as the older samples. Following extensive land clearance in the area after 1869 there has been a decrease in the regularity of bush fires, but the intensity of the fires has increased, and elements continue to be removed from the system through this process. In addition, nutrient species are exported by harvesting and grazing (Clymans et al., 2011; Heckman et al., 2003). Thus while modern agriculture is a significantly different land management practice to that of pre-European

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Aborigines, the outcome of nutrient depletion of groundwater in the study area is the same.

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5 Conclusions

At the study site a geochemical mass balance was carried out to investigate the role of granite weathering on groundwater and surface water geochemical evolution. A small number of samples from this site showed the influence of granite weathering (through pyrite oxidation), but for the majority of the samples, once rainfall inputs were taken into account, all major cations and anions are depleted. Cation exchange and mineral precipitation are ruled out as possible causes for this depletion, with the most likely mechanism being uptake by plant biomass.

Continued uptake of chemical species by vegetation should result in a buildup of these species in the soil and biomass, but in fact the soil is depleted as well, so there must be an export mechanism. For this study site we hypothesise that regular burning by Aboriginal land users was responsible for much of this export, given that the majority of the groundwater samples were recharged before European settlement.

This study has shown that the uptake of species through vegetation growth and removal through fire regimes has a dominating influence on groundwater and surface water chemistry and on geochemical cycling in southeast Australia. These results are likely to be applicable to similar low precipitation, high transpiration biomes elsewhere in Australia and globally, and this should be explored further.

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Neither the NCGRT, AINSE nor DPI Victoria (as funding sources) were involved in the design of this specific study, nor were they involved in the collection or analysis of the resulting data.

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Author contributions

J. F. Dean carried out sampling, majority of the lab work, data analysis and wrote the article. J. A. Webb contributed significantly to data analysis and article writing, and contributed to project design. G. Jacobsen carried out the ^{14}C analysis. R. Chisari carried out the tritium analysis. P. E. Dresel contributed to the project design and carried out the implementation of infrastructure at the site. All authors discussed the results and commented on the manuscript.

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Table 1. Groundwater and surface water sampling details, field parameters and major ion compositions.

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Table 2. Dates on groundwater samples obtained in this study. Samples designated “Modern” have ^{14}C activity > 100 pMC, indicating they are younger than 1950. Samples designated “young” have ^{14}C activity > 95 pMC and all contain measurable tritium.

Sample ID	$a^{14}\text{C}$ (pMC)	1 σ -error	Radiocarbon age	1 σ -error	Radiocarbon age assumption	Activity of ^{3}H (Bq kg^{-1})	1 σ -error
Group A							
2272	81.26	± 0.28	1665	± 30		0.007	BD
2273	77.43	± 0.28	2055	± 30			
2275	89.01	± 0.36	935	± 35			
2276	93.11	± 0.31	575	± 30		0.011	BD
2278a	92.27	± 0.93	650	± 90		0.026	BD
2278b							
2280	98.56	± 0.33	115	± 30	young	0.148	± 0.01
2282	94.81	± 0.32	430	± 30	young	0.072	± 0.006
2283	91.85	± 0.34	685	± 30		0.009	BD
2284	90.7	± 0.34	785	± 30			
2285	*	*	*	*		0.018	BD
2289	40.15	± 0.24	7330	± 50			
2290	41.93	± 0.23	6980	± 45			
2291	94.97	± 0.31	415	± 30	young	0.047	± 0.005
2292	7.53	± 0.08	20770	± 90		0.001	BD
2293	91.39	± 0.32	725	± 30		0.087	± 0.007
2294	77.38	± 0.28	2060	± 30		0.007	BD
2295	64.36	± 0.24	3540	± 30		0.021	BD
2296	95.78	± 0.28	345	± 25	young	0.133	± 0.011
2297	49.45	± 0.20	5655	± 35		0.0354	± 0.005
Group B							
2277	104.52	± 0.43	0	Modern		0.339	± 0.015
2279	104.93	± 0.35	0	Modern		0.304	± 0.014
2281	91.77	± 1.03	690	± 100		0.094	± 0.007

* CO_2 too low; BD = below detectable limit.

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Table 3. Rainfall chemistry used in this study.

Sample ID	Ca ²⁺ (mol)	Cl ⁻ (mol)	HCO ₃ ⁻ (mol)	K ⁺ (mol)	Mg ²⁺ (mol)	Na ⁺ (mol)	Si (mol)	SO ₄ ²⁻ (mol)
Rainfall – Cavendish	1.50e-5	1.20e-4	4.00e-5	5.00e-6	1.50e-5	1.20e-4	ND	ND
Rainfall – Hamilton	2.45e-5	1.28e-4	UR	3.09e-5	2.41e-5	1.09e-4	8.32e-7	2.52e-5
Rainfall – Horsham	3.44e-5	9.39e-5	UR	6.39e-6	1.18e-5	9.52e-5	ND	1.55e-5
Median Rainfall	2.45e-5	1.20e-4	4.00e-5	6.39e-6	1.50e-5	1.09e-4	8.32e-7	2.03e-5

ND = not determined, UR = unreliable data.

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Table 4. Major element (wt %) composition of weathered and unaltered granite from the study site.

Species	Weathered ^a	Unweathered ^b	% change in composition
SiO ₂ (%)	72.2	74.53	15.84996666
TiO ₂ (%)	0.31	0.285	30.07884456
Al ₂ O ₃ (%)	18.69	13.415	66.61283768
Fe ₂ O ₃ (%)	1.65	1.73	14.05850579
MnO (%)	0.01	0.045	-73.42475219
MgO (%)	0.06	0.34	-78.89612674
CaO (%)	0.06	1.095	-93.44719917
Na ₂ O (%)	0.15	4.16	-95.68791051
K ₂ O (%)	0.46	4.28	-87.147018
P ₂ O ₅ (%)	0.02	0.05	-52.16455393
LOI (%)	7.23		

^a Median of 3 analyses; ^b from Hergt et al. (2007).

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Table 5. Groundwater depletion of all species is evident after subtraction of rainfall and rock weathering inputs in Group A. Group B shows some evidence of weathering inputs.

Group A (20 samples)	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Median groundwater concentrations (mol L ⁻¹ × 10 ⁵)	22.2	258	687	4960	7230	175	53.3	22.6
Median normalised groundwater concentration (mol L ⁻¹ × 10 ⁵)	0.04	0.40	1.28	8.91	12.00	0.37	0.08	0.04
Median rainfall (mol L ⁻¹ × 10 ⁵)	0.64	2.45	1.50	10.92	12.00	2.03	0.08	4.00
Net species addition/depletion after rainfall subtraction (mol L ⁻¹ × 10 ⁵)	-0.60	-2.05	-0.22	-2.01	0	-1.66	0	-3.96
Group B (3 samples)	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Median groundwater concentrations (mol L ⁻¹ × 10 ⁵)	5.84	6.09	23.8	138	107	63.9	19.8	18.2
Median normalised groundwater concentration (mol L ⁻¹ × 10 ⁵)	0.19	0.29	1.44	15.44	12.00	6.64	1.40	2.73
Median rainfall (mol L ⁻¹ × 10 ⁵)	0.64	2.45	1.50	10.92	12.00	2.03	0.08	4.00
Net species addition/depletion after rainfall subtraction (mol L ⁻¹ × 10 ⁵)	-0.45	-2.16	-0.06	4.52	0	4.61	1.32	-1.27

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Table 6. Surface water depletion of species after rainfall subtraction prevents weathering rate calculations.

	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Dwyer's Ck. composition (mol L ⁻¹ × 10 ⁵)	4.60	158	346	1950	2760	98.6	4.28	26.2
Normalised Dwyer's Ck. composition (mol L ⁻¹ × 10 ⁵)	0.02	0.69	1.51	8.47	12.00	0.43	0.02	0.11
Median rainfall (mol L ⁻¹ × 10 ⁵)	0.64	2.45	1.50	10.92	12.00	2.03	0.08	4.00
Net species addition/depletion after subtraction of rainfall (mol L ⁻¹ × 10 ⁵)	-0.62	-1.76	-0.01	-2.45	0	-1.60	-0.06	-3.89
	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Lambing Hut Ck. composition (mol L ⁻¹ × 10 ⁵)	15.0	546	1060	7380	9700	518	21.5	44.3
Normalised Lambing Hut Ck. composition (mol L ⁻¹ × 10 ⁵)	0.02	0.68	1.32	9.13	12.00	0.64	0.03	0.05
Median rainfall (mol L ⁻¹ × 10 ⁵)	0.64	2.45	1.50	10.92	12.00	2.03	0.08	4.00
Net species addition/depletion after subtraction of rainfall (mol L ⁻¹ × 10 ⁵)	-0.62	-1.77	-0.18	-1.79	0	-1.39	-0.05	-3.95

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Table 7. Group B groundwater samples show some input from pyrite oxidation and plagioclase weathering.

Group B (3 samples)	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Net species addition/depletion after rainfall subtraction (mol L ⁻¹ × 10 ⁵)	-0.45	-2.16	-0.06	4.52	0	4.61	1.32	-1.27
Release of ions by pyrite and plagioclase weathering (mol L ⁻¹ × 10 ⁵)	0	1.43	0	4.52	0	4.61	9.04	0
Net species addition/depletion after subtraction of ions released by pyrite and plagioclase weathering (mol L ⁻¹ × 10 ⁵)	-0.45	-3.59	-0.06	0	0	0	-7.72	-1.27

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Sample ID	SI: Calcite	SI: Gypsum	SI: Aragonite	SI: Halite
Group A				
2272	-1.80	-0.72	-1.95	-4.00
2273	-1.44	-0.90	-1.59	-4.06
2275	-4.16	-1.49	-4.31	-4.29
2276	-1.26	-1.23	-1.41	-4.53
2278a	-5.49	-2.41	-5.64	-4.74
2278b	-5.15	-2.05	-5.30	-4.69
2280	-2.65	-1.41	-2.80	-4.09
2282	-4.14	-2.24	-4.29	-5.75
2283	*	-2.02	*	-4.31
2284	*	-1.10	*	-3.85
2285	-4.50	-1.60	-4.66	-3.95
2289	-2.96	-1.37	-3.11	-4.13
2290	-2.88	-1.36	-3.03	-4.11
2291	-4.95	-2.09	-5.10	-4.77
2292	-0.79	-1.27	-0.94	-4.73
2293	-3.31	-1.88	-3.46	-4.65
2294	-2.98	-1.49	-3.13	-4.17
2295	-2.31	-1.53	-2.45	-4.17
2296	-2.65	-1.73	-2.80	-4.12
2297	-0.79	-0.80	-0.94	-3.94
Group B				
2277	-5.14	-3.51	-5.29	-7.61
2279	-4.15	-3.07	-4.29	-7.47
2281	-5.43	-2.12	-5.58	-5.16
Surface Water				
Dwyer's Ck.	-2.61	-1.79	-2.76	-4.97
Lambing Hut Ck.	-2.27	-0.85	-2.42	-3.93

* pH too low for analysis.

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Table 9. Element depletion expressed as a percentage of total molar input of rainfall.

Group A (20 samples)	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	SO ₄ ²⁻	H ₄ SiO ₄	HCO ₃ ⁻
Percentage of total rainfall input	1.9	7.3	4.5	32.5	6.0	0.2	11.9
Percentage of rainfall input depleted in groundwater	93.8	83.7	14.7	18.4	81.7	100	99.0
Macro- or micro-nutrient (Atwell et al., 1999; Marschner, 1989)	macro	macro	macro	micro	macro	micro	macro

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Table 10. Burning frequency required for common elements in *Eucalyptus camaldulensis*; biomass values from Briggs and Maher (1983) and Fekeima et al. (2012).

	Ca	K	Mg	Na	S
Rainfall input ($\text{kg ha}^{-1} \text{yr}^{-1}$)	9.3	1.7	1.9	14.7	3.3
Rainfall deficit ($\text{kg ha}^{-1} \text{yr}^{-1}$)	5.5	1.5	0.3	3.1	3.5
Leaf biomass (kg ha^{-1})	15.4	11.9	6.8	5.5	3.2
Burning frequency (yr)	2.8	7.9	22.7	1.8	0.91



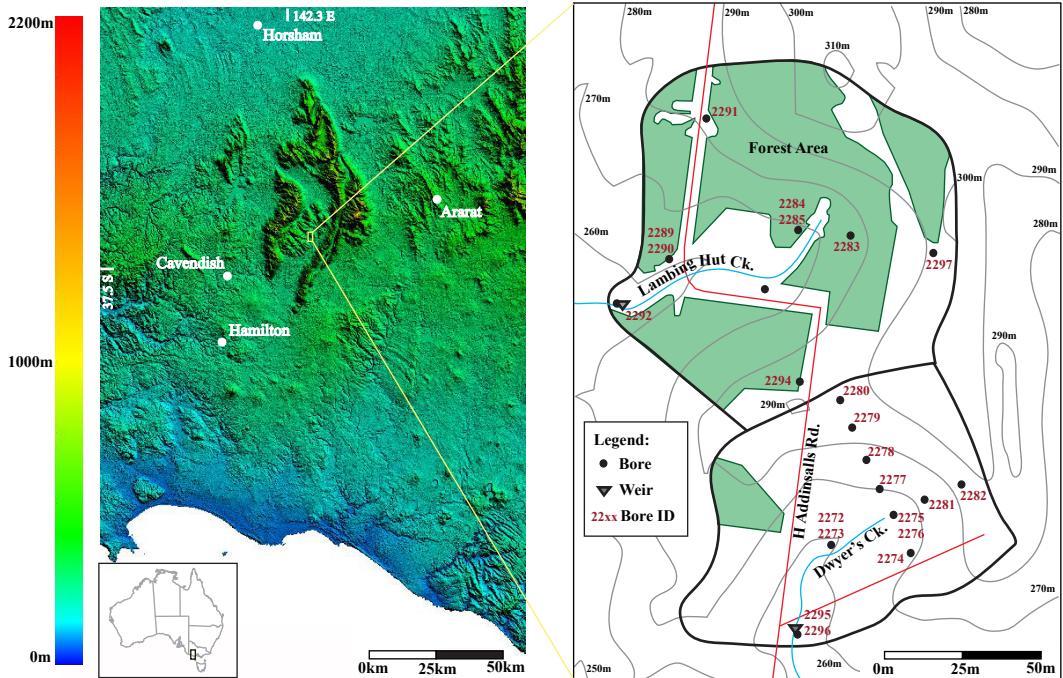


Fig. 1. Left – location of the study site in Southwestern Victoria, Australia. Right – location of the bores, streams and weirs.

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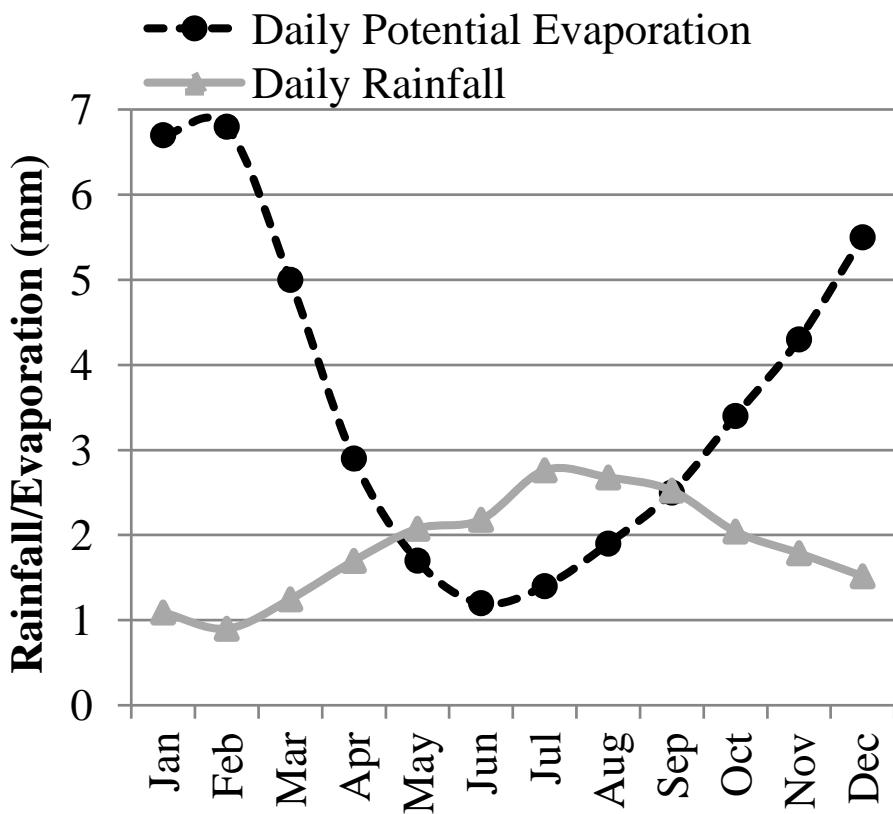


Fig. 2. Average daily rainfall and potential evaporation for the study region, based on data from 1965–2000, Hamilton, Victoria, Bureau of Meteorology.



Fig. 3. Painting of Victoria Valley prior to land clearance (Eugene von Guérard, 1866; Courtesy of Sotheby's Australia).

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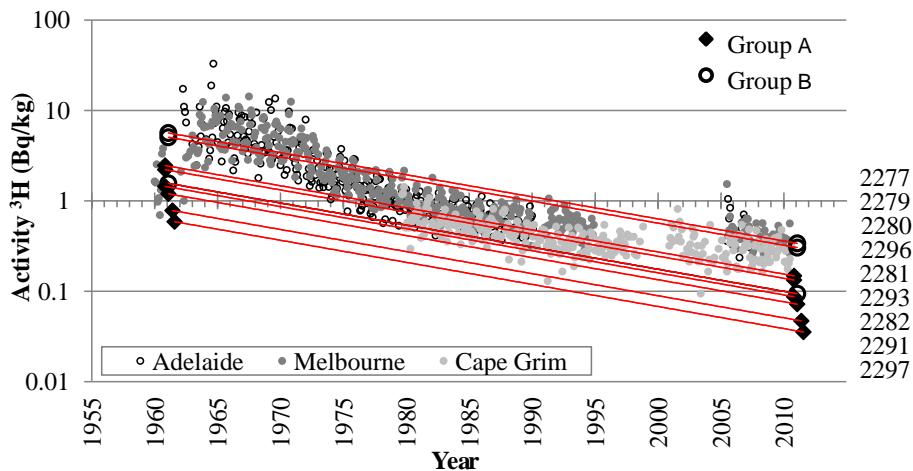


Fig. 4. Tritium decay curves for the nine samples with detectable tritium levels (Table 2); each curve is calculated for 50 yr of decay. The atmospheric tritium values are shown also to indicate possible recharge times; unpublished rainfall data from ANSTO. The precision of the tritium dates varies; sample 2297 was recharged in 1960 or earlier, whereas sample 2281 was recharged from 1975–1995 or during 1960 and earlier.

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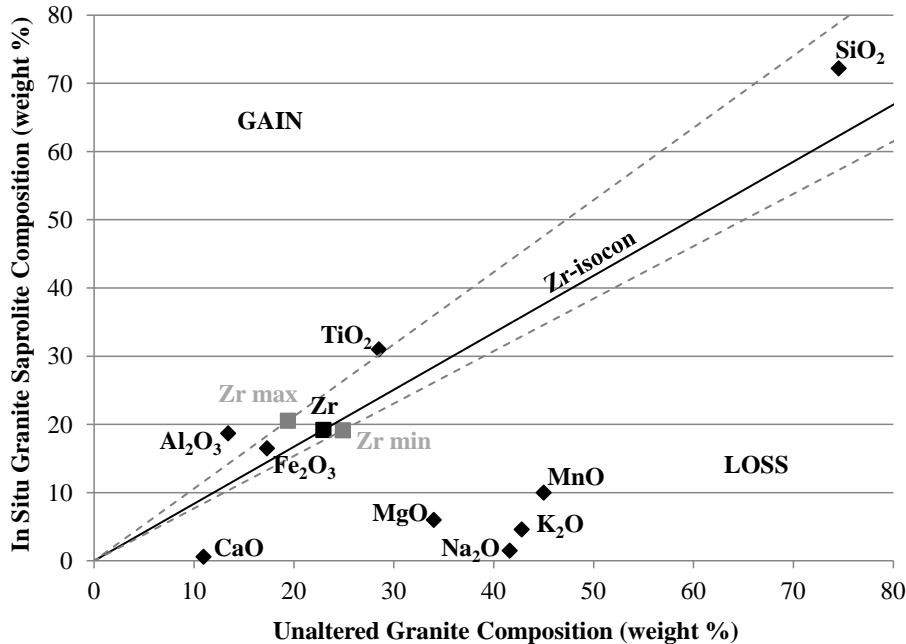
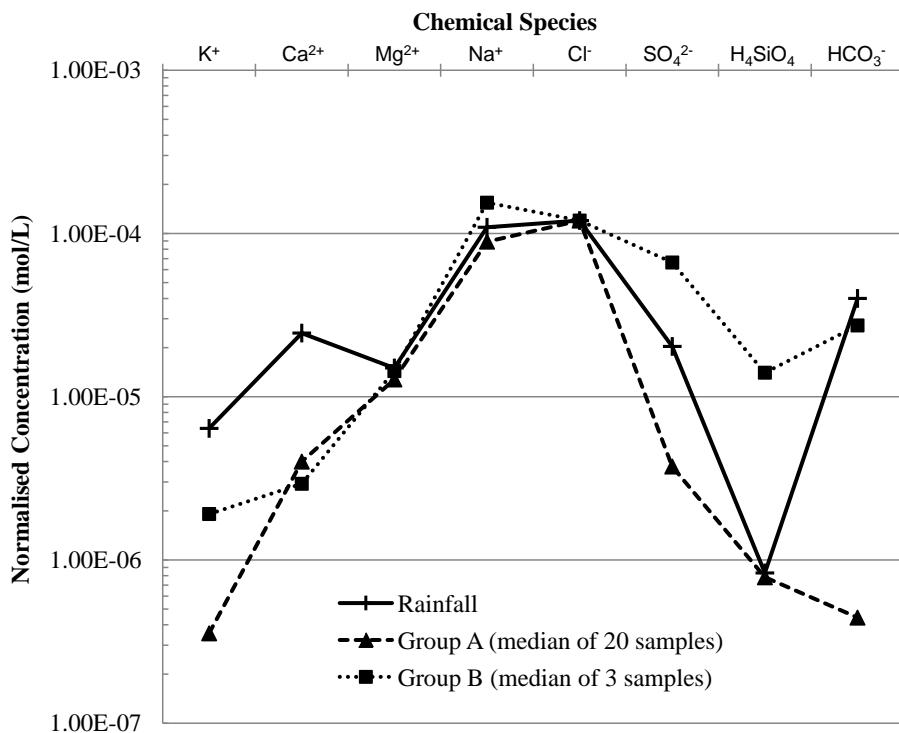


Fig. 5. Comparison of element concentrations of the in situ granite saprolite (median of 3 analyses) and the unaltered granite (Hergt et al., 2007) from the study site (determined by XRF analysis). Zr is assumed to be immobile and an isocon (Grant, 1986; Webb and Golding, 1998) is defined from the origin through this point. Above this line the granite saprolite is enriched in that element, below the line it is depleted. Minimum and maximum isocons are defined by the equivalent Zr ratios from both sets of analyses. In order to better show some elements visually on this graph both values were multiplied by 10, 100 or 1000. As these are ratios, so long as both values have the same multiplication applied to them, the result is not affected.

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**Fig. 6.** Schoeller plot of sampled waters normalised to local rainfall Cl^- (see Sect. 4.2).

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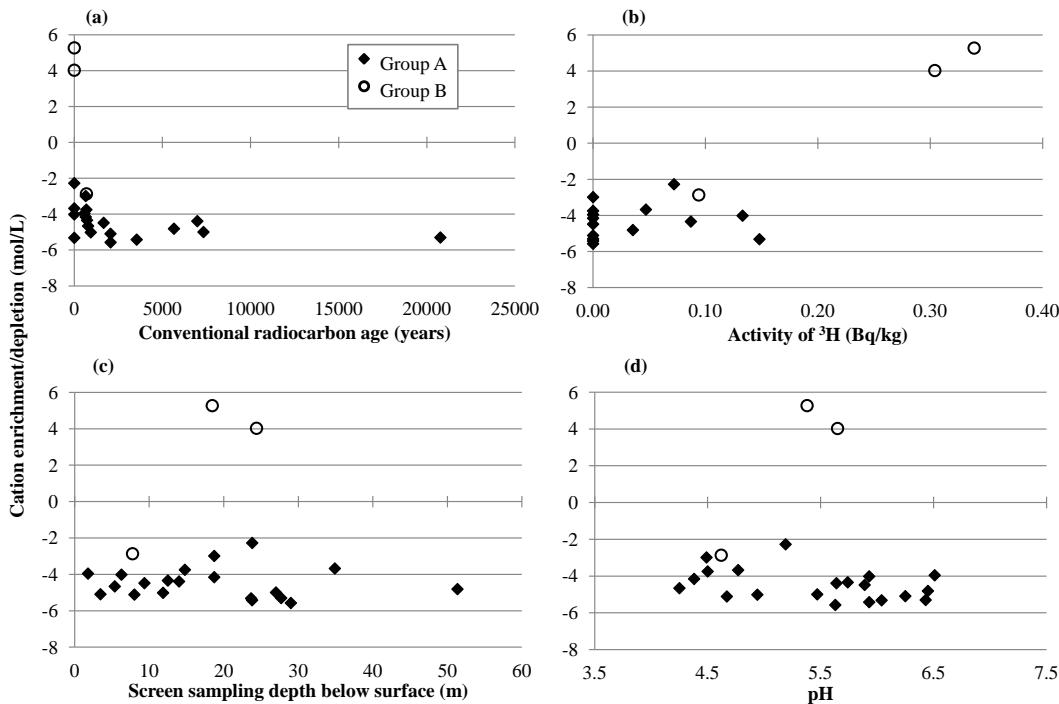


Fig. 7. The cation depletion in the groundwater samples (after subtracting rainfall and rock weathering inputs) shows no clear trend with age (**a, b**), sampling depth (**c**), or pH (**d**). The zero values in graphs (**a**) and (**b**) indicate values outside the range of the respective dating techniques. A detectable level of tritium indicates that the water is “modern” – recharged in the last ~ 50 yr (Clark and Fritz, 1997; see Sect. 3.1.3). Those samples that contained measurable tritium and also sufficient ${}^{14}\text{C}$ to give a radiocarbon date indicate mixing of modern and older groundwater (Table 2).

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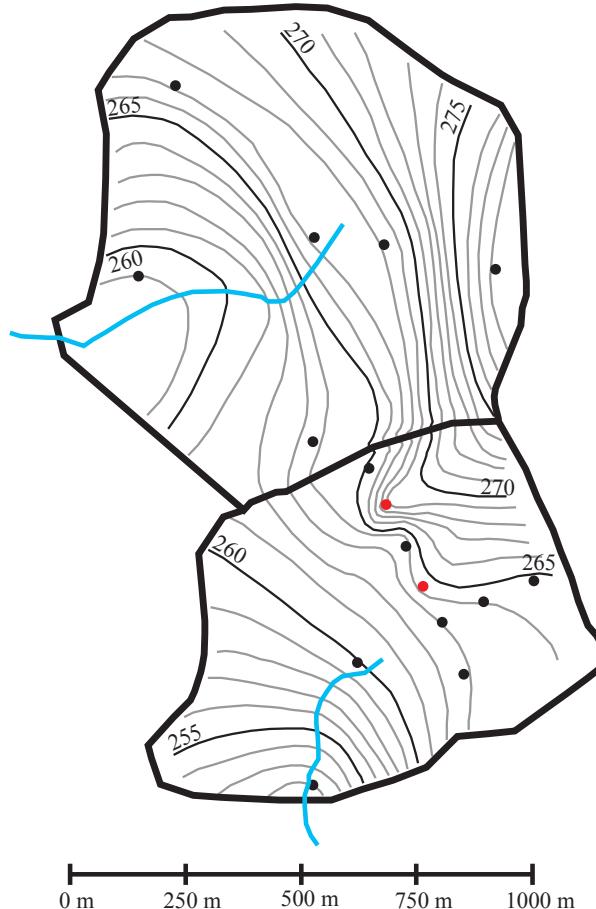


Fig. 8. Groundwater potentiometric surface map for September 2012. Note the northeast corner of the farm catchment where the fracture flow evident in bores 2279 and 2277 (red dots) exhibit preferential pathways in the equipotential lines.