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Hydrology and Earth System Sciences Discussions

Interactive comment on "Dying to find the source – the quantitative use of rhodamine WT as a proxy for soluble point source pollutants in closed pipe surface drainage networks" *by* C. H. Mines et al.

Anonymous Referee #1

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Recent technological advances have made in situ, time dense, water-quality measurements relatively easy. Studies evaluating the performance of in situ technology, particularly fluorescence sensors, which can be strongly influenced by environmental conditions, are critical to interpreting results. Rhodamine WT has long been used as a conservative tracer, but only recently has the technology been developed to measure fluorescence in the field; thus, a rigorous assessment of performance and potential interferences is warranted. As such, the paper entitled "Dying to find the source – the quantitative use of rhodamine WT as a proxy for soluble point source pollutants in closed pipe surface drainage networks" is timely and of interest. The paper is well

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written, the study design and statistics are valid, and the overall conclusions are sound. However, I have two main concerns:

1) There is no evaluation or discussion of turbidity, which has known and potentially substantial interference with fluorescence.

2) The stability of fluorescence experiments were conducted on both environmental and deionized water, while the pH experiments were conducted using only environmental water samples and the temperature and salinity experiments were conducted using only deionized water. There is the potential for interactive effects of environmental conditions on fluorometric response and using only environmental water or deionized water for experiments will miss these effects.

The authors need to include a discussion of turbidity interference on fluorescence and the reason for not including turbidity in the study. Likewise, the authors need to provide the rationale behind the choice of waters used in experiments and a discussion of the potential influence on results. More specific scientific comments and technical corrections are listed below. I recommend this paper for publication in Hydrology and Earth System Sciences after some revision.

Specific Scientific Comments:

1. (Abstract, page 4536, lines 13-14) "If these effects were combined in an additive manner, the maximum potential underestimation and overestimation of RWT concentration are approximately 30% and 20%, respectively" This concept is not discussed in the text of the paper.

2. (Introduction) The key to this study is the evaluation and field use of an in situ fluorometric sensor specific to Rhodamine WT that may perform differently than standard fluorometric approaches. This point should be clearly emphasized in the introduction because it underscores the fundamental importance of the study.

3. (Materials and Methods, Section 2.1 In situ instrumentation) The YSI 6130 has

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known turbidity interferences (∼0.03 ug/L per NTU, but potentially larger under highly turbid conditions, www.ysi.com); however, turbidity was not considered in this study. Given the emphasis on quantitation, the authors need to discuss why turbidity was not included in the study. Understanding turbidity interferences would be particularly important when conducting studies under stormwater runoff/high flow conditions.

4. (Materials and Methods, Section 2.3 Laboratory methodology) What were the ambient light conditions during the stability study?

5. (Materials and Methods, Section 2.3 Laboratory methodology) Why were the pH experiments conducted only on the Swan River water and the temperature and salinity experiments conducted only on deionized water? There are likely interactions between environmental conditions and fluorometric response that were potentially overlooked with this approach, particularly for temperature. Background fluorescence may be highly influenced by temperature. In addition responses may be different under turbid conditions.

6. (Materials and Methods, Section 2.4 Field methodology) I recognize that flow data are unavailable, but a general description of flow conditions (ie low, moderate, high, runoff) in the piped drainage network during the experiment would be useful to the reader.

7. (Results and Discussion, Section 3.1 Stability of fluorescence) It is worthwhile to point out that response was generally similar between the DI and Swan River waters, suggesting little fluorescence interference due to natural environmental conditions (at least for the water sample used in the experiment). The only exception is perhaps the 10 ug/L Swan sample (note this concentration is similar to background observed in Whaleback Lake), which as the authors point out is likely explained by the lower signal:noise ratio in this sample.

8. (Results and Discussion, Section 3.6 Field release, lines18-24) While the first release was only an order of magnitude greater than the background levels, it was still

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∼6-fold greater than background. Based on the lack of variability in the ambient data presented and the performance of the 6136 in the laboratory, the authors can state with some confidence that both peaks were the result of RWT addition and not background fluctuations.

9. (Results and Discussion, Section 3.7 Background water quality data) I suggest presenting this information before section 3.6 to provide context for the reader.

10. Figures 5-6. The reduced variance around the 0 temperature difference is clearly evident in these graphs; consider discussing this point in the text.

Technical Comments:

1. In situ should be italicized throughout the text.

2. (Abstract, page 4536, Lines 15-17) The last sentence of the abstract is somewhat confusing. Suggest the following modification: The field release study succeeded in detecting RWT at concentrations two orders of magnitude greater than background fluorescence. Based on longitudinal dispersion theory, observed RWT peak concentrations were within 10% of predicted peaks.

3. (Introduction, page 4536, line 20) Suggested modification : "...has become widespread in most developed areas of the world."

4. (Introduction, page 4536, line 24) Suggest removing "in water bodies"

5. (Introduction, page 4537, line 25) Need a comma after "factors"

6. (Results and Discussion, page 4545, line 12) Need a comma after "(Shiau et al., 1993)"

7. (Results and Discussion, page 4545, line 20) Need commas before and after "however" (...pH must, however, be...)

8. (Results and Discussion, page 4547, line 13) Suggest replacing "significantly" with

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"substantially" in this context.

9. (Results and Discussion, page 4547, line 19) Need a comma after "(equivalent to 0.012 N NaCl)"

10. (Results and Discussion, Section 3.5 Salinity effects) The discussion of the Smart and Laidlaw (1977) studies is somewhat confusing; clarify what the differences were in the two studies they conducted that had contradictory results.

11. (Results and Discussion, Section 3.6 Field release, line 10) Clarify that the peak concentration given for the 2nd release is for the first peak.

12. (Results and Discussion, Section 4. Conclusions, page 4550, lines 11-15) This is a long sentence. I suggest modifying as follows: The rapid changes in water quality at the study site, coupled with the potentially significant effects of local water quality conditions on detected RWT concentration highlight the value of in situ fluorometric methods to quantitative release studies; the researcher can assess the measured concentration against real-time water-quality conditions.

13. Figure 1. Symbols indicating detection and release points should be more distinctive.

14. Figure 4. The reverse order scaling on the x-axis is not intuitive and may be initially confusing to some readers.

15. Figure 5. At first glance, this graph appears to show an inverse relation between temperature and fluorometric response. The fact that the graph is showing calibration temperature – sample temperature really needs to be emphasized to ensure readers interpret the graph properly.

16. Figure 8. Suggest changing figure description to: Continuously measured RWT concentration at Whaleback Lake. . .

17. Figure 9. Suggest removing ORP from the figure because it is not discussed in the

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text.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 6, 4535, 2009.