Review of: Using groundwater age to understand sources and dynamics of nutrient contamination through the catchment into Lake Rotorua, New Zealand
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We wish to thank the reviewers for their very thorough and insightful comments demonstrating excellent choice of reviewers with expertise in the local hydrogeology, hydrochemistry, and age tracer interpretation. The comments have helped us to improve the manuscript significantly.

Response to comments by reviewer 1:

General Comments: This article concerns the transit time and hydrochemistry of groundwater within the highly sensitive Rotorua Lake Catchment within the Taupo Volcanic Zone of New Zealand. Through the application of high resolution age dating, multivariate statistical analysis (HCA), hydrochemistry and hydrogeology a cogent picture of the controls over the two key limiting nutrients (N and P) to Lake Rotorua are provided thereby providing a strong framework for future management of the Lake.
We wish to thank the reviewer for these encouraging words.

Overall I find the sampling protocols, the number of samples and the use of historical data to be more than adequate. The quality of the interpretative methods are also well established and referenced, although **I would like to see some comment (background) provided as to the reasons for the differences in hydrochemical facies (lava, ignimbrite and lacustrine "Huka" type)**. Some explanation of the mechanisms responsible for the differing hydrochemical signatures would seem relevant given the significance placed on the hydrochemical facies as a means of discriminating recharge area and inferring flowpaths. Furthermore, although I agree that denitrification is likely to be minimal I feel the use of **absolute phrases such as '..absence of electron donors..'** to be inappropriate (please see explanation in marked up text). Although a minor issue I think the removal of 'absolute' statements would help improve the manuscript. **Clarification of the age dating methods** used and a **more hydrogeologically focused geology section** would improve the manuscript (please see below).

We agree with the reviewer that some explanation of the mechanisms responsible for the differing hydrochemical signatures would be relevant and we had looked into this aspect already before submission of the manuscript. However, very little is known currently about this aspect. We have not found any useful references, nor have we established a suitable theory sufficiently advanced to be discussed in this paper. Reviewer 2 had similar comments regarding the correlations between groundwater age and pH and hydrochemistry. We believe that our findings will shed new light into the processes that control the hydrochemistry reaction rates in the various geologic units, and stimulate new research in in this topical issue within the hydrochemical community. We have made the following amendment to the text:

…In rhyolite lava formations, geochemical reactions lead to increased pH, Si, and F in groundwater significantly faster than in ignimbrite, indicating higher reaction rates for dissolution of these elements from lava formations. While this is important for understanding water-rock interaction, we do not yet have sufficient information on the lithogeochemistry to develop a mechanistic understanding of the reaction processes.

In regards to the ‘absolute phrases’, we agree with the reviewer and have changed these (see minor comments).

In regards to the age dating methods, these are described sufficiently in Morgenstern and Daughney 2012, and references therein. A summary is given in section 3.1., without causing too much duplication.

In regards to ‘a more hydrogeologically focused geology section’, we believe we have summarised all of the available and necessary context, starting in the Geology section with the description of the geologic units and the eruption history that controls the sequence of the geologic units, and in the Hydrogeology section all available information about the geometry and hydraulic properties of the significant units. To cover knowledge gaps, we ‘make insightful inferences from results about the hydrogeology’ as noted by reviewer 2.

The combination of groundwater (baseflow, spring) age and hydrochemistry provides important insights into the origin and likely transit times for N and P to Lake Rotorua. The discovery of a dominantly geogenic source of P to the Lake is highly significant in terms of lake management. Specifically, the land use interventions for minimising N versus P loss may be very different. Furthermore, the identification of a considerable time lag and that a large proportion of the groundwater (baseflow and springs) feeding the lake was recharged prior to intensification is a key finding.

In short and subject to the Editors considerations, I recommend the acceptance of this manuscript subject to the few minor comments raised above and within the marked up manuscript as I believe it provides a high quality and cogent argument for the groundwater and nutrient delivery dynamics of the Rotorua Catchment and fits within the aims of HESS.

Again, we thank the reviewer for these encouraging words.

Minor comments marked within the text:

P9908 L01: Is the use of the term continuously accurate? Has there been a monotonic decline in water quality metrics or stepped change?

The trend is not perfectly monotonic, therefore we changed to:

The water quality of Lake Rotorua has steadily declined…

P9908 L26-28: recommend.. ' absence of 'bioavailable' or 'metabolisable' electron donors along flow paths.

We changed to:

…indicating absence of bioavailable electron donors along flow paths that could facilitate…

P9909 L 11: Is it useful to include a comment that nitrate loads to the lake are likely to double etc over x time period?

We amended accordingly:

About half of the currently discharging water is still pristine old water, and after this old water is completely displaced by water affected by land use, the nitrogen load of Hamurana Stream will approximately double.

P9909 L23: Reference or data source required.

We amended accordingly:

We measured nitrate concentrations of 6-10 mg/L NO_3-N in three young groundwater samples under dairy farms in the SE catchment.

P9912 L5: Reference

We believe there is no reference for this. We have amended the text for better explanation:

…after WWII; water recharged before this post-war upsurge in intensive agriculture has low tritium and low nitrate concentrations.

P9928 L21: we inferr. "the thin nature..." Inference so please note. However, the reviewer has seen many examples within the TVZ/Rotorua area where the thinning of lacustrine (Huka type) sediments above lava domes or stratigraphic highs results in outflows or hydrothermal fluids or meteoric waters.

Text changed accordingly: …lake shore; we infer that the thin nature…

We have not been able to trace such a reference.

P9929 L1: lava domes within the TVZ commonly act as conduits for cold water inflows or geothermal fluid upflows. Domes also provide cross stratal pathways for fluid flow by 'bridging' confining layers (Huka type sediments) so this reasoning seems sound.

Text amended accordingly:

The small lava feature may be fractured, discontinuous, or act as a water conduit, allowing water discharge from the ignimbrite behind.

P9930 L1-2: Microbial populations for reduction reactions are ubiquitous but perhaps in this instance are limited by the availability of metabolisable e-donor. Hence, I think some caution is required regarding absolute statements such as: "...absence of microbial reduction reactions..." on the basis of DO alone. Further, although the data is sparse I note that values as low as 5 mg/L D.O. suggest there has already been some reductive removal?? (May have occured prior to infiltration)? Also, from Fig. 6a it appears that the youngest waters from the ignimbrite and lava units have lower DO than older waters of the same hydrochemical facies. This is difficult to reconcile if it is a meaningful trend - I suspect there are some other complexities.

We agree microbial populations are ubiquitous but reduction reactions are insignificant in this geologic formation. We changed our statement accordingly:

… indicating microbial reduction reactions are insignificant in this volcanic aquifer

We also agree that DO significantly below 5mg/L indicates that oxygen has been removed to some degree, and that this probably occurred prior to infiltration, during passage through the soil. We point this out at a later stage.

In regards to increasing DO for the ignimbrite data, we feel the data doesn't allow deducing such a trend as significant.

P9930 L10: Agree with overall interpretation but just cautious of being 'absolute' - e.g. "....no potential.." might be better replaced by "..limited potential.."

Changed accordingly:

No trend of decreasing DO with increasing groundwater age was observed, suggesting absence of significant amounts…

P9930 L15-19: Interesting to note an increase in DO as waters get older? How is this explained?

As explained above, we don't think the data is sufficient to identify such a trend as significant.

P9931 L27-28: Just a comment: I wonder if deeper seated diffuse degassing of magamatic volatiles (esp. CO2) into shallow GW systems of the TVZ influence the relationship between alk. and GW age?

P9932 L16: Bicarbonate may be derived from diffuse degassing - d13C or other may be of use here. I note Chiodini et al., studied the input of magmatic CO2 to the regional aquifer systems of Italy and discriminated significant input across a broad region - why not also the TVZ? As we know, CO2 is a vapour phase constituent that becomes decoupled from mineralised (alklai-Cl) parent fluids (Na, F, etc) and dissolves into shallow, overlying meteoric aquifers.

These are interesting thoughts. However, while it is worth mentioning the increasing concentration of bicarbonate with groundwater age as observed for other rock-forming elements, it is beyond the scope of this paper to differentiate between the various sources of carbon.

P9934 L17-19: I'd think about referencing a land-use change report here.

Text amended: …increased conversions to dairy farming during the 1980s and 1990s (Rutherford et al., 2011).

P9935 L8-12: This observation is consistent with a high P-retention scores for ashfall (allophanic/imogolite(proto-imogolite)) soils and thick vadose zones across this region which would be very efficient at buffering P loss. Very different to coarse alluvial or peat aquifer systems with thin vadose zones where direct-P leaching from fert is more likely.

This is a good confirmation of our finding and we amended the text accordingly:

This finding is consistent with the usually high P-retention scores for ashfall soils and thick unsaturated zones across this region, which are very efficient at buffering P loss. P-retention in soils was also observed in the New Zealand National Groundwater Monitoring Programme across other soil types (Morgenstern and Daughney, 2012).

P9936 L1: emotive?

We stayed with this term. Merriam Webster defines insidious as "developing so gradually as to be well established before becoming apparent" and this seems to describe the groundwater contamination well.

P9939 L14-18: Again, ..'..absence of electron donors.." is perhaps not the best phrase? Unless you truly believe there is little if any reduced Fe mineral, clays or organic matter? I'd be more inclined to say limited electron donor abundance or at least negligible bio-available e-donors.

Changed accordingly:

…absence of significant microbial reactions due to limitation of electron donors in the aquifer…

Response to comments by reviewer 2:

Paper Summary:
This paper uses estimates of groundwater age to make inferences about the sources and timing of different chemical determinands entering Lake Rotorua, New Zealand, with a focus on nutrients associated with lake eutrophication. The authors assembled an impressive isotopic and hydrochemical dataset spanning several decades from streams, springs, and wells throughout the lake region. They use hierarchical cluster analysis (HCA) to map three geographical clusters - lava, ignimbrite, and sediment - with similar hydrochemisty. They assume a binary mixing model of age distribution of natural environmental tracers (primarily tritium) to estimate the mean residence time (MRT) at sample points, and they highlight interesting associations between MRT and streamwater chemistry in different clusters. They use their deep expertise in the regional geology to make insightful inferences from results about the hydrogeology. Finally, they present estimates of future nitrate loading to the lake based on their fitted age distributions and the fraction of water that is yet to be released since land-use intensification. Important new reported findings include (1) oxic conditions in the groundwater and (2) a link between the main recharge areas in the Mamaku ignimbrite and groundwater discharge into the lake.
In addition to the reviewer's comment, we believe that the important new reported findings also include: source of nutrients (anthropogenic versus geologic); large lag time with detailed age distribution, and prediction of future nutrient loads.

General Comments:
This paper is a good case study in the application of tracer methods and hydrochemical data to relate groundwater age to a common water quality management challenge. I believe it has the potential to merit publication in HESS subject to major revisions related to the study methods, contributions, and data analysis. I discuss each below in sequence.

Study methods:
The major findings of the paper hinge on the validity of the HCA analysis and the MRT estimates. As such, I believe the paper should elaborate on the methods and limitations of these techniques. Starting with HCA, the authors report using Ward's linking rule to partition the samples into four groups (page 9927, line 17-19). I believe that additional details and references on the method would help readers both relatively familiar with HCA and relatively unfamiliar (myself included). Particular points to include would be (1) on what basis are the clusters identified, (2) what human judgment was required in doing the clustering, and (3) what statistical measures can be provided to help the reader judge the significance of the clustering. Finally, for clarity, I would recommend moving discussion of HCA methods out of the Results and Discussion section and into the Methods section of the paper.

The HCA method with all details and relevant assumptions has been described in a separate paper which is dedicated especially to the HCA analysis: Donath et al. (2014, under review) and references therein. This paper provides all of the detail about how HCA was conducted, and so this information does not need to be reproduced in the present article. For this reason, and to keep the focus of this paper on the age tracer method, HCA was not included in the methods section of this manuscript. As this paper is still under review, we provide a pdf of the manuscript.

Related to the MRT estimate, I believe the paper needs more compelling justification for its selection of the binary mixing model. I think the authors should strengthen the reasons given for using the binary mixing model (discussed below) and/or add additional reasons.

* Model fit: The binary mixing model was selected in part because it matched the data (page 9922, line 18-25). This would be more meaningful if shown in the context of model complexity (i.e., with some statistical measure that accounts for degrees of freedom). I am concerned that the goodness of fit may mean little when applying a 5- parameter model to explain just 4 to 10 observations (as seems to be the case based on the number of samples shown in Figures 3 and 4).

In the following we strengthen the reason for the choice of the binary mixing model. We agree in principal with the reviewer's comment that for part of the sites a five-parameter model is an over-fit. However, at least ten sites have sufficient tritium time series data to demonstrate that a simple two-parameter model (e.g., EPM, DM) cannot fit the stream data. A two-parameter model would be an over-simplification of the more complex hydrogeological situation of the Lake Rotorua volcanic aquifers. We have added: The complex volcanic aquifers of the Lake Rotorua catchment, which have evolved through volcanic activity, require a more complex system response function. A combination of two exponential piston flow models was used.

The binary mixing model is frequently used as system response function, and is justified in the Rotorua volcanic aquifers by the presence of shallow young and deep old groundwater discharges. It is true that most of the sites have insufficient data and do not allow calibration of all five parameters. However, some sites have sufficient data (Figs. 3 and 4) to justify a binary model with a young and an old age distribution. We then consistently applied the mixing parameters, calibrated for these sites, to all the sites, and vary only two parameters, the mean residence times of the young and the old water, to match the measured data. We think this is the most sensible approach, and increasing MRT with decreasing TU shows that the model assumptions are sensible. One has to also keep in mind that very little is known about mixing parameters; very few tritium time series data covering the passage of the bomb tritium exist internationally, and the presented data from Lake Rotorua are among the highest quality data that are available.

* Model structure: The authors argue that the binary mixing model is consistent with the fact that the aquifer has both deep and shallow aquifers (page 9922, line 18-25). This point seems to be contradicted by their earlier assertion that the complexity of the aquifer precludes horizontal-layer-based modeling (page 9918, line 24). The authors should resolve this apparent discrepancy. Further, the paper should make a more compelling argument for using a different model than they applied in all the rest of New Zealand (see Page 9925, line 15-17). One way to do this would be to demonstrate that the Lake Rotorua geology is an outlier when compared with the rest of the country.

We do not see a conflict in regards to the horizontal layers. We state: … precluding a simple horizontal layer based model. We added:
… precluding a simple horizontal-layer-based succession model throughout the catchment usually applicable in sedimentary basins.

We have made clear in the text that the Lake Rotorua geology is an outlier due to its evolution through complex volcanism.

* Hydrochemical validation: The paper points out that the good trends between MRT estimates and hydrochemistry are an indication of robust age estimates (page 9932, line 28-29). I also find this somewhat compelling, but the trends themselves are not necessarily what one might expect for all clusters. Further, this point raises the question about whether the paper is using groundwater age to test hypotheses about sources, or the other way around. Therefore despite the good trends observed, I think the other concerns raised here about model selection still need addressing.

We agree with the comment that he good trends between MRT and hydrochemistry are compelling. However, to avoid circular arguments, we have toned this statement down to: Good trends of hydrochemistry versus groundwater age may be an indirect indication of robust age interpretations.

Recognizing that the choice of age distribution model may be somewhat subjective, I also think the paper needs more thoughtful discussion on the possible equifinality of different model structures and parameter sets. This would help give the reader a sense of how robust their MRT estimates are to changes in model parameterization and selection. For parameterization, this could involve finding the parameter sets that fit the data equally well (in a statistical sense) and reporting the distribution of MRTs that they predict. For model structure, this could involve comparing the MRT estimates for the common models that the authors have already considered (e.g., binary, exponential piston, and dispersion). If these factors were taken into account in the MRT error estimates presented by the authors (beginning page 9925, line 27), that should be made explicit, along with whatever other factors included in those error estimates.

This issue is addressed above in our comment regarding the model structure.

Contributions:

The scientific contributions of the paper to the literature should be more clear. Much of the discussion of nutrients (the titular focus of the paper) in the abstract, section 4, and the conclusion seems to reach qualitatively similar conclusions about lag times and future predictions as those attributed in the introduction (page 9909, line 19) to Morgenstern at al 2006. I assume this work represents some expansion or independent confirmation of previous findings, but their exact nature should be more apparent. The paper does highlight two seemingly noteworthy discoveries: evidence of the link between recharge in the Mamaku ignimbrite and main groundwater discharges to the lake, and the high DO levels in the groundwater (with its implications for denitrification). If these or other findings are deemed to be the main contribution of the paper, they should be better established as important and unanswered research questions in the introduction. For example, the conclusion makes an uncited reference to “longstanding controversies” about the connectivity between the recharge areas and the lakeside springs (page 9938, line 25). These controversies should be described in the introduction through literature review to help the reader grasp the importance of the findings and the weight of the new evidence vis a vis previous findings.

It is correct that the findings of this manuscript are an expansion of the Morgenstern et al. 2006 report. Note that this is only an internal company report and that these findings have not been published yet.
We believe that the findings of this paper for HESS have been made apparent in the conclusion and in the abstract sections, including origin of groundwater discharges (ignimbrite, lava, sediment); origin of N and P (anthropogenic versus geologic); large lag time; only insignificant denitrification must be expected even during such long travel times; prediction of future N load. Reviewer 1 commented favourably on our findings: …cogent picture of the controls over the two key limiting nutrients (N and P) to Lake Rotorua are provided thereby providing a strong framework for future management of the Lake.
In regards to "longstanding controversies", we have added the references accordingly.

Data Analysis:
In general the presentation and interpretation of the data presented is very insightful. There were however two seemingly important discrepancies or oversights in the analysis that should be addressed.

First is the geographic proximity of different hydrochemistry clusters in Figure 5. To the north of the lake we see relatively close sediment/ignimbrite sample locations. To the east of the Ngongotaha lava dome we see relatively close sediment/ignimbrite and sediment/lava formations. These should be explained in the discussion. Based on Figure 1 I guess they may represent different water sources (i.e., spring, stream, or well). In that case, it would helpful to give the sample site indicators in Figure 5 different shapes (i.e., square, circle, diamond) according to the water source type.

The reviewer has highlighted that a compact and clear summary of the drainage pattern as derived from the geographic proximity of the hydrochemistry clusters is missing. The drainage patterns are explained in detail in section 4.2. We have amended/added the following text to the conclusion section:
After long-standing controversies (e.g. White et al., 2004; Rutherford et al., 2011), hierarchical cluster analysis of the water chemistry parameters has provided evidence about the recharge areas and hydraulic connections of the large springs near the northern shore of Lake Rotorua. Streams and shallow wells that gain most of their flow and recharge within the lacustrine sediments display a characteristic hydrochemical signature. Hydrochemistry of the water draining the Ngongotaha lava dome also has a characteristic signature due to interaction with lava formations. Only where the lava dome intercepts the paleo-lake sediments is the groundwater flow from the lava formation forced to the surface due to the low permeability of the sediments. The water from the ignimbrite also displays a characteristic hydrochemical signature. Similarly to the discharges from the lava formation, the water from the ignimbrite discharges near the intercept of the ignimbrite formation with the paleo-lake sediments, indicating the groundwater flow from the ignimbrite is forced to the surface due to the low permeability of the sediments. The largest springs, discharging in the north-west of the lake, emerge close to the lake shore within the sediment area, but the ignimbrite signature of these water discharges implies that these springs drain the Mamaku ignimbrite plateau, which has negligible surface runoff, through the lake sediment layers in slope areas where the sediments are thinner and weaker.

There is no correlation between water source (i.e., spring, stream, or well) and water type (HCA cluster). Therefore we decided to keep this figure as simple as possible. Interested readers are able to trace the water source via Fig. 1.

Second is the “other” cluster category graphed in Figure 8. I could not find any identifying information about “other”, despite the fact that is constitutes most of the “young” water with high nitrate concentrations. If we just consider the three clusters discussed in the paper, then the relationship between nitrate and MRT is much less dramatic, and possibly the opposite of what might be expected in the sediment cluster. Therefore the authors should clarify the meaning of “other” and add interpretations of the nitrate results for each of the cluster categories individually, as they have done for the other species. If the “other” category are the samples influenced by geothermal activity that were excluded from their analysis (page 9931, line 11-13) then the authors should justify why they include it here and why it seems to show the highest sensitivity to MRT.

Thanks to the reviewer for identifying that the explanation for ‘other’ had gone missing. We have added the following text which explains the points raised by the reviewer:

Fig. 8 also includes data (labelled 'other') from the sites in the Lake Rotorua catchment that could not be assigned to one of the HCA clusters because these sites had not been analysed for the full suite of hydrochemical parameters required for input into HCA. In several surveys only nitrate was measured to obtain higher spatial resolution in nitrate distribution. The analysis of all hydrochemical parameters, as required for HCA, was mainly undertaken at the large discharges into the lake that contain old water, and only few of these sites contain water young enough to show the impact of recent land use intensification. Therefore the ‘other’ samples were added to Fig. 8 to better represent younger waters. In addition, samples from the eastern catchment having a geothermal signature are also included in the cluster ‘other’. The geothermal influence is minimal and does not affect the nitrate signature, and hence does not bias the display of results in Fig. 8.

Adding interpretations of the nitrate results for each of the cluster categories individually would not be sensible because only little dairy farming occurred near the lake shore in the sediment formation, and no dairy farming at all at the Ngongotaha lava dome from which all the lava cluster samples originate. This would bias the result.

Minor comments:

Page 9921, line 11-14. The sentence starting “This method is: : :” is not clear. Consider rewording.

Text amended:

…This method is particularly useful for interpretation of ages of groundwater in the Lake Rotorua catchment where most of the groundwater discharges lack any other information on mixing of groundwater with varying flow path lengths and of different age such as ratio of confined to unconfined flow volume, or screen depth for wells.

Page 9921, line 23-25. The authors should specify whether the scaling factor is empirically derived or calibrated (and if so, to what).

Text amended:

… factor of 0.87 to account for variation in atmospheric tritium concentrations due to latitude and orographic factors as deduced from measurements from rain at various locations in New Zealand (e.g. Morgenstern et al., 2010).

Page 9922, line 13. The authors should explain the importance of the 0.4 TU threshold, which isn't clear from the context.

Text amended:

…the data for Hamurana water intake spring (blue in Fig. 3) are all below 0.4 TU which is below the detection limit of many tritium laboratories (http://www-naweb.iaea.org/napc/ih/IHS_programme_ihl_tric.html)

Page 9922, line 27 – The authors should give a sense of how many samples were collected at each site. Figure 4 suggests it is on the order of 3-4 samples per site. If this represents typical values, it suggests that the five-parameter binary mixing model may be overfitting the data, and that inferences based on that model may be suspect. (See also related discussion in the General Comments section.)

Text amended:

…sampled multiple times near the inflow into the lake, typically 3-4 times (Figs. 3 and 4).

In regards to over-fitting, refer to models section in the major comments above.

Page 9926, line 10-11. The authors should consider showing some examples of the match between the CFC and SF6 results. While they say that CFC and SF6 samples were used, it's not clear exactly if or how their use differed from the tritium.

The focus of this study is on surface water discharges. Therefore the gas tracers CFCs and SF6 play a minor role in this study because they are not suitable for water dating in these streams and rivers. This is outlined on P.9911 L16-20. Further, the gas tracer ages in groundwater indicate travel time through the saturated zone only. With the large unsaturated zones in the Lake Rotorua catchment, large differences between tritium and gas ages are expected. Differentiating between tritium and gas ages is not the subject of this study, therefore only a reference is given that includes the data and age interpretations (Morgenstern et al., 2004). We have added the following paragraph which summarises the results that are relevant to this study.

Substantial fractions of that long residence time in the groundwater system may occur during passage through the thick unsaturated zones (50 – 100 m) as indicated by CFC and SF_6 results measured at groundwater wells and springs (Morgenstern et al., 2004). CFCs and SF_6 in groundwater are still exchanged with the atmosphere during passage through the unsaturated zone, therefore CFC and SF_6 ages represent travel time through the saturated zone only. Large observed differences between CFC and SF_6 ages, compared to tritium ages of up to 40 years and greater for the older waters, therefore indicate travel time of the groundwater through the unsaturated zone of >40 years for the older groundwater discharges.

Page 9925, line 18-27. This section is repeating what was already said in page 9922 line 16-25 and page 9921 line 11-17, with very similar phrasing. Suggesting combing all this information into a single part of the methods section.

According to the reviewer comments, these sections have been streamlined, with duplications removed and the relevant information re-arranged to the relevant sections.
page 9921 line 11-17 The duplication has been removed from this part:
~~The exponential piston flow model was used because, with its age distribution, it has produced good matches to most (about a hundred) tritium time series data from springs and wells throughout New Zealand, including all hydrogeological situations (Morgenstern and Daughney, 2012).~~
page 9922 line 16-25 The part relevant to the method section has been extended accordingly, and the duplication has been removed.
Throughout New Zealand, for springs and wells in almost all hydrogeological situations, the exponential piston flow model, with its age distribution, has produced good matches to most (about a hundred) tritium time series data. It was not, however, possible to obtain adequate matches in the ignimbrite area of the Rotorua catchment using such a simple exponential piston flow model. Alternatively, using the dispersion model did not improve the matches. The complex volcanic aquifers of the Lake Rotorua catchment, which have evolved through volcanic activity, require a more complex system response function. ~~However, using a binary mixing model of parallel contribution from two expo nential piston flow models resulted in excellent matches. We justify this binary mixing model by inferring two different flow contributions in the catchment to the stream and spring flow, mainly from deep old groundwater, and a contribution from younger groundwater from shallow aquifers, as indicated by very deep groundwater tables in the area (generally> 50 m) but at the same time also minor stream flows maintained by shallow aquifers.~~
Page 9925, line 18-27. This section was retained, containing the results.

Page 9925, line 26-27 and onto next page. The authors should elaborate on how they determined their error calculations. (See also related discussion in the General Comments section.)

We have amended this section to the error sources considered in this estimate:

…For the MRTs, errors caused by our tritium measurement error and uncertainty in tritium input are typically…

Page 9926, line 12-13. The authors should explain the importance of the 0.4 TU threshold, which isn't clear from the context.

This is now explained in comment above (Page 9922, line 13)

Page 9927, line 13-15 (and more broadly). The presentation would be more clear if the statistical and graphical techniques applied to the data were introduced in the methods section. (See also related discussion in the General Comments section.)

The HCA method with all details and relevant assumptions has been described in a companion paper which is dedicated to the HCA analysis: Donath et al. (2014, under review) and references therein. For this reason, and to keep the focus of this paper on the age tracer method, HCA was not included in the methods section of this manuscript.

Page 9930, line 16-17. It's not clear what the authors mean by "Constant DO of between 50 and 100% in very young and old groundwater: : :".

This has been amended for better clarification:

… Absence of a trend of decreasing DO with increasing groundwater age, but rather constant DO in very young and old groundwater of between 50 and 100%...

Page 9930, line 23 and onto next page. It would be interesting to elaborate on possible reasons for the different relationships observed between age and pH.

Yes it would be interesting to elaborate on the relationship between age and pH. However, we have not yet found a reason for these relationships. Similar relationships we describe in Morgenstern and Daughney (2012). This is a very interesting topic and we are certain that this subject will be picked up by fellow hydrochemists, or in one of our separate investigations that specifically deals with the relationship between groundwater age and hydrochemistry.

Page 9931, line 11-13. This seems redundant. The authors make it clear that geothermally influenced samples would not be analyzed on page 9929 line 18-20.

While it may be beneficial to some readers to remind them here that samples with indication of geothermal influence have been excluded, we agree it is not strictly necessary and have removed this sentence: ~~In the following discussion, samples indicative of geothermal influence are excluded because they follow different thermodynamic equilibrium.~~

Page 9932, line 12-13. It would be interesting to hypothesize why the Na relationship is linear.

This is an oversight on our side. A linear relationship is not sensible. Therefore we changed this to a logarithmic fit, even though the data is insufficient to distinguish between a linear and log fit.

Page 9932, line 14-19. The statement that the origin of Na is purely geologic seems to contradict page 9932 line 5-6, which noted that higher Na in young groundwater can be caused by land use. The authors should clarify.

In other parts of NZ we have observed elevated Na in groundwater that is also elevated in nitrate (Morgenstern and Daughney, 2012) suggesting impact by land use. However, the Lake Rotorua data set suggests that this is not the case in the Lake Rotorua catchment. For clarification we have amended the text by:

… Note that elevated Na in young groundwater can also be caused by land-use impacts as observed in other parts of New Zealand (Morgenstern and Daughney, 2012). …

Page 9932, line 21-23. The authors should reconsider the generalization that "all samples" follow a similar trend of hydrogeochemistry with MRT. The lava cluster, for example, seems to have a negative correlation between bicarbonate and sodium with MRT, but positive correlation between pH and SiO_2 with MRT.

We have corrected this to:

~~All~~ The samples in each of these geologic units…