

Summary of manuscript corrections

We have addressed the various comments in our response to the reviewers and have incorporated most the suggestions in the revised paper (as summarised in [blue](#)). Given that many of the minor comments related to sentences that were long or which contained multiple clauses, we have also done additional editing to remove some of these. Finally, we have included a data availability section after the Conclusions as was requested on a previous paper.

Editorial Comments

(1) while it is true that tritium does carry quite some information content about the age of water, I think the often communicated "one sample is enough" message needs to be toned down a bit (p.5,l.6). of course one sample is better than no sample, but given the observational and modelling uncertainties involved, it will only give us a very rough estimate. in principle, models could be calibrated using one O-18 value as well. the question is then, however, how much confidence do we have in this one sample and how strongly can it constrain redundant parameterizations? the same is of course true for tritium.

We didn't really intend the comment in that way. What we are trying to convey is that ^3H can now be used in a similar way to other radioisotope tracers (e.g. ^{14}C or ^{36}Cl) where an age or mean transit time estimate can be derived from individual measurements. We agree that you cannot adequately characterise a catchment with one sample (with ^3H or any of the other radioisotope tracers). However, the use of ^3H in this way facilitates studying the catchment at different flow conditions and probably allows more sites to be studied. We have discussed this in more detail on pages 5 and 6 and tried to emphasise the differences in approaches between the time series and the single measurement approach. The time-series approach has the advantage that it can be used to determine the most appropriate LPM by comparison of observed and predicted ^3H vs. time. However, it requires an assumption of time invariance which may not always be reasonable. The single measurement approach does not require an assumption of time invariance but it cannot be used to determine the most appropriate LPM.

In the southern hemisphere, it is questionable whether the time series approach would work for ^3H in the future due to the much lower ^3H activities of the bomb pulse waters, which have now all but disappeared. For example, the calculated decrease of ^3H activities for a water with a mean transit time of 10 years between 2016 and 2026 as predicted by the EPF and EM models used in the paper with the Melbourne ^3H record is only 0.2 TU. The corresponding decline for a northern hemisphere site (e.g. Ottawa) is around 3 TU. Additionally, the time vs. ^3H trends of the different models in the southern hemisphere are similar within analytical uncertainty.

Both approaches have advantages and drawbacks and there is no "best" method. The use of ^3H is obviously in a transitional phase as the bomb pulse disappears from requiring a time-series approach to being used as a conventional age tracer. Hopefully, we have conveyed that in the paper.

(2) in your replies you mention that MTT studies in peatlands are rare. this is not exactly true. most of the british MTT work (e.g. soulsby, tetzlaff, birkel and myself) is located in peatlands.

We did cite a number of these but have added a couple more. If one does a survey of the literature the number of studies specifically on peatland catchments is much less than on other landscapes, but there clearly are some. We have rephrased the start of this section to reflect that (page 6, lines 18-19).

(3) in one comment reviewer 2 highlighted the missing description of the model calibration strategy - i.e. how were the parameters determined? what were the objective functions used? what was the calibrated model performance? you did not address this point in your replies: you only mention your assumptions on the choice of the model but not on how you obtained the parameters. please add that in the revised manuscript.

As we noted in the response to the reviewers, it is not possible to calibrate the model using the ^3H data. Using ^3H as a “conventional” radioisotope tracer requires one to assign a plausible lumped parameter model (as is the case for other commonly-used tracers such as ^{14}C in older waters). We have approached the calculation of mean transit times by utilising a range of lumped parameter models and considering the different results as part of the uncertainties in the transit time calculations. This goes back to the point regarding the differences between the use of single ^3H activities in the southern hemisphere and the need/ability to use time series ^3H data in the northern hemisphere. Our choice of models was based on those most commonly used for determining mean transit times (e.g. as reviewed by McGuire and McDonnell, 2006). LPMs such as the exponential-piston flow model correspond to the likely geometry of the flow system and is the preferred model. We have tried to be more explicit on this point in Sections 1.1 (pages 5 & 6), 2.3 (page 11), 4.2 (page 17-19) and 5 (page 24). We also added the mean transit times from the other LPM’s to Table 2 and discuss them explicitly in the paper (page 17).

(4) p.6,l.11-17 would indeed better fit into the methods section as suggested by reviewer 2

We made this change

(5) apart from that i think you can leave the introduction section and its sub-sections structurally as is.

We left the other sections as in the original manuscript.

Reviewer 1 (Edison Timbe)

The manuscript HESSD “Contrasting transit times of water from peatlands and eucalypt forests in the Australian Alps determined by tritium: implications for vulnerability and the source of water in upland catchments” by Cartwright and Morgenstern, 2016, assesses, in terms of mean transit times, the hydrological differences between wet-lands (peatlands) and eucalypt forest ecosystems. Although this study is mainly based on lumped parameter models for which uncertainties are commonly large, the inclusion in the analysis of diverse datasets like major chemical elements, stable and radioactive isotope data, allows the authors to crosscheck findings from different perspectives. The authors perform an appropriate analysis of the contrasting mean transit times found between both analyzed ecosystems, allowing to hypothesize about the hydrological functioning of the related aquifers and flow paths. Considering the scarce studies dealing with wetlands and more specifically, peatlands (e.g., as compared to mountain forest head water catchments), this study is very timely and therefore I recommend it for publication after some minor revisions which I detail below.

In response to this comment and the more extensive comments from the second reviewer regarding lumped parameter modelling and uncertainties. This additional discussion now appears in Section 4.2 (page 17, lines 4-7 and page 19, lines 12-14).

Specific questions/issues

Page 2, line 8. Define the acronym TU when first used, e.g., Tritium Units (TU). Besides, consider using an acronym for ^3H activity/activities, this term is widely used along the manuscript (around 100 times).

We defined “TU” on first usage both in the abstract (page 2, line 7) and the main text (page 4, line 11). We did not abbreviate activities as it is generally not done so for ^3H .

Please avoid beginning a sentence or a paragraph with an acronym or an abbreviation, this basic grammar rule is circumvented throughout the manuscript. Just to mention some few paragraphs starting with acronyms: pag. 8, line 17; pag. 11, lines 16 and 25, pag. 12, lines 10 and 19.

We changed these occurrences and others throughout the paper

Furthermore, three from four paragraphs of the Section 4.3 begin with “ ^3H activities of...”

We varied the style of sentences to improve readability (now section 3.3, pages 13-14).

Page 4, lines 20 to 22. There are very few studies dealing with the appropriate tracer data resolutions to obtain reliable transit time estimations through lumped parameter models. Please consider mentioning the study by Timbe et al., 2015, who investigated this topic using stable isotopes of water.

We thank the reviewer for pointing out this paper which we have referenced (page 4, line 23).

Page 5, lines 17 to 19. Consider adding another citation, there is a more recent study for a similar ecosystem (peatlands), located in the tropics by Mosquera et al., 2016, in which mean transit times of less than one year have been also found (it uses Oxigen-18 and Deuterium as tracers).

We became aware of the Mosquera et al. (2016) paper following the submission of our paper and have now referenced it in the discussion on page 6, line 28.

Page 9, lines 12 to 15. Is it really possible to outline small catchment, like 0.5 km², from the mentioned coarse google resolution?

The Google Earth Pro images are high resolution and when used in conjunction with the topographic maps, the catchment areas are clearly defined. The exact catchment areas are not particularly important as there is no correlation of ^3H activities with area (this is a recurring theme in our studies of Australian catchments).

We have added the detailed catchment maps as a supplementary Figure.

Technical Corrections

Page 2, line 6. Please write out the full name when the acronyms are first mentioned. E.g., define acronym ^3H : “This study uses Tritium (^3H) to estimate...”

This was done on first use in the abstract (page 2, line 6) and main text (page 4, line 11).

Page 2, line 13. Should say: “are higher in the eucalypt forest stream than in the peatland...”

We rephrased this sentence (page 2, lines 13-14)

Page 6, line 2. Rephrase: "This study is based in the upland areas of the Victorian Alps, southeast Australia and was designed to..." to something like: "This study, located in the upland areas of the Victorian Alps (southeast Australia), was designed to..."

We rephrased this sentence to "This study was designed to test the hypothesis that peatlands in the Victorian Alps, southeast Australia represent a relatively long-lived store of water" which more clearly conveys the aims of the study (page 7, lines 11-12).

Page 7, line 17. Please check this "the soils alci include..."?

We split this material up and corrected the typo "alci". It now reads "These soils overlie weathered regolith that is a few tens-of-centimetres to a few metres thick. There are also minor deposits of colluvium and alluvium along the streams (Shugg, 1987). Groundwater flow is restricted to the weathered zones and fractures in the granites and metasediments; the minor alluvial and colluvial sediments are more permeable but represent only a minor part of the landscape" which is clearer (page 8, lines 23-27)

Page 8, line 15. Please check, sentence is currently written in present tense: "Observations indicate that this is at or close..."

This is now in the past tense to be consistent with the rest of the paragraph (page 9, line 27)

Page 8, line 16. Correct: "At least three bore volumes of water WERE extracted prior to sampling"

This was corrected as suggested (page 10, lines 1-2).

Page 8, lines 20 to 22. Rephrase the complete sentence written in these lines.

We rephrased this as "Enrichment of ^3H was by a factor of 95, which results in a detection limit of 0.02 TU, while the use of deuterium-calibration for each sample results in a 1% reproducibility of the tritium enrichment." (page 10, lines 6-8).

Page 9, line 3. This device is more commonly known as Thermo-Finningar Delta plus.

The device is as named on the manual etc.

Page 10, line 9. Delete "transit times" once, it is repeated.

This was corrected (page 11, line 22).

Page 11, lines 16. Please rephrase the description of the stable isotope values, it is a bit confusing in its current state. I would first describe the range for O-18 and then for Deuterium (e.g., from -8.3 to -5.0 per mil for O-18 and from -43 to -23 per mil for Deuterium).

We corrected this as suggested (page 13, line 11).

Page 12, line 1. Rephrase "Three 2 week to 3 months aggregated samples..."

To also address comments by reviewer 2, we have changed this to “The ^3H activities of three multi-month rainfall samples from Mount Buffalo are 2.85 TU (12 month sample collected in February 2015), 2.88 TU (9 month sample collected in November 2015), and 2.99 (17 month sample collected in December 2013) (Table 1). Three samples of rainfall collected over periods of 2 weeks to 3 months in 2014 also from Mount Buffalo have ^3H activities of 2.52 to 2.90 TU (Table 1).” (page 13, lines 21-25).

The word “aggregated” was probably not clear and is also used to describe mixing of the waters in the catchment, so we have removed it when referring to the rainfall.

Page 12, line 4. Correct “activities in rainfall FOR this region”.

We corrected this as suggested (page 13, line 27).

Page 12, line 14. Delete the word “and” at the end of the sentence.

This was corrected (Page 14, line 10).

Page 15, line 14. Define acronym “Eqs” when first used.

In other HESS papers “Eqs” is generally used without definition (i.e., it is one of the standard acronyms). We left this as is.

Page 15, line 19. “Given that the water WAS sampled” or “Given that waters WERE sampled”?

Changed to “waters were” (page 17, line 14).

Page 16, lines 3 to 5. Rephrase the sentence contained in these lines.

Changed to “For a water with a ^3H activity of 3 TU, propagating the analytical uncertainty of $\pm 2\%$ produces an uncertainty in mean transit times of ± 0.3 years” (page 18, lines 8-9).

Page 16, line 8. “yields mean transit times of up to 3.9 years” Do you mean 4.0 years (Table 2, last column)?.

Changed to 4.0 years (page 18, line 14).

Page 17, line 1. Insert a comma after the word “increase”.

Corrected as suggested (page 18, line 18)

Page 20, line 15. Delete the word “at” after “mean transit times”.

Corrected as suggested (page 23, line 9)

Page 21, lines 25 – 26. Rephrase: “...comparable studies such as this will become possible there which will allow...”

We changed this section to reflect some of the changes in the manuscript made in response to Reviewer 2. The section (page 24, lines 18-25) now has more emphasis on some of the general issues around tritium dating.

Figure 1. Units are missing in the legend for elevation.

These have been added and the definition of AHD (Australian Height Datum) has been added to the caption for Fig. 1.

Figures 4 and 6a: Correct the axes labelling

For some reason hidden layers (from Adobe CS) became visible in these figures following uploading (they were not visible in the files that were uploaded or .pdf's that I generated from these on my computer). We have removed the hidden layers in the final version of the figures.

Reviewer 2

The paper presents a comparison between mean transit time, MTT, between peatlands and eucalyptus forest in the Australian Alps. The authors used tritium as a tracer to model MTT using a lumped parameter approach. The authors also integrate geochemistry data and water stable isotopes in the analysis to yield important interpretations related to water storage and availability in these ecosystems. The paper is relevant to the scientific community because it provides information about underrepresented ecosystems with scarce hydrologic data. The paper could eventually make an important contribution to the scientific literature. However, I believe there are issues with the paper structure and writing style. Thus I recommend major revisions before it can be considered for publication.

One of the reviewer's major comments relates to the structure of the paper. HESS does not have a fixed house style and looking through recent issues, the structure that we have used is one that is common but not ubiquitous. As outlined below in response to the specific comments, we made some of the suggested changes to the style of the paper.

I provide below some specific comments and suggestions:

Abstract: Lines 1-2: the first sentence sounds redundant (use of word "that"). Please rewrite.

The second "that" has been changed to a "which" (Page 2, line 2).

Line 8: define the acronym before using it (TU).

We defined "TU" on first usage both in the abstract (page 2, line 7) and the main text (page 4, line 11).

1. Introduction:

I believe the introduction should provide more information about the use of geochemical data in the context of mean transit time modelling.

Page 3, line 21-23: This sentence should be rewritten.

We clarified this sentence (Page 3, lines 21-23). It now reads "If water transit times are short, then the peatlands may dry significantly during droughts making them prone to degradation and vulnerable to bushfires."

Page 4, section 1.1: I think the authors should include a paragraph about the recent advances and challenges in the determination of transit times and the use of lumped parameter models. For instance, the authors should clarify that the calculated times are most likely representative of base flow conditions and spell out the underlying assumptions in the use of these models. There is a vast new literature dealing with time variant modelling of transit times.

We have addressed these comments as follows:

- We now include a discussion of both non-steady state conditions (page 5) and aggregation (page 6) that references the studies of Kirchner (2016, Hydrology and Earth System Sciences, 20, 279-297), Kirchner, (2016, Hydrology and Earth System Sciences, 20, 299-328), and Stewart et al. (2016, Hydrology and Earth System Sciences Discussion, doi:10.5194/hess-2016-532)
- We have also added a section point out the differences in approach in determining mean transit times using a time-series approach vs. individual ^3H analyses (pages 5-6). The use of single ^3H measurements does not require an assumption of time invariance but importantly cannot be used to determine the most appropriate lumped parameter model via comparison between the observed and predicted ^3H activities (i.e., one has to assume a suitable lumped parameter model). This essentially utilises ^3H in a similar way to ^{14}C and other radioisotope tracers (which we note on page 5, lines 18-19). From a practical point of view it would be difficult to commence time-series ^3H studies in the southern hemisphere due to the much lower activities of the bomb pulse (as we have noted on page 5, lines 24-28).

As noted below a, section discussing the impacts of aggregation on the calculations appears on pages 19-20 and Figure 8 (new).

We have noted that we are characterising baseflow conditions (page 7, line 13) and reiterated this point on page 16, lines 13-16.

Page 4, line 19-22: there is a missing “the” before “use”. In addition are there any relevant references to this statement?

We corrected the typo, and following the suggestion of Reviewer 1 have referenced the Timbe et al. (2015) study (page 4, line 23).

Page 4 line 19: consider using “to determine” instead of “to determining”

This was changed (page 4, line 25).

Page 6: I suggest you eliminate section 1.3 and have the objectives of the study be the last paragraph of the introduction.

We elected to keep the section heading as it separates this material from the more general discussion of mean transit times.

Page 6 line 11-17: this information should appear before the paragraph with the objectives. Could be part of the last paragraph in page 5.

We removed this paragraph and incorporated the material in the description of the field area (page 9, lines 13-19)

I suggest this section be part of Methods.

We have made this section the first part of the Methods (section 2.1) as suggested.

Page 6 line 19-22. I suggest you rewrite this sentence.

We changed this to “Water from streams draining peatlands and eucalypt forests was sampled ...” (page 7, lines 22-23).

Page 7 line 1-2, line 13-14: Please use the correct notation for the scientific name of species.

We italicised the species names throughout section 2.1.

3. Methods

Line 9: Explain “aggregated” over what time frame? In addition, how many, when, how frequent were the samples collected?

We have clarified this to “Samples of rainfall representing the total precipitation over periods of several weeks to months (Table 1) were collected from a rainfall collector at Mount Buffalo (Fig. 1)” (page 9, lines 21-22) and also added a note regarding sample collection to Table 1.

Line 9-10: That just means grab samples, right?

We have used the term “Grab samples” (page 9, line 22).

Page 9 section 3.2. More information is required about the modeling procedure, how were the best parameters identified, what objective function was used, how many possible parameter combinations were implemented, can you include dotted plots? How did you choose among the 3 different transit time functions (exponential, piston flow, and dispersion). Why did you choose these 3 and not others?

As discussed above, to calculate mean transit times from single ^3H measurements one has to assume a LPM model (i.e. it cannot be constrained from the observed ^3H measurements in the same way as when time series data are used). This has been made more explicit in section 1.1 (page 5) and we have reiterated it here (page 11, lines 14-21). Our choice of models spans those most commonly used in the literature and are ones that accord with our understanding of the flow systems. For example the exponential-piston flow model is appropriate for near vertical recharge through the unsaturated zone and exponential flow in the unconfined shallow aquifers and soils. Additionally, where ^3H time series data are available, these models have reproduced the ^3H activities of river water and groundwater (e.g. Maloszewski and Zuber, 1982; Maloszewski et al. 1983; Zuber et al., 2005; Stewart et al. 2007; Morgenstern et al., 2015).

Unfortunately, there is no procedure to identify the best parameters from the ^3H (or other data). Our approach (which is hopefully now explicit throughout) is to use a range of lumped parameter models and to recognise that this introduces uncertainty into the estimates of mean transit times (which we discuss in Section 4.2).

4. Results

Here is where the major structural issues arise: The results section does not present any of the MTT related findings. This is odd considering that this is precisely the main topic of the paper. Residence time results are mentioned in the abstract, discussion, and conclusions. The manuscript must include a residence time results section in which the modelling findings are presented.

The paper is structured such that it presents the data first (Section 3) and then discusses it (Section 4). While this is not a strict requirement in HESS, it is a common structure used by many journals. While it is possible to write papers that mix results and interpretation into a single section, the drawback of doing this is that the reader may be unclear as to what is data and what is interpretation or that the paper begins to present interpretations ahead of describing the data that was used to make those interpretations. Much of what precedes section 4.2 is required to produce the interpretations in that section.

For those reasons we have kept the structure as is but have provided a brief explanation as to what is in each section at the start of Sections 3 and 4.

Page 11 lines 2-5: This sentence is awkward. Please rewrite.

We have rephrased this to "Watchbed Creek drains the peatlands at Falls Rocky A (Fig. S1b), and there is a near-complete streamflow record for this site between 1940 and 1986." (page 12, lines 21-23).

Page 11, line 8: Avoid starting the sentence with a delta symbol, instead say "Water stable isotopes (^{18}O and ^2H).

A similar point was raised by Reviewer 1. We have gone through the paper to ensure that sentences do not start with symbols, numbers or acronyms.

Page 11: section 4.2. Figure 3 should be cited sooner.

We have cited this at the top of Section 3.2 (page 13, line 11).

In addition it is not clear when or how many samples were collected.

The samples are listed in Table 1 together with their sampling dates and we have now included numbers of samples in Figs 3 and 4. We have also clarified that these are individual samples in the caption to Fig. 3 and Table 1.

Page 11 line 11-12: is this slope different from the GMWL. The MMWL in Fig. 3 is very steep is that correct. In addition, the text says that the samples line to the left of this line which is not true.

The data are to the left of the MMWL. The line through the samples is a best fit to the data with a slope of 5 (it is not the MMWL). We have added an explanation of this in the caption to Fig. 3 and have modified the Figure so that the MMWL and the trend line are more clearly distinguished.

Page 11 line 13: please provide the range if deuterium excess.

These were added to the text (page 13, lines 17-19).

Page 11 line 22-25: This sentence is too long.

This now reads “As is commonly the case in southeast Australia (Cartwright et al., 2012; Leaney and Herczeg, 1999), the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of all waters including rainfall lie to the left of the global and Melbourne meteoric water lines” (page 13, lines 14-16).

Page 12 line 5: the word “and” makes no sense.

This was a long sentence that have made clearer by splitting (page 13, line 16).

Page 12 Lines 3-10: Did you test the data for normality to make sure a parametric test was appropriate?

Although there is no indication that the data are not normally distributed, the datasets are too small for the statistics to be rigorous. Rather than presenting the p values, we have now just pointed out that the ^3H activities between the sites overlap (page 14, lines 6-9).

Page 12 line 11-14: this sentence is too long.

We have split this into two sentences (page 14, line 9).

Discussion:

Page 13 line 19-21: Please avoid single sentence paragraphs.

The first paragraph to section 4 is a single sentence, but it introduces the section and we have retained it.

Page 14 line 22: reword sentence.

We split this sentence up, it now reads “Some peatland waters have lower $\delta^2\text{H}$ values than those of the rainfall. These potentially record recharge by rainfall that has a high proportion of low $\delta^2\text{H}$ stratospheric moisture. Such rainfall would also be expected to have higher ^3H activities than average rainfall” (page 16, lines 18-21).

Page 15: The MTT results should be move to the result section. Also the selection of the best model should be justified both physically and statistically. What objective function was use to qualify the goodness of fit?

As discussed above, we have elected to keep this material here as it is an interpretation. In terms of the approach to calculating mean transit times, as discussed above we have stressed that it is not possible to select a best model in a similar way to the way that it can be done using time-series data (this is has now been made more explicit in sections 1.1, 2.3, and 5). As to the choice of models, we provided more information as to why we used the models in Section 2.3 and the start of section 4.2. Not being able to constrain the most appropriate lumped parameter model represents an uncertainty in the calculations and we have explicitly noted that in section 4.2 (page 18, lines 4-7 and page 19, lines 7-16) and also in Section 5 (page 24, lines 17-27). We have also added the calculated mean transit times from the different models to Table 2.

Tables: in general the captions need to be more comprehensive. For instance, the caption for Table 1 should indicate if the isotopic values averages? If so what is the time period over which they were calculated, how many samples are included, and are there metrics of uncertainty.

These data are from single samples. The error bars on the figures reflect analytical errors not sample variability (as is stated in the figure captions). We have made this clearer in the caption to Table 1.

We added more explanation to Table 2 also.

Figures

Figure 1: Please use different markers to indicate the location of peatlands and eucalyptus forest.

It is too difficult to show the outcrops of peat at this scale. As noted in the response to Reviewer 1, we have included annotated high-resolution Google Earth images that show the distribution of peatlands and eucalypt forest more clearly as a Supplement.

Figure 2b. Please use probability scale in the x-axis.

We have modified the Figure

Fig. 3 not clear what the dash (–) line is.

The dashed line is a linear best fit to the rainfall samples. We have explained this in the figure caption.

The error bars for the grab samples should be representative of the accuracy (from the analysis of duplicate samples).

This is the case (as is noted in the figure caption).

If the precipitation signature corresponds to weighted means, then the error should be weighed errors.

They were analysed as individual samples (this has been added to the caption of Table 1).

Please add the number of samples (n=xx) associated to each (peat, Eucalypts, rain)

We have added this to the figure.

Figure 4: Not sure what the equation and $R^2 = 0.89$ mean versus the $R^2 = 0.69$. The legend has a "series 3" and "linear (series 3)", automatically generated from excel, that are not identified.

As explained above, some hidden layers appeared in the final versions of these figures when they were uploaded. We have removed them.

Contrasting transit times of water from peatlands and eucalypt forests in the Australian Alps determined by tritium: implications for vulnerability and the source of water in upland catchments

5 **Ian Cartwright^{1,2} and Uwe Morgenstern³**

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Abstract

Peatlands are a distinctive and important component of many upland regions that commonly contain distinctive flora and fauna which are different from those of adjacent forests and grasslands. Peatlands also represent a significant long-term store of organic carbon. While their environmental importance has long since been recognised, water transit times within peatlands are not well understood. This study uses tritium (^3H) to estimate the mean transit times of water from peatlands and from adjacent gullies that contain eucalypt forests in the Victorian Alps (Australia). The ^3H activities of the peatland water range from 2.7 to 3.3 Tritium Units (TU), which overlap the measured (2.9 to 3.0 TU) and expected (2.8 to 3.2 TU) average ^3H activities of rainfall in this region. Even accounting for seasonal recharge by rainfall with higher ^3H activities, the mean transit times of the peatland waters are <6.5 years and may be less than 2 years. Water from adjacent eucalypt forest streams has ^3H activities of 1.6 to 2.1 TU, implying much longer mean transit times of 5 to 29 years. Cation/Cl and Si/Cl ratios are higher in the eucalypt forest streams than the peatland waters and both of these water stores have higher cation/Cl and Si/Cl ratios than rainfall. The major ion geochemistry reflects the degree of silicate weathering in these catchments that is controlled by both transit times and aquifer lithology. The short transit times imply that, unlike the eucalypt forests, the peatlands do not represent a long-lived store of water for the local river systems. Additionally, the peatlands are susceptible to drying out during drought which renders them vulnerable to damage by the periodic bushfires that occur in this region.

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1. Introduction

Globally, peatlands occupy parts of the upland areas of many river catchments and provide water to the headwater streams in those catchments. It is estimated that peatlands cover $\sim 4 \times 10^6$ km² or $\sim 3\%$ of the world's land area (Dixon et al., 1994). Peatlands have received much attention because they represent a major (1.8 to 4.5×10^{11} tonne) long-lived store of terrestrial organic carbon (Gorham, 1991; Page et al., 2002). Peatlands commonly contain distinctive flora such as sphagnum moss, sedges, and orchids that may not occur in surrounding forests or grasslands (Grover and Baldock, 2013; Grover et al., 2005; McDougall, 1982). Due to their unique flora, there may be also differences in fauna between the peatlands and the surrounding regions.

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Draining of peatlands is a major environmental concern. This can occur directly due to anthropogenic activities such as peat extraction and the conversion of peatland to agricultural land or forest. Additionally, since peatlands form in high rainfall environments, drainage can occur due to a reduction in rainfall. Draining of peatlands destroys the habitats of flora and fauna and also causes oxidation of the organic matter, which in turn releases CO₂ to the atmosphere (Gorham, 1991; Grover and Baldock, 2010). In addition, the dried peat is susceptible to bushfires that commonly occur during droughts and which can destroy the peatlands (Van Der Werf et al., 2010).

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Peatlands comprise ~ 520 km² or $\sim 2.5\%$ of the alpine region of the southeast Australian mainland (Fig. 1) (Costin, 1972; Grover et al., 2005; Western et al., 2009). The peat generally occupies shallowly-sloping areas in the upland plains that are poorly drained. While it forms only a minor part of the Australian landscape, understanding the water balance in the Australian peatlands is important for assessing the potential impacts of environmental change. If water transit times are short, then the peatlands may dry significantly during droughts making them prone to degradation and vulnerable to bushfires. Additionally, the peatlands provide water to numerous small upland streams. Most of the upland peatlands are flanked by eucalypt forests that occupy steeper slopes and gullies. Eucalypts have high transpiration rates and groundwater recharge rates in eucalypt-dominated areas are low (Allison et al., 1990), which results in relatively long water transit times (on the order of years to decades) in eucalypt-dominated catchments (Cartwright and Morgenstern, 2015).

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1.1 Determining mean transit times

The mean transit time represents the average time required for water to flow through the aquifer or soil from where it recharges to where it discharges at the surface (e.g., at a spring, stream or lake) or is sampled from a bore (Cook and Bohlke, 2000; Maloszewski and Zuber, 1982; McDonnell et al., 2010).

5 Documenting mean transit times is important for understanding and managing catchments. The time required for nutrients or contaminants to be transported from recharge areas to streams is a direct function of the transit time (Morgenstern and Daughney, 2012). Additionally, catchments with long transit times are more likely to be resilient to short-term (years to decades) variations in rainfall but will respond to climate or landuse changes that cause longer-term (decades to centuries) changes in groundwater recharge and flow.

Tritium (^3H) has a half-life of 12.32 yr which, together with the fact that it is part of the water molecule, makes it an ideal tracer for determining transit times of young shallow groundwater, soil water, or

surface water (Clark and Fritz, 1997; Cook and Bohlke, 2000; Morgenstern et al., 2010). Other potential tracers for determining transit times of young waters, such as ^3He , chlorofluorocarbons, and SF_6 are gases that degas to the atmosphere and are thus difficult to use for water sampled from streams.

Because the seasonal variation of stable isotope ratios or major ion concentrations in recharge is attenuated with increasing transit times, time-series of stable isotope ratios or Cl concentrations are

also commonly used to estimate mean transit times (e.g., McGuire and McDonnell, 2006; Hrachowitz et al., 2010, 2013; Kirchner et al., 2010). However, this is only practicable where mean transit times

are shorter than ~ 5 years, as longer transit times attenuates the seasonal variation of these tracers (Stewart et al., 2010). Additionally, the use of these tracers requires a detailed (preferably at least weekly) record of stable isotope and/or major ion geochemistry in rainfall for a period which exceeds that of the transit times of water in the catchment (e.g. Timbe et al., 2015).

Coupled with models that describe the distribution of flow paths within an aquifer, commonly referred to as lumped parameter models (Cook and Bohlke, 2000; Maloszewski, 2000; McGuire and McDonnell,

2006), ^3H may be used to determine transit times of waters that are up to ~ 100 years old. The ^3H activities in rainfall over the last several decades have been measured globally (e.g. International Atomic Energy Association, 2016; Tadros et al., 2014), which allows the ^3H input to catchments over

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time to be estimated. Rainfall ^3H activities peaked in the 1950s to 1960s due to the production of ^3H in atmospheric thermonuclear tests (commonly termed “bomb pulse” ^3H).

There are two different approaches in using ^3H to estimate mean transit times. In the northern hemisphere, the ^3H activities of remnant bomb pulse waters are currently above those of modern rainfall. This situation results in individual measurements of ^3H activities in groundwater or surface water yielding non-unique estimates of transit times (Morgenstern et al., 2010). Mean transit times may, however, be determined using time-series of ^3H measurements (e.g., Maloszewski and Zuber, 1982; Michel, 1992, McGuire and McDonnell, 2006). The use of time-series measurements is potentially advantageous as, in addition to determining a mean transit time, it allows the most appropriate lumped parameter model to be assessed by comparison of the predicted and observed changes to ^3H activities over time (Maloszewski and Zuber, 1982). However, the time series approach inherently assumes that the flow system is identical at each sampling time (which is unlikely in dynamic near-surface systems where there are fluctuations of the water table). Where the system is not time invariant, it is difficult to calculate meaningful mean transit times (Kirchner, 2016b).

The bomb pulse ^3H activities in the southern hemisphere were several orders of magnitude lower than in the northern hemisphere (Clark and Fritz, 1997; Tadros et al., 2014), and the ^3H activities of the remnant bomb-pulse waters have now decayed below those of modern rainfall. This permits ^3H to be used in a similar manner to other radioactive isotope tracers such as ^{14}C or ^{36}C whereby a residence or transit time may be estimated from individual ^3H activities (Morgenstern et al., 2010). Since the ^3H activities reflect the net residence time in the catchment there is not a requirement for the flow system to be time invariant. However, this approach to determining mean transit times does not permit the optimal lumped parameter model to be determined, as is the case when time-series ^3H measurements at similar flow conditions are available. The attenuation of the bomb-pulse ^3H in the southern hemisphere is such that constraining the lumped parameter models using time-series measurements of ^3H is probably no longer practicable. For example, the predicted decrease in ^3H activities for a water with a mean transit time of 10 years between 2016 and 2026 calculated using the lumped parameter models and ^3H input employed in this study is only ~ 0.2 TU, and the predicted ^3H vs time trends are similar for the different models. Instead, a plausible lumped parameter model

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must be proposed based on factors such as the geometry of the flow system or information from previous time-series studies. Given that the different lumped parameter models yield different mean transit times for the same ^3H activity, this introduces uncertainties. However, because the ^3H activities of the remnant bomb pulse waters are below those of modern rainfall, the relative transit times of southern hemisphere waters are largely independent of assumed flow models (i.e., water with a low ^3H activity has a longer mean transit time than water with a high ^3H activity).

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Rivers aggregate water from different flow systems and the mean transit times of water contributed by individual tributaries may vary considerably. Kirchner (2016a) discussed the impacts of aggregation for mean transit times calculated from time-series major ion and stable isotope data. That study demonstrated that the mean transit time calculated from the aggregated water was generally lower than the actual mean transit time (i.e. that which would be calculated from the weighted average of each of the end-members contributing to the mixture). Aggregation also affects mean transit times calculated from individual ^3H activities. Mean transit times calculated from the ^3H activity of the aggregated water are again generally lower than the actual mean transit times with the error increasing as the difference between the mean transit time of the individual end members increases (Stewart et al., 2016).

1.2 Transit times in upland peat

Compared with catchments developed on other vegetation types, the transit time of peatland water, especially upland or mountain peat, is less well known. Due to peatlands containing poorly-drained organic rich soils and occupying shallow slopes, it is sometimes assumed that peatland waters have long transit times. However, there has been little assessment of that assumption (e.g., as discussed by Western et al., 2009). Using ^3H activities, transit times of years to decades were proposed for water from metre to tens-of-metre thick peat deposits in Quebec, Canada (Dever et al., 1984), Dartmoor, UK, (Charman et al., 1999), Lithuania (Mažeika et al., 2009), and Minnesota, USA (Siegel et al., 2001). From the preservation of seasonal $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, Aravena and Warner (1992) estimated that the water from the upper ~0.1 m of peat from Ontario, Canada, was <1 year old. Mean transit times from an upland peat-bearing catchment in Zhuruca, Ecuador, were estimated at <1 year using oxygen isotopes (Mosquera et al., 2016). Mean transit times from the extensively-studied upland catchments,

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in the United Kingdom, which include extensive regions of peat, were estimated using time series of stable isotopes and Cl as <5 years (e.g., Soulsby et al., 2006; Kirchner et al., 2010; Hrachowitz et al., 2013; Tetzlaff et al., 2014; Benettin et al., 2015). However, the mean transit times of the water specifically draining the peat in those catchments are generally not known. Morris and Waddington

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(2011) modelled water transit times in peat and suggested that they vary from <1 year for the upper 0.1 m to several years in deeper layers, which is broadly consistent with the above estimates. While not estimating transit times, Western et al. (2009) concluded on the basis of hydrograph analysis and water balance calculations that peatlands in southeast Australia did not act as long-term water stores for the local streams.

1.3 Objectives

This study was designed to test the hypothesis that peatlands in the Victorian Alps, southeast Australia represent a relatively long-lived store of water. Specifically, we utilise ³H to provide the first estimates of the mean transit times of water draining Australian peatlands during summer baseflow conditions and compare these with mean transit times of streams that drain adjacent eucalypt forests.

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Documenting mean transit times is important for determining the relative importance of the peatlands and eucalypt forests in providing water to the local rivers and also in assessing potential environmental impacts resulting from landuse or climate change. In addition, we assess whether the major ion geochemistry of the water may be used as a first-order proxy for mean transit times and discuss the controls on mean transit times in these upland areas.

2. Methods

2.1 Setting

Water from streams draining peatlands and eucalypt forests was sampled in the Mount Buffalo (Ovens Catchment: Fig. S1a), Falls Creek (Kiewa and Upper Murray Catchments: Fig. S1b), and Dargo (Mitchell Catchment: Fig. S1c) regions of the Victorian Alps (Fig. 1). Catchment areas in the peatlands and eucalypt forests are similar, ranging from 0.5 to 6.4 km² (Table 1). The Falls Creek and Dargo areas consist of indurated Ordovician metasedimentary rocks, Devonian granites, and minor Tertiary basalts,

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Mean transit times in adjacent catchments in the Ovens Valley dominated by eucalypt forests (Fig. 1) were estimated using ³H as being between 4 and 30 years, with higher mean transit times recorded during summer low flow conditions (Cartwright and Morgenstern, 2015). That study focussed on the major tributaries to the Ovens River that had catchment areas between 6 and 435 km², and the transit times in the upper reaches of the catchments where streamflow commences remains unknown. Additionally, it was not established whether there are differences between mean transit times for water draining the peatlands and the eucalypt forests in those upper catchments.

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whereas the Mount Buffalo plateau comprises Devonian granite (van den Berg et al., 2004; Energy and Earth Resources, 2016).

Peatlands are developed in poorly-drained low-relief upland areas of the Victorian Alps with eucalyptus forests occupying steeper valleys that dissect the uplands and the higher better-drained areas at the margins of the peatland (Grover and Baldock, 2013; Grover et al., 2005; McDougall, 1982; Western et al., 2009). The peatlands are characterised by sphagnum mosses (*Sphagnum cristatum*), rushes (*Empodisma minus* and *Baloskion australe*), and heaths (*Epacris paludosa* and *Richea continentis*) (McDougall, 1982). Most of the peatlands in the Alpine region are <2 m thick. The upper few centimetres comprise little decomposed plant material (the fibric zone). The fibric zone grades downwards through the hemic zone (typically 50 cm to 1 m thick) where the soils are organic-rich, fibrous, with abundant discernible roots into a denser soil (the sapric zone) comprising mainly decomposed organic matter with clays and fragments of rock. The peat typically has a thin (<20 cm thick) layer of weathered rocks at its base but mainly overlies little-weathered basement rocks. The hydrology of the peat comprises the upper acrotelm, which alternates between saturated and unsaturated as the water table rises and falls, and the lower permanently-saturated catotelm (e.g., Grover et al., 2005). The boundary between the acrotelm and catotelm is generally in the hemic zone.

In the alpine regions of southeast Australia the dominant eucalypt species include Mountain Ash (*Eucalyptus regnans*) at altitudes of <1000 m and Alpine Ash (*Eucalyptus delegatensis*) and Snow Gum (*Eucalyptus pauciflora*) at higher altitudes (McDougall, 1982). The soils of the eucalypt forests include sandy lithosols; these are thin, well-drained, and poor in organic matter and largely occur on the upper slopes of the gullies and on the elevated areas surrounding the peatlands. In the centres of the gullies, the soils also include alpine humus loams that contain higher contents of organic matter and which are less well drained. The soils overlie weathered regolith that is a few tens-of-centimetres to a few metres thick. There are also minor deposits of colluvium and alluvium along the streams (Shugg, 1987).

Groundwater flow is restricted to the weathered zones and fractures in the granites and metasediments; the minor alluvial and colluvial sediments are more permeable but represent only a minor part of the landscape.

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Average precipitation is 1250 mm yr⁻¹ at Falls Creek, 1650 mm yr⁻¹ at Mount Hotham (near Dargo), and 1790 mm yr⁻¹ at Mount Buffalo (Bureau of Meteorology, 2016) (Fig. 1). Approximately 60 to 70% of precipitation occurs in the austral autumn to winter (May to September) with a proportion of the winter precipitation occurring as snow. February and March have the lowest precipitation (4 to 6% of the annual total in each month). No currently active river gauges exist in these upland areas and previous flow measurements were only from a few streams at Falls Creek (Department of Environment, Land, Water, and Planning, 2016). These limited records show that river flow varies seasonally with the majority of streamflow occurring in the winter months; however, flows persist over summer (Fig. 2a) and the streams generally do not record zero flows (Fig. 2b). Water from some of the peatlands at Falls Creek drains into the Rocky Valley Reservoir (~2.8x10⁷ m³), which is used to provide water to the Falls Creek resort and the Kiewa Valley hydroelectric system. Water from some of the peatlands at Mount Buffalo feeds Lake Catani, which is an artificial recreational lake with a volume of ~2x10⁶ m³.

Mean transit times in the Ovens Valley which is dominated by eucalypt forests (Fig. 1) were estimated using ³H as being between 4 and 30 years, with higher mean transit times recorded during summer low flow conditions (Cartwright and Morgenstern, 2015). That study focussed on the major tributaries to the Ovens River that had catchment areas between 6 and 435 km², and the transit times in the upper reaches of the catchments where streamflow commences remains unknown. Additionally, it was not established whether there are differences between mean transit times for water draining the peatlands and the eucalypt forests in those upper catchments.

2.2 Sampling and analytical techniques

Samples of rainfall representing the total precipitation over periods of several weeks to months (Table 1) were collected from a rainfall collector at Mount Buffalo (Fig. 1). Grab samples of stream water from the peatlands and eucalypt forests were taken from flowing reaches. Water was also sampled from within the peat using a hand-operated siphon pump with a soft PVC inlet hose that was inserted into a rigid 5 cm diameter PVC piezometer with a ~20 cm screen pushed directly into the peat. The piezometer was inserted to the maximum possible extent (i.e., until resistance prevented it from being pushed deeper). Field observations indicated that this was at or close to the base of the peat and

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within the hemic zone and catotelm. At least three bore volumes of water were extracted prior to sampling.

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Tritium activities (Table 1) were measured on water samples that had been vacuum distilled and electrolytically enriched using liquid scintillation spectrometry (Quantulus ultra-low-level counters) at Geological and Nuclear Sciences, New Zealand (Morgenstern and Taylor, 2009). The ^3H activities are expressed in tritium units (TU) where 1 TU represents a $^3\text{H}/^1\text{H}$ ratio of 1×10^{-18} . Enrichment of ^3H was by a factor of 95, which results in a detection limit of 0.02 TU, while the use of deuterium-calibration for each sample results in a 1% reproducibility of the tritium enrichment. Precision (1σ) is $\sim 1.8\%$ at 2 TU.

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Major ion concentrations (Table 1) were measured at Monash University using a ThermoFinnigan ICP-OES (cations), ThermoFinnigan ICP-MS (Si), and a ThermoFischer ion chromatograph (anions). Samples for cation and Si analysis were filtered through 0.45 μm cellulose nitrate filters and acidified to $\text{pH} < 2$ using double-distilled 16M HNO_3 . Samples for anion analysis were filtered but unacidified. The precision of the major ion concentrations determined by replicate analyses of samples is $\pm 2\%$ and the accuracy as determined by analysis of certified water standards is $\pm 5\%$.

Stable isotope ratios of water (Table 1) were determined using a ThermoFinnigan DeltaPlus Advantage mass spectrometer at Monash University. A ThermoFinnigan Gas Bench was used for the ^{18}O analyses. Waters were equilibrated with He-CO_2 at 32°C for 24 to 48 hours and the gas subsequently analysed by continuous flow. A ThermoFinnigan H-Device was used for the ^2H analyses. H was produced from water via reaction with Cr at 850°C and analysed by dual-inlet measurement. Internal standards that have been calibrated using IAEA SMOW, GISP and SLAP standards were employed to normalise the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (following Coplen, 1988). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are expressed in ‰ relative to V-SMOW with a precision (1σ) determined from replicate analyses of samples of $\pm 0.1\text{‰}$ ($\delta^{18}\text{O}$) and $\pm 1\text{‰}$ ($\delta^2\text{H}$). The deuterium (D) excess is defined as $\delta^2\text{H} - 8 \delta^{18}\text{O}$ (Clark and Fritz, 1999).

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Catchment areas (Table 1) were estimated from Google Earth satellite images (Figs S1a to S1c) and 1:30,000 topographic map sheets on which the streams are clearly distinguished. Attempts to define

catchment areas using a digital elevation model (DEM) did not reproduce the drainage pattern in the peatlands due to the low topography relative to the DEM resolution.

2.3 Estimating mean transit times using ³H

Water flowing through aquifers or soils follows flow paths of varying length and thus the water discharging into streams or sampled from bores has a range of transit times (McGuire and McDonnell, 2006). Mean transit times were calculated using lumped parameter models (Maloszewski, 2000; Maloszewski and Zuber, 1982; Zuber et al., 2005) as implemented in the TracerLPM Excel workbook (Jurgens et al., 2012). For steady-state groundwater flow, the ³H activity in water at the catchment outlet at the time of sampling ($C_o(t)$) may be estimated using the convolution integral:

$$C_o(t) = \int_0^{\infty} C_i(t-\tau) g(\tau) e^{-\lambda\tau} d\tau \quad (1),$$

In Eq. (1), C_i is the ³H activity of recharge, τ is the transit time, $t-\tau$ is the time when water entered the catchment, λ is the ³H decay constant (0.0563 yr^{-1}), and $g(\tau)$ is the response function that describes the distribution of transit times in the flow system.

As discussed above, the use of single ³H activities to estimate mean transit times requires that a lumped parameter model be assigned. The following lumped parameter models were considered in this study: the exponential flow model; the exponential-piston flow model; and the dispersion model. Together these represent the most commonly used lumped parameter models in determining mean transit times (e.g. as reviewed by McGuire & McDonnell, 2006). In catchments where time-series data are available, these models generally reproduce the predicted variation in ³H activities over time (e.g., Maloszewski and Zuber, 1982; Maloszewski et al. 1983; Zuber et al., 2005; Stewart et al. 2007; Morgenstern et al., 2015).

The exponential flow model predicts transit times in homogeneous unconfined aquifers of constant thickness with uniform recharge, where water from the entire aquifer discharges to the stream or is sampled by a bore. Flow through aquifers where flow paths are the same length and no mixing occurs results in all water discharging to the stream at any given time having the same transit time and is

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described by the piston flow model. Transit times in aquifers that have regions of both piston and exponential flow are described by the exponential-piston flow model, for which the response function is:

$$g(\tau) = 0 \quad \text{for } \tau < \tau_m(1-f) \quad (2a)$$

$$5 \quad g(\tau) = (f\tau_m)^{-1} e^{-\tau/f\tau_m + 1/f - 1} \quad \text{for } \tau > \tau_m(1-f) \quad (2b),$$

where τ_m is the mean transit time and f is the proportion of the aquifer volume that exhibits exponential flow. At $f = 1$, this model becomes the exponential flow model, while at $f = 0$, it becomes the piston flow model. TracerLPM specifies the ratio of exponential to piston flow as the EPM ratio (equivalent to $1/f - 1$).

10 The dispersion model is based on the solution to the one-dimensional advection-dispersion transport equation. The response function for the dispersion model is:

$$g(\tau) = \frac{1}{\tau \sqrt{4\pi D_p \tau / \tau_m}} e^{-\frac{(1 - \tau/\tau_m)^2}{4D_p \tau / \tau_m}} \quad (3),$$

where D_p is the dispersion parameter defined as $D_p = D/(v x)$, where D is the dispersion coefficient ($m^2 \text{ day}^{-1}$), v is velocity ($m \text{ day}^{-1}$) and x is distance (m). This model is generally considered to be a less realistic representation of flow systems, however it does commonly reproduce the observed distribution of tracers (Maloszewski, 2000).

3. Results

This section presents the streamflow and geochemistry data (Table 1) from the Victorian Alps; interpretation of these data appears in later sections.

20 3.1 Streamflow

As noted above, very few streamflow measurements exist in these catchments. Watchbed Creek drains the peatlands at Falls Rocky A (Fig. S1b) and there is a near-complete streamflow record for this site between 1940 and 1986. The average discharge for Watchbed Creek over that time period was

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5.64x10⁶ m³ yr⁻¹ (Department of Environment, Water, Land and Planning, 2016). For the average annual rainfall of 1.25 m yr⁻¹ (Bureau of Meteorology, 2016), the runoff coefficient (i.e., the volume of rainfall that is exported by the stream) was 78%. This is much higher than the runoff coefficients in the eucalypt-dominated catchments of the upper Ovens Valley which range from 6 to 64% (Cartwright and Morgenstern, 2015). That Watchbed Creek exports more rainfall than streams from the eucalypt forests is also apparent in the flow duration curves (Fig. 2b). Relative discharges from Watchbed Creek are around an order of magnitude higher than those from Simmons Creek in the upper Ovens catchment. Simmons Creek has a slightly larger catchment area (6 km² vs. 3.5 km²) and receives similar rainfall but drains eucalypt forest.

3.2 Stable isotope ratios

Stable isotope ratios are presented in Table 1 and Fig. 3. Rainfall has δ¹⁸O values of -7.9 to -6.5‰ and δ²H values of -40 to -34‰. The δ¹⁸O and δ²H values of the peatland water range from -8.3 and -5.0‰ and -43 to -26‰, respectively. The eucalyptus forest streams have smaller ranges of δ¹⁸O and δ²H values (-7.4 to -5.7‰ and -38 to -29‰, respectively). As is commonly the case in southeast Australia (Cartwright et al., 2012; Leaney and Herczeg, 1999), the δ¹⁸O and δ²H values of all waters, including rainfall, lie to the left of the global and Melbourne meteoric water lines. Overall the waters define an array with a slope of ~5 and have D-excess values between 14 and 24‰ with a median of 19‰. These D-excess values are significantly higher than the mean D-excess of the Melbourne meteoric water line of 9.6‰ (Hughes and Crawford, 2012).

3.3 Tritium activities

The ³H activities of three multi-month rainfall samples from Mount Buffalo are 2.85 TU (12 month sample collected in February 2015), 2.88 TU (9 month sample collected in November 2015), and 2.99 (17 month sample collected in December 2013) (Table 1). Three samples of rainfall collected over periods of 2 weeks to 3 months in 2014 also from Mount Buffalo have ³H activities of 2.52 to 2.90 TU (Table 1). The sample with the lowest ³H activity represents mainly snow and low-temperature rainfall collected over a 2 week period in July 2014. The ³H activities are within the expected range of ³H activities in rainfall for this region of 2.8 to 3.2 TU (Tadros et al., 2014). Aside from the July 2014 rainfall

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sample that represents the two weeks of winter precipitation, there is an inverse correlation ($R^2 = 0.69$) between the ^3H activities and $\delta^2\text{H}$ of rainfall (Fig. 4). ~~Since~~ the rainfall with the higher $\delta^2\text{H}$ values has lower D-excess values, ~~there is also~~ a correlation between D-excess and ^3H activities. Rainfall from elsewhere in southeast Australia defines broadly similar trends in $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ values and $\delta^2\text{H}$ vs ^3H values (Table 1, Figs 3, 4).

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The peatland waters have ^3H activities that vary from 2.70 to 3.32 TU (median = 2.75 TU) at Mount Buffalo, 2.90 to 3.17 (median = 3.04 TU) at Falls Creek, and 2.47 to 3.36 (median = 2.77 TU) at Dargo (Table 1, Figs 4, 5). The overall median ^3H activity is 2.88 TU. The ^3H activities of the peatland water from the three sites are closely similar. Additionally, there are no significant differences in ^3H activities of water collected from within the peat and that collected from the streams draining the peat. The ^3H activities of waters collected in February 2015 and those collected in November 2015 also overlap. The ^3H activities of the peatland waters are locally higher than those of the rainfall samples and several of those waters also have lower $\delta^2\text{H}$ values and higher D-excesses than the rainfall (Figs 3, 4).

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The eucalyptus forest streams have ^3H activities of between 1.56 and 2.35 TU (median = 2.10 TU) (Table 1; Figs 4, 5) that are lower than those of the peatland waters. The ^3H activities of the eucalyptus streams overlap with those of river water from the streams in the upper Owens catchment at low flow conditions in December 2013 and February 2014, which range from 1.63 to 2.28 TU (median = 2.09 TU) (Cartwright and Morgenstern, 2015; Fig. 5).

3.4 Major ion geochemistry

Cl concentrations of the peatland waters are between 0.5 and 1.1 mg l^{-1} , which are similar to those of rainfall from Mount Buffalo (0.8 to 1.1 mg l^{-1}) (Fig. 5a, Table 1). Peatland water from Falls Creek has lower Cl concentrations (0.5 to 0.9 mg l^{-1}) than that from the other areas; however, there is no significant difference between the Cl concentrations of the water extracted from within the peat and that draining the peatlands. Na concentrations of the peatland water range from 0.8 to 2.1 mg l^{-1} , which are higher than those of rainfall (0.6 to 1.0 mg l^{-1}) (Fig. 5b). The eucalypt forest streams have higher Cl (1.1 to 2.6 mg l^{-1}) and Na (3.2 to 5.7 mg l^{-1}) concentrations than any of the peatland water (Figs. 5a, 5b). Molar Na/Cl ratios range from 1.7 to 3.5 in the peatland water and 3.9 to 6.8 in the

eucalypt forest streams (Fig. 5d). These Na/Cl ratios are higher than those of Buffalo rainfall, which has Na/Cl ratios of 1.0 to 1.1 that are similar to those generally recorded in southeast Australia (Blackburn and McLeod, 1983; Crosbie et al., 2012).

5 Molar Cl/Br ratios vary between 340 and 650 in the peatland water and between 550 and 780 in the eucalypt forest streams (Fig. 5c). These ratios are similar to those of Buffalo rainfall (570 to 650) and also similar to the ocean Cl/Br ratio of ~650 (Davis et al., 1998). Other cation/Cl ratios are also higher in the eucalypt forest streams compared with the peatland water, and the water from both these sources has higher cation/Cl ratios than rainfall. Si concentrations in Buffalo rainfall are <0.1 mg l⁻¹ (Fig. 5e) and molar Si/Cl ratios are ~0.1 (Fig. 5f). By contrast, Si concentrations and Si/Cl ratios in the 10 peatland water and eucalypt forest streams are significantly higher (up to 9.8 mg l⁻¹ and 9.5, respectively: Figs 5e, 5f).

There are broad inverse correlations between ³H activities and Na, Cl, and Si concentrations and Na/Cl and Si/Cl ratios (Fig. 5). In general the differences in geochemistry between the peatland water and eucalypt forest streams are more marked than the geochemical variations within those groups. For 15 example, the Si vs. ³H trend for the combined peatland water and eucalypt forest streams has a R² of 0.63, whereas R² values for Si vs. ³H in the peatland water and the eucalyptus forest streams are 0.05 and 0.32, respectively. The correlations between major element concentrations and ³H activities are stronger in the eucalypt forest streams (R² values of 0.32 to 0.87) than in the peatland waters (R² values of 0.05 to 0.24). The trends in ³H activities vs. major ion concentrations or ratios in the 20 eucalyptus forest streams from the Victorian Alps are similar to those of the upper Ovens catchment as a whole.

4. Discussion

25 ~~This section combines the major ion geochemistry, stable isotope data, and ³H activities to determine the mean transit times of the waters from the peatlands and eucalyptus forest streams and assesses the major geochemical processes that impact these waters.~~

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4.1 Modern rainfall ³H activities

Understanding the ³H activities of the water that recharges the catchments is critically important in estimating mean transit times. The three longer-term (9 to 17 month) rainfall samples have ³H activities of between 2.85 and 2.99 TU, which lie within the predicted ³H activity of rainfall in this area of 2.8 to 3.2 TU (Tadros et al., 2014). However, the observation that the peatland water has ³H activities that are locally up to 3.35 TU indicates that it is not possible to use the rainfall ³H activities as the ³H activity of recharge for all of the peatland waters.

There may be spatial variations in rainfall ³H activities, especially between the three areas. The observation, however, that peatland water at Mount Buffalo from <5 km from the rainfall gauge has a ³H activity of up to 3.32 TU suggests that this cannot be the only explanation. The higher ³H activities in the peatland waters potentially reflect preferential recharge by spring rainfall. Maximum ³H activities in Australian rainfall are recorded in early spring (August to September) as this is the time of maximum transport of water vapour with high ³H activities from the stratosphere to the troposphere (Tadros et al., 2014). Stratospheric moisture also has lower $\delta^2\text{H}$ values and higher D-excesses than tropospheric moisture (Bony et al., 2008). Thus the variation in the relative ratios of stratospheric to tropospheric moisture would also explain the observations that rainfall samples with higher ³H activities have lower $\delta^2\text{H}$ values (Fig. 4) and higher D-excess values (Fig. 3).

Some peatland waters have lower $\delta^2\text{H}$ values than those of the rainfall. These potentially record recharge by rainfall that has a high proportion of low $\delta^2\text{H}$ stratospheric moisture. Such rainfall would also be expected to have higher ³H activities than average rainfall. While it is difficult to precisely constrain the ³H of seasonal recharge, extending the rainfall $\delta^2\text{H}$ vs. ³H trend defined by the Mount Buffalo rainfall samples in Fig. 4 to the lowest $\delta^2\text{H}$ value of the peatland waters (-43‰) yields a ³H activity of ~3.4 TU, which is similar to the highest ³H activities recorded in the peatland waters. This is ~14% higher than the ³H activities of the rainfall samples, which is well within the seasonal variation of ³H activities of Australian rainfall (Tadros et al., 2014).

That some of the peatland waters with high ³H activities have higher $\delta^2\text{H}$ values is likely due to subsequent evaporation (Fig. 4). As discussed below, the major ion geochemistry also implies that

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evaporation has affected these waters. Evaporation at a humidity of 50 to 70%, which is characteristic of these Alpine areas in summer (Bureau of Meteorology, 2016), produces arrays of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with slopes of 4 to 5 (Clark and Fritz, 1999). Thus the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the waters (Fig. 3) probably reflects both initial variations in stable isotope ratios and subsequent evaporation. Assuming that the mass-dependant isotope fractionation of $^3\text{H}/^1\text{H}$ is approximately double that of $^2\text{H}/^1\text{H}$, a 10% increase in $\delta^2\text{H}$ values would equate to a ~2% increase in ^3H activities, which is approximately the analytical precision.

4.2 Mean transit times

Mean transit times (Table 2, Fig. 6a) were initially calculated using an exponential-piston flow model with an EPM ratio of 0.33 via Eqs (1 and 2). The soils and shallow aquifers are unconfined and likely to exhibit exponential flow below the water table; however, recharge through the unsaturated zone will most likely resemble piston flow. A similar flow model successfully reproduces time-series of ^3H activities in upland catchments in New Zealand (Morgenstern et al., 2010). Given that the waters were sampled at baseflow conditions during the late spring or summer, which represent the driest months, it was assumed that there was a single store of water present rather than a mixture of recent rainfall and older water. While the exponential-piston flow model plausibly represents the flow systems, it is not possible in independent test its veracity. Hence, mean transit times were also calculated using the exponential flow model with a higher proportion of piston flow (EPM ratio of 1), the exponential flow model, and the dispersion model with $D_0 = 0.1$ and 1.0 which are appropriate values for flow systems of this scale (Maloszewski, 2000) (Table 2, Fig. 6a).

The annual average ^3H activities of rainfall in Melbourne, which is ~200 km to the southwest, from the International Atomic Energy Agency Global Network of Isotopes in Precipitation program as summarised by Tadros et al. (2014) were used as the ^3H input. Rainfall ^3H activities reached ~62 TU in 1965 and then declined exponentially to present-day values (Tadros et al., 2014). The calculations initially adopted a present-day ^3H activity of recharge of 3.4 TU (as discussed above). A ^3H activity of 3.4 TU was also used for recharge from prior to the atmospheric nuclear tests.

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Mean transit times from the exponential piston flow model with an EPM ratio of 0.33 are up to 6.4 years with a median of 3.0 years (Table 2). For the range of ^3H activities in these peatland waters, between the mean transit times estimated from the different lumped parameter models are similar

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(Table 2, Fig. 6a). The exponential-piston flow model with an EPM ratio of 1 yields mean transit times of up to 6.0 years with a median of 2.9 years. The exponential flow model produces mean transit times of up to 7.4 years with a median of 3.1 years. The dispersion model yields mean transit times of up to 6.0 years with a median of 2.8 years ($D_p = 0.1$) and 8.0 years with a median of 3.5 years ($D_p = 1.0$).

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For a water with a ^3H activity of 3 TU, propagating the analytical uncertainty of $\pm 2\%$ produces an uncertainty in mean transit times of ± 0.3 years. Uncertainties in calculated mean transit times for the high ^3H samples mainly arise from the assumed ^3H activity of the recharging water (Fig. 6b), which as discussed above is difficult to constrain precisely. This will be illustrated for the exponential-piston flow model with an EPM ratio of 0.33, but similar variations would be observed for the other models.

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Utilising a ^3H activity of 3.0 TU for modern and pre-bomb pulse rainfall based on the ^3H activities of the rainfall samples (Table 1), yields mean transit times of up to 4.0 years with a median of <1 year

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(Table 2). However, in this case a large number of peatland waters have ^3H activities that are higher than the rainfall activities and for those waters, a ^3H activity of 3.0 TU for the recharging water is not realistic. Adopting a ^3H activity of 3.2 TU, which is the upper limit of the estimate for annual rainfall in this area (Tadros et al., 2004) yields mean transit times of up to 5.4 years with a median of 1.8 years. In this case two peatland waters (Dargo D and Buffalo Cresta A) have ^3H activities that are higher than the assumed recharge ^3H activities. Given the likelihood that seasonal recharge has occurred and thus the ^3H activity of the recharging water may be locally variable, it is unrealistic to differentiate mean transit times of <1 year.

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By contrast with the peatland waters, the eucalypt forest streams have much longer mean transit times that are relatively insensitive to the assumed ^3H activity of recharge (Fig. 6b). For the exponential-piston flow model with an EPM ratio of 0.33 and a modern and pre-bomb pulse rainfall activity of 3.0 TU (which assumes recharge has the ^3H activity of average rainfall), mean transit times range from 5.3 to 28.6 years with a median of 9.5 years (Table 2). Adopting a ^3H activity for recharge of 3.2 TU, the mean transit times range from 6.9 to 28.8 years with a median of 10.8 years and if the

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^3H activity of recharge was 3.4 TU, the mean transit times are 7.8 to 28.9 years with a median of 11.5 years. These mean transit times are within the range of those of the much larger (6 to 1240 km²) catchments in the upper Owens Valley that are also dominated by eucalypt forest. Mean transit times of river water in December 2013 and February 2014 in the upper Owens Valley calculated using the same exponential-piston flow model and a ^3H activity of recharge of 3.0 TU are 7 to 30 years (Cartwright and Morgenstern, 2015).

For the eucalypt forest streams there are larger uncertainties in mean transit times produced by the different lumped parameter models (Table 2, Fig. 6a). The range in mean transit times for a water with a ^3H activity of 2 TU calculated from the exponential flow model, the exponential-piston flow model with EPM ratios of 0.33 and 1, and the dispersion model with $D_p = 0.1$ and $D_p = 1$ is ~4.5 years. For a water with a ^3H activity of 1.5 TU the range in mean transit times from those models is ~13 years. Uncertainties as to the most appropriate lumped parameter model thus represent a significant source of uncertainty in these calculations. However, overall the water in these streams has mean transit times of years to decades and is significantly older than that from the peatlands. Propagating the analytical uncertainty in ^3H activities (Table 2) also results in uncertainties in mean transit times of ± 0.5 years for a water with a ^3H activity of 2 TU.

Aggregation of water with different mean transit times also introduces uncertainty in the calculated mean transit times (Kirchner, 2016a; Stewart et al., 2016). Figure 8 illustrates the impact of mixing different proportions of water with mean transit times of between 10 and 50 years (appropriate for the eucalypt forest waters) on the calculated mean transit times. The actual mean transit time represents the mean transit time that calculated from the weighted average of the transit times of the mixed waters. The apparent mean transit time is calculated from the ^3H activity of the mixed water again using the exponential piston flow model with an EPM ratio of 0.33. The apparent mean transit times are less than the actual mean transit times with the greatest difference (~13%) occurring when there are approximately equal proportions of two end members with mean transit times of 10 and 50 years. The difference between actual and apparent mean transit times decreases when multiple end-members are aggregated (shaded field). For example the apparent mean transit time calculated from an equal mixture of nine waters with transit times of 10, 15, 20, 25, 30, 35, 40, 45, and 50 years is 28.9

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years, which is within 4% of the actual mean transit time of 30 years. The relative difference between apparent and actual mean transit times are similar when other lumped parameter models are used. Mixing waters with a range of mean transit times between 1 and 5 years (which would be appropriate for the peatland waters) produces similar relative differences. Overall, aggregation introduces uncertainties that are similar to those resulting from other uncertainties in the calculations (discussed above).

Overall, there are uncertainties in the calculated mean transit times resulting from uncertainties in the ³H activity of recharge, the most appropriate lumped parameter model, and aggregation. However, the conclusion that the mean transit times of water in the eucalypt forest catchments range from several years to decades and are significantly longer than those in the peatlands remains robust. Mean transit times of the peatland waters are unlikely to be more than a few years and may be mainly less than 2 years depending on the ³H activity of recharge. As noted above, the ³H activities of the water from the piezometers in the peatlands are similar to the water that drains the peat. The water that drains the peat is likely derived mainly from the acrotelm (Western et al., 2009; Grover and Baldock, 2013), presuming that the piezometers which were inserted into the lower levels of the peat sampled water from the catotelm, this observation implies that the catotelm is not a store of older water.

4.3 Major ion tracers

The major ion geochemistry allows the main geochemical processes to be understood and also can provide first-order estimates of mean transit times. Overall, the observation that the Cl/Br ratios in the peatland water and the eucalypt forest streams have molar Cl/Br ratios that cluster around those of the rainfall implies that, in common with the majority of groundwater and surface water in southeast Australia, the vast majority of Cl is derived from the rainfall and concentrated by evapotranspiration (Cartwright et al., 2006; Herczeg et al., 2001). Other potential sources of Cl (such as dissolution of halite in the unsaturated zone) produce water with high Cl/Br ratios and can thus be discounted.

The higher Cl concentrations in the eucalypt forest streams compared with that from the peatland water reflects higher net evapotranspiration rates in the eucalypt forest catchments. Some of the

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increase in the concentration of the other major ions such as Na in the eucalypt forest streams and peatland water over those in rainfall will also be due to evapotranspiration. The adsorption of Br by organic matter (Gerritse and George, 1988) may locally increase Cl/Br ratios if the pool of organic matter is increasing. By contrast, a net degradation of organic matter releases Br producing lower Cl/Br ratios. The wider range of Cl/Br ratios in the peatland water may reflect that, locally, the volume of organic matter is increasing whereas elsewhere it is degrading. The far more homogeneous Cl/Br ratios in the eucalypt forest streams indicate that either the organic matter content of those catchments is relatively stable or that the waters are better mixed and any local variations in Cl/Br ratios have been homogenised. This homogenisation is consistent with longer mean transit times in the eucalypt forest streams.

The increase in cation/Cl and Si/Cl ratios in the peatland and eucalypt forest waters over those in rainfall is interpreted to be due to silicate weathering (c.f., Herczeg and Edmunds, 2000). As rainfall contains $<0.1 \text{ mg l}^{-1} \text{ Si}$, evapotranspiration will not increase Si concentrations appreciable and the vast majority of the Si will be derived from silicate weathering. The eucalypt forest streams have higher cation/Cl and Si/Cl ratios compared with the peatland water and thus records higher degrees of weathering. This is likely due to two factors. Firstly, the eucalypt forest catchments are developed on weathered regolith and the flow of water through the regolith will promote mineral dissolution. Common minerals in the regolith include plagioclase and alkali feldspars (Cartwright and Morgenstern, 2012) and the dissolution of these will provide Si, Na, Ca, and K. By contrast, the peatlands are developed on less weathered rocks, which limits the potential for mineral dissolution; although there clearly has been sufficient weathering to produce the elevated cation/Cl and Si/Cl ratios. There is commonly a thin ($<20 \text{ cm}$ thick) layer of regolith at the base of the peat and fragments of basement rock within the lower layers of the peat that are likely being weathered by the peatland water. Secondly, the longer mean transit times in the eucalypt forest catchments allow the silicate weathering reactions to progress further than in the peatlands.

4.4 Controls on mean transit times

As with the Ovens catchment as a whole, there is no correlation between ^3H activities and catchment areas either within or between the eucalypt forest and peatland catchments (Fig. 7). Elsewhere,

inverse correlations between catchment slope and mean transit times have been documented (McGuire et al., 2005). Catchment slopes have not been calculated in this study (and would be difficult to do so in the peatlands given the limitations of the DEM). However, the observation that the eucalypt forests occur in gullies that invariably have steeper slopes than the peatlands but contain water with longer mean transit times indicates that, in this case, catchment slopes cannot explain the difference in mean transit times between the two catchment types.

The difference in the mean transit times between the peatland water and the eucalypt forest streams is likely the combination of two factors. Firstly the high evapotranspiration rates of the eucalypt forests (Allison et al., 1990) results in low recharge rates that in turn increase the transit times.

Secondly, differences in the depth of weathering in the catchments and the development of deeper flow paths is also likely to be important. Most of the peatlands are developed on relatively unweathered basement rocks and the majority of the water is stored within the peat itself (Grover and Baldock, 2013; Western et al., 2009). Given that most of the peat is <2 m thick, this results in a shallow reservoir of water underlain by bedrock with very low hydraulic conductivities. By contrast, groundwater in the eucalypt gullies is partially hosted in weathered regolith that is locally several metres thick. The gullies may be developed where weathering is greater due to the presence of joints and/or faults that will also host groundwater flow (Shugg, 1987). The presence of weathered and fractured bedrock on steep slopes conceivably allows long groundwater flow paths to develop that will increase transit times.

The correlation between major ion concentrations and ^3H activities may allow a first-order estimate of relative mean transit times to be made, which is useful in extending studies such as this to adjacent catchments. Caution must be exercised, however, in using the datasets as a whole as the geochemistry may partially reflect differences in the characteristics of the peatland and eucalypt forest catchments (specifically whether the water flows through the regolith or is contained within the peat) rather than solely the mean transit times. Nevertheless, in the catchments studied here there are broad correlations between ^3H activities and major ion concentrations within both the peatland water and the eucalypt forest streams, which would permit estimations of relative mean transit times.

Streamflow (Q) is related to the mean transit time (MTT) and the volume of water held in storage (V) via $Q = V / \text{MTT}$ (Maloszewski and Zuber, 1982). This relationship is commonly used to estimate V where MTT has been calculated and Q measured (e.g., Morgenstern et al., 2010). However, in ungauged peatland catchments such as these it is possible to estimate Q if the volume of peat can be estimated and MTT is known. The area drained by the stream at Falls Rocky A is $3.5 \times 10^6 \text{ m}^2$ and for a peat thickness of 0.5 to 1 m (which is consistent with observations at this site), $V = 1.75$ to $3.5 \times 10^6 \text{ m}^3$. Adopting a range of mean transit times of 0.5 to 2.5 years (Table 2) yields estimates of Q of 7.0×10^5 to $7.0 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$, which span the measured average discharge of $5.64 \times 10^5 \text{ m}^3 \text{ yr}^{-1}$. Presuming that the parameterisation is appropriate, the correspondence between calculated and observed streamflows occurs when mean transit times are < 1 year, which suggests that the ^3H activities of rainfall which recharges the peat are not significantly higher than those discussed above. Carrying out these calculations on the Victorian peatland water is difficult as Q tends to ∞ as the MTT approaches 0. In ungauged peatland catchments where mean transit times are longer, however, this would be a viable method of estimating Q .

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5. Conclusions

The mean transit times in peatland water in southeast Australia are less than 6.5 years and in many cases substantially shorter. The short mean transit times implies that the peat is susceptible to drying if there are successive years of below average rainfall. In turn this makes the peat vulnerable to damage during the periodic bushfires that also occur during the summers in drought periods. The majority of southeast Australia underwent a major drought (the “millennium drought”) between 1995 and 2010 (Bureau of Meteorology, 2016) during which time there were major bushfires in the Australian Alps, especially in 2003 and 2009. Although mainly affecting the eucalypt forests, locally these bushfires also impacted the peatlands (Arthur Rylah Institute, 2016).

The observation that the water from within the peat yields similar mean transit times to that draining the peat implies that there is not likely to be older water stored within the deeper layers. This may be because the peat in the Victorian Alps is shallow and consequently stores little water. The peatlands do not act as a long-lived store of water to the river systems. Given their small total area, there would

be little impact of peatland drying to the hydrology of the lower reaches of the adjacent catchments. However, drying of the peat could impact the hydrology of the small upland streams that form an integral part of the landscape and ecosystems of the alpine areas. The observation that even in small eucalypt forest catchments the stream water has mean transit times of several years to decades indicates that they are likely to be more resilient to short-term variations in rainfall. As a whole, the river catchments in the Victorian Alps are eucalypt dominated, which implies that the river systems are likely to be sustained by baseflow even during prolonged drought periods, and indeed many of these streams continued to flow through the millennium drought.

More generally this study illustrates that the combination of ^3H and major ion geochemistry allows both the timescales of water movement and the hydrogeochemical processes in these catchments to be understood. As noted by Western et al. (2009), there is a common perception that, due to their high water contents and organic rich soils, peatlands represent long-term water stores and indeed this was the premise that this study set out to test. However, this is not the case in this study and possibly not elsewhere. For example, the upland catchments in the United Kingdom that include extensive peat areas have transit times are <5 years (Kirchner et al., 2012; Soulsby et al., 2006; Hrachowitz et al., 2013; Benettin et al., 2015) and the Zhurucaay area in Ecuador where mean transit times are <1 year (Mosquera et al., 2016).

The study has determined transit times using individual ^3H measurements, which is possible in the southern hemisphere due to the decline of the bomb-pulse ^3H . While this removes the requirement of collecting data over several years and does not require the assumption of steady-state flow systems, it is not possible to test the appropriateness of the lumped parameter models. Differences between the mean transit times estimated from the different lumped parameter models is one of the main uncertainties, especially where the mean transit times are in excess of a few years. Uncertainties in the ^3H activities of recharge and errors caused by aggregation of water with different mean transit times also impact these calculations (as they do the calculations based on time-series data). Irrespective of these uncertainties, the fact that the relative difference in mean transit times between waters is readily calculated is valuable in understanding catchments.

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6. Data Availability

All geochemical data used in this study are contained in Table 1. Streamflow data are publicly available from the Victorian State Government Department of Environment, Land, Water and Planning (<http://data.water.vic.gov.au/monitoring.htm>).

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Author contributions. U. Morgenstern was responsible for the ^3H analyses. I. Cartwright undertook the sampling program and oversaw the analysis of the other geochemical parameters. I. Cartwright and U. Morgenstern prepared the manuscript.

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Figure Captions

Fig. 1. Location of study sites in northeast Victoria superimposed on the digital elevation model. Places: Br = Bright; Da = Dargo; MB = Mount Buffalo; MtB = Mount Beauty; MH = Mount Hotham; My = Myrtleford. FFA and FFB are the Falls Forest sampling sites A & B, other sampling sites are in the indicated study areas (see Supplementary Figure S1). Catchment boundaries from Department of Environment, Land, Water and Planning (2016), elevations are relative to the Australian Height Datum (AHD).

Fig. 2a. Streamflow at Watchbed Creek which drains peatlands at Falls Creek (Fig. 1) between 1984 and 1987. **2b.** Flow duration curves for Watchbed Creek and Simmons Creek, which drains eucalyptus forest in the Upper Ovens (Fig. 1). Data from Department of Environment, Land, Water and Planning (2016).

Fig. 3. $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ values of waters from the Australian Alps (data from Table 1) relative to the global meteoric water line (GMWL: Clark and Fritz, 1997) and the Melbourne meteoric water line (MMWL: Hughes and Crawford, 2012). Each data point represents an individual sample collected on the date indicated in Table 1. Error bars are analytical uncertainties (0.2‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$). Rainfall samples: B = Mount Buffalo multi-month samples, W = 2 week winter precipitation sample, O = other samples from southeast Australia. Dashed line (slope, s , = 5) is fit to all of the data by linear regression.

Fig. 4. ^3H activities vs $\delta^2\text{H}$ values of waters from the Australian Alps (data from Table 1). Error bars are analytical uncertainties (1‰ for $\delta^2\text{H}$ and ^3H from Table 1). Rainfall samples: B = Mount Buffalo multi-month samples, W = 2 week winter precipitation sample, O = other samples from southeast Australia. Linear regression line is fit to the multi-month Mount Buffalo samples. Arrowed lines show changes in ^3H activities and $\delta^2\text{H}$ values due to evaporation (Evap) and radioactive decay of ^3H .

Fig. 5. ^3H activities vs. Cl (5a), Na (5b), Si (5e) concentrations and Cl/Br (5c), Na/Cl (5d), Si/Cl (5f) ratios (data from Table 1). Arrowed lines illustrate trends expected from major geochemical processes. Ovens data are from the upper Ovens Valley streams in December 2013 and February 2014 (Cartwright

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and Morgenstern, 2015); the geochemistry of these larger streams is similar to the eucalypt forest streams in the Victorian Alps.

Fig. 6a. Comparison of mean transit times from different lumped parameter models, calculated using Eqs 1 to 3 assuming a ^3H activity of recharge of 3.0 TU (based on the rainfall samples). DM = Dispersion model with D_p of 0.1 and 1.0; EM = Exponential flow model; EPF = Exponential-piston flow model with EPM ratio = 0.33 and 1.0. **6b.** Mean transit times from the exponential flow model (EPM = 0.33) with ^3H activities of modern recharge ranging from 3.0 to 3.4 TU. Shaded fields show ^3H activities in the peatlands waters and eucalyptus forest streams, arrow is the median ^3H activity in the peatland waters (data from Table 1).

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Fig. 7. ^3H activities vs. catchment areas for the peatlands and eucalyptus forest catchments. Area error bars assume a $\pm 10\%$ measurement error, ^3H error bars are from the analytical uncertainties. Data from Table 1.

Fig. 8. Impact of aggregation on calculated mean transit times. Apparent mean transit times are calculated from the ^3H activities of mixtures of waters with actual mean transit times of between 10 and 50 years using the exponential-piston flow model with and EPM ratio of 0.33. Actual mean transit times are calculated from the weighted average mean transit times in the mixed water. The binary curve represents variable mixtures of the two end-members, the shaded field represents mixtures of multiple waters with mean transit times of between 10 and 50 years. The red line represents agreement between apparent and actual mean transit times.

Supplementary Material

Fig. S1. Annotated Google Earth® images of Mount Buffalo (Fig. S1a), Falls Creek (Fig. S1b), and Dargo (Fig. S1c) catchments showing extent of the peatlands and the sampled eucalypt forest catchments. Sampling site abbreviations (sites in Table 1). Fig S1a: Cres = Buffalo Cresta, Cry = Buffalo Crystal, BF = Buffalo Forest. Fig. S1b: Cope = Falls Cope, Lan = Falls Langford, Rky = Falls Rocky, FF = Falls Forest. Fig. S1c: D = Dargo, DF = Dargo Forest.

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Table 1. Geochemistry of water samples from the Australian Alps

Site ^a	Date	Area ^b	³ H	$\delta^2\text{H}$	$\delta^{18}\text{O}$	EC	Na	Mg	K	Ca	Si	Cl	Br	NO ₃	SO ₄
		km ²	TU	‰ V-SMOW	‰ V-SMOW	$\mu\text{S cm}^{-1}$	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹	mg l ⁻¹
Peatlands															
<i>Mount Buffalo</i>															
Buffalo Cresta A	26/11/2015	1.5	3.32±0.053	-26	-5.0	19.12	1.12	0.125	0.192	0.621	2.714	0.94	0.0031	0.040	0.072
Buffalo Cresta A	23/02/2015	1.5	2.84±0.058	-41	-7.7	13.72	2.06	0.125	0.168	0.645	2.831	0.95	0.0039	0.048	0.185
Buffalo Cresta B(P) ^b	23/02/2015		2.75±0.055	-41	-7.7	22.33	1.96	0.152	0.273	1.123	3.244	1.08	0.0037	0.285	0.304
Buffalo Cresta C	23/02/2015	2.1	2.75±0.056	-40	-7.5	19.92	1.06	0.121	0.160	0.432	1.632	0.95	0.0036	0.063	0.080
Buffalo Cresta D(P)	26/11/2015		2.70±0.048	-37	-7.3	15.21	1.79	0.131	0.184	0.653	2.601	1.14	0.0038	0.073	0.194
Buffalo Crystal A	23/02/2015	3.5	2.74±0.055	-35	-6.6	12.01	1.97	0.153	0.178	0.684	2.031	1.01	0.0038	0.066	0.207
Buffalo Crystal B	23/02/2015	0.2	2.93±0.058	-30	-5.7	12.65	2.06	0.130	0.250	0.354	3.466	0.99	0.0037	0.320	0.245
<i>Falls Creek</i>															
Falls Cope	24/02/2015	1.9	3.14±0.061	-41	-7.2	9.62	0.92	0.247	0.119	0.519	1.417	0.47	0.0031	0.084	0.076
Falls Langford A	24/02/2015	0.5	3.10±0.060	-39	-7.1	21.42	1.43	0.512	0.203	0.882	2.496	0.64	0.0035	0.250	0.271
Falls Langford B(P)	24/02/2015		2.98±0.059	-43	-8.3	8.52	0.88	0.223	0.160	0.490	0.812	0.70	0.0033	0.165	0.167
Falls Rocky A	24/02/2015	3.5	2.96±0.059	-42	-8.0	7.65	0.79	0.194	0.057	0.463	1.097	0.55	0.0026	0.307	0.111
Falls Rocky A	25/11/2015	3.5	2.90±0.050	-42	-8.1	11.25	0.78	0.149	0.075	0.318	2.103	0.51	0.0018	0.164	0.163
Falls Rocky B(P)	25/11/2015		2.86±0.049	-42	-8.2	7.47	0.62	0.136	0.118	0.255	1.029	0.54	0.0023	0.035	0.130
Falls Rocky C(P)	25/11/2015		3.17±0.055	-35	-6.5	9.54	0.79	0.257	0.245	0.540	1.125	0.51	0.0025	2.097	0.185
Falls Rocky D	25/11/2015	2.6	3.14±0.059	-33	-6.5	16.47	1.04	0.227	0.223	0.403	1.113	0.93	0.0033	0.087	0.079
<i>Dargo</i>															
Dargo A	25/11/2015	5.5	2.84±0.048	-40	-7.7	21.17	1.15	0.930	0.133	1.427	3.259	1.10	0.0040	0.804	0.142
Dargo B	25/11/2015	1.2	2.69±0.043	-43	-8.1	31.9	1.34	1.381	0.334	2.112	2.147	0.91	0.0038	0.493	0.050
Dargo C(P)	25/11/2015		2.47±0.040	-39	-7.0	29.2	1.56	1.667	0.308	1.900	3.012	0.93	0.0038	0.388	0.063
Dargo D	25/11/2015	2.7	3.36±0.053	-35	-6.9	13.9	0.77	0.343	0.097	1.095	2.788	0.83	0.0025	1.845	0.192

Eucalypt Forest															
Buffalo Forest A	24/02/2015	3.3	2.21±0.048	-35	-6.3	42.7	3.89	2.056	0.618	1.727	4.433	1.16	0.0045	0.052	0.740
Buffalo Forest A	26/11/2015	3.3	2.35±0.042	-34	-6.4	39.5	3.27	1.878	0.470	1.536	4.844	1.30	0.0048	0.038	0.763
Falls Forest A	24/02/2015	3.3	1.56±0.037	-38	-7.4	65.2	5.70	3.230	0.543	3.686	5.060	2.60	0.0097	0.104	0.499
Falls Forest B	24/02/2015	1.5	2.10±0.047	-37	-7.5	45.7	3.24	2.092	0.445	2.149	4.233	1.09	0.0045	0.038	0.608
Falls Forest C	25/11/2015	6.4	2.26±0.040	-31	-6.2	45.3	3.41	1.855	0.566	1.623	6.236	1.20	0.0048	0.418	0.901
Falls Forest D	25/11/2015	5.8	1.70±0.035	-37	-7.3	56.0	4.78	2.793	0.400	3.092	9.540	1.22	0.0045	0.022	0.581
Dargo Forest A	25/11/2015	6.1	2.00±0.036	-29	-5.7	44.1	4.12	1.898	0.542	1.654	5.328	1.24	0.0045	0.240	0.408
Rainfall															
Buffalo	Feb 2015 (12) ^d		2.85±0.057	-36	-7.0	11.58	0.68	0.011	0.058	0.214	0.081	0.98	0.0039	0.015	0.081
Buffalo	Nov 2015 (9)		2.88±0.051	-35	-6.5	12.20	0.53	0.117	0.108	0.361	0.077	0.80	0.0028	0.106	0.171
Buffalo	Dec 2013 (17)		2.99±0.046	-38	-7.3		0.87					1.10			
Buffalo	Feb 2014 (2)		2.90±0.049	-37	-7.1										
Buffalo	Jul 2014 (<1)		2.52±0.043	-40	-7.9										
Buffalo	Sep 2014 (3)		2.71±0.044	-34	-6.8										
Melbourne ^e	Jul 2013 (12)		2.72±0.045	-33	-6.3										
Otways ^e	Sep 2014 (6)		2.45±0.041	-22	-4.4										
Latrobe ^e	Aug 2015 (12)		2.76±0.043	-36	-6.8										

Notes: ^a Sampling regions on Fig. 1; ^b Catchment area; ^c P = Piezometer sample; ^d Month collected and number of months represented by the sample; ^e Other rainfall from SE Australia. The rainfall samples represent aggregated samples collected over the number of months indicated, all other samples are individual samples.

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Table 2. Calculated mean transit times

Site ^a	Date	Mean Transit Time (yrs)							
		<u>LPM</u> ^b	EPM (3.4) ^c	EPM (3.2)	EPM (3.0)	EPM (3.4)	EM (3.4)	DM (3.4)	DM (3.4)
Parameter ^d		<u>0.3</u>	<u>0.3</u>	<u>0.3</u>	<u>1</u>			<u>0.1</u>	<u>1</u>
Peatlands									
<i>Mount Buffalo</i>									
Buffalo Cresta A	26/11/2015	<1	ND ^c	ND	<u><1</u>	<u><1</u>	<u><1</u>	<u><1</u>	<u><1</u>
Buffalo Cresta A	23/02/2015	3.4	2.2	1.0	<u>3.3</u>	<u>3.5</u>	<u>2.7</u>	<u>4.0</u>	<u>4.0</u>
Buffalo Cresta B(P)	23/02/2015	4.1	2.9	1.6	<u>3.9</u>	<u>4.4</u>	<u>3.9</u>	<u>4.9</u>	<u>4.9</u>
Buffalo Cresta C	23/02/2015	4.1	2.9	1.6	<u>3.9</u>	<u>4.4</u>	<u>3.9</u>	<u>4.9</u>	<u>4.9</u>
Buffalo Cresta D(P)	26/11/2015	4.4	3.2	1.9	<u>4.2</u>	<u>4.8</u>	<u>4.2</u>	<u>5.4</u>	<u>5.4</u>
Buffalo Crystal A	23/02/2015	4.2	3.0	1.7	<u>3.9</u>	<u>4.4</u>	<u>3.9</u>	<u>5.3</u>	<u>5.3</u>
Buffalo Crystal B	23/02/2015	2.8	1.6	<1	<u>2.7</u>	<u>2.9</u>	<u>2.8</u>	<u>3.3</u>	<u>3.3</u>
<i>Falls Creek</i>									
Falls Cope	24/02/2015	1.4	<1	ND	<u>1.4</u>	<u>1.5</u>	<u>1.4</u>	<u>1.5</u>	<u>1.5</u>
Falls Langford A	24/02/2015	1.7	<1	ND	<u>1.7</u>	<u>1.7</u>	<u>1.7</u>	<u>1.9</u>	<u>1.9</u>
Falls Langford B(P)	24/02/2015	2.4	1.3	<1	<u>2.4</u>	<u>2.5</u>	<u>2.4</u>	<u>2.9</u>	<u>2.9</u>
Falls Rocky A	24/02/2015	2.6	1.4	<1	<u>2.5</u>	<u>2.7</u>	<u>2.5</u>	<u>3.0</u>	<u>3.0</u>
Falls Rocky A	25/11/2015	3.0	1.8	<1	<u>2.9</u>	<u>3.1</u>	<u>2.9</u>	<u>3.5</u>	<u>3.5</u>
Falls Rocky B(P)	25/11/2015	3.3	2.1	<1	<u>3.2</u>	<u>3.5</u>	<u>3.2</u>	<u>3.9</u>	<u>3.9</u>
Falls Rocky C(P)	25/11/2015	1.3	<1	ND	<u>1.3</u>	<u>1.3</u>	<u>1.3</u>	<u>1.4</u>	<u>1.4</u>
Falls Rocky D	25/11/2015	1.4	<1	ND	<u>1.4</u>	<u>1.5</u>	<u>1.4</u>	<u>1.5</u>	<u>1.5</u>
<i>Dargo</i>									
Dargo A	25/11/2015	3.4	2.2	1.0	<u>3.3</u>	<u>3.6</u>	<u>3.2</u>	<u>4.0</u>	<u>4.0</u>
Dargo B	25/11/2015	4.5	3.3	2.0	<u>4.3</u>	<u>4.9</u>	<u>4.3</u>	<u>5.6</u>	<u>5.6</u>
<u>5.2</u> Dargo C(P)	25/11/2015	6.5	5.4	4.0	<u>6.0</u>	<u>7.4</u>	<u>6.0</u>	<u>8.0</u>	<u>8.0</u>

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Dargo D	25/11/2015	<1	ND	ND	<1	<1	<1	<1
<i>Eucalypt Forest</i>								
Falls Forest A	24/02/2015	28.9	28.8	28.6	<u>26.0</u>	<u>39.0</u>	<u>37.2</u>	<u>40.2</u>
Falls Forest B	24/02/2015	11.5	10.8	9.6	<u>9.9</u>	<u>16.4</u>	<u>10.0</u>	<u>17.7</u>
Buffalo Forest A	24/02/2015	9.7	8.8	7.5	<u>8.7</u>	<u>13.0</u>	<u>8.6</u>	<u>14.7</u>
Falls Forest C	25/11/2015	9.1	8.1	6.6	<u>8.0</u>	<u>11.3</u>	<u>7.9</u>	<u>13.2</u>
Falls Forest D	25/11/2015	22.6	22.2	21.6	<u>17.2</u>	<u>30.7</u>	<u>16.7</u>	<u>31.4</u>
Dargo Forest A	25/11/2015	14.0	12.4	11.2	<u>11.3</u>	<u>18.8</u>	<u>11.1</u>	<u>19.6</u>
Buffalo Forest A	26/11/2015	7.8	6.9	5.3	<u>7.0</u>	<u>9.4</u>	<u>7.0</u>	<u>10.8</u>

^a Sites on Fig. 1 as Supplementary Figure S1

^b Lumped parameter model (DM = Dispersion model; EM = Exponential flow model; EPF = Exponential-piston flow model)

^c Assumed ³H activity of modern recharge in brackets

^d EMP or D_p parameter

^e Not determined as ³H activity higher than assumed value of recharge

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