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Discussions

Interactive comment on "Using groundwater age to understand sources and dynamics of nutrient contamination through the catchment into Lake Rotorua, New Zealand" by U. Morgenstern et al.

Anonymous Referee #2

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Review of: Using groundwater age to understand sources and dynamics of nutrient contamination through the catchment into Lake Rotorua, New Zealand. U. Morgenstern, C.J. Doughney, G. Leonard, D. Gordon, F.N. Donath, and R. Reeves

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

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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.

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.

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).

* 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.

* 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

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concerns raised here about model selection still need addressing.

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.

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 "long-standing 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

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findings and the weight of the new evidence vis a vis previous findings.

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.

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.

Minor comments:

In addition to these major comments above, following are minor comments for the authors' consideration.

Page 9910, line 12. I believe that Sophocleous 2012 has been retracted.

Page 9910, line 14. Consider changing "defines" to "is defined by".

Page 9919, line 17: possible typo

Page 9920, line 26: possible typo

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

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

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

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.)

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.

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.

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.)

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

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.)

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...".

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.

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.

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

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.

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.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 9907, 2014.