Measurement and modeling of denitrification hotspots and NO_3 uptake in low-order streams

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Background

Denitrification, which is the step-wise reduction of soluble nitrogen oxides NO_3 and NO_2 to gaseous N_2 (complete) or either gaseous NO or N_2O (incomplete), is a process paramount to bacterial metabolism and functioning and has been shown to be the primary means for permanent nitrogen removal in lotic systems (Craig et al. 2008). Denitrification in streams often occurs in disproportionately small areas of the stream bed in which conditions are most suitable for NO_3 reduction (i.e. "hotspots"), such as high NO_3 or organic matter concentration.

Due to the small size and distinct biogeochemical features of these hotspots they can be very difficult to model (Groffman et al. 2009). Current approaches to the modeling of nitrogen processing in streams (e.g. OTIS) use 1-dimensional (1-D) techniques in which NO_3 is lost over a given reach length but assumed homogenous in the vertical and lateral directions. As variables such as NO_3 and dissolved oxygen (DO) concentration, temperature, shear stress and others exhibit spatial heterogeneity in all directions, accurate 3-D modeling must be utilized to depict and propagate these variabilities over time.

Methods

Time-series data was collected for velocity (Nortek Downward-Looking Acoustic-Doppler Velocimeter (ADV)), NO_3 (Unisense NO_x Biosensor), DO (Unisense OX-N Microsensor), and temperature (MSCTI, Precision Measurement Engineering) in the Outdoor StreamLab (OSL) at St. Anthony Falls Laboratory over three summers. Environmental sensors were mounted to the ADV shaft using a bracket system (Figure 1). Hydraulic structures were installed in the stream and discharge was controlled via an inlet valve. Varying discharge and hydraulic conditions allowed for NO_3 to be measured over a range of velocities (Table 1).

Velocity data measured by the ADV was filtered using the modified phase-space threshold method (Parsheh et al. 2010). Velocity fluctuations were averaged over the time-series at each data point and extrapolated to the bed to determine shear velocity (Biron et al. 2004). The local boundary Reynolds value was ascertained from the shear velocity and depth at each vertical column within a transect.

Sediment cores were extracted from the stream using a 1" PVC tube and immediately placed in a 4°C cooler. These cores were tested for potential denitrification using the Denitrification Enzyme Activity (DEA) method in which acetylene is used to block the conversion of N_2O to N_2 (Groffman et al. 2006). N_2O concentration was then found using a gas chromatograph and compared with the sediment dry weight to determine an overall denitrification potential in the sediment sample.

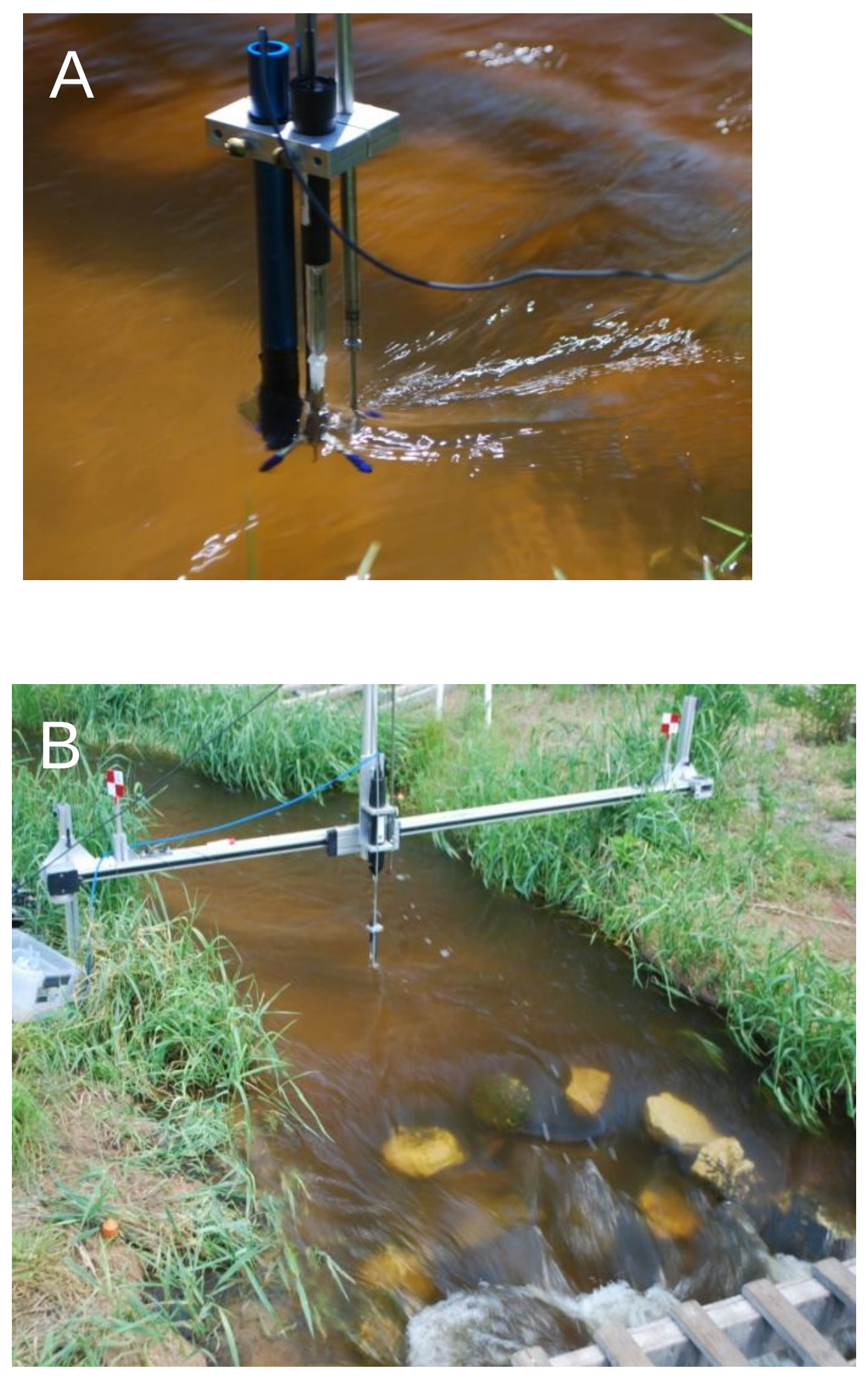

Figure 1: Photographs illustrating A) the bracket system, which holds (from left) the NO_x biosensor, DO microsensor, and temperature sensor along with B) the traverse system, which mounts the ADV and allows for transversal and vertical measurements within the stream and near structures (cross vane shown in this photograph). Stream flow is from left to right in both photographs.

Year	Structure(s) Installed	Discharge (lps)	NO_3 (mg-N/L)	u (m/s)	Transects Measured
2009	1 bendway weir	150	0.74	0.09	1
2010	3 bendway weirs	284	0.46	0.52	3
2011	2 cross vanes	25	1.03	0.1	2
2011	2 cross vanes	284	0.85	0.45	5

Table 1: Hydraulic scenarios run in the OSL in which NO_3 profiles were taken. Values for NO_3 concentration and streamwise velocity (u) are averaged over all cross-sections measured. Bendway weirs were installed in the central meander while the cross vanes were installed in former riffle sections.

Field Results

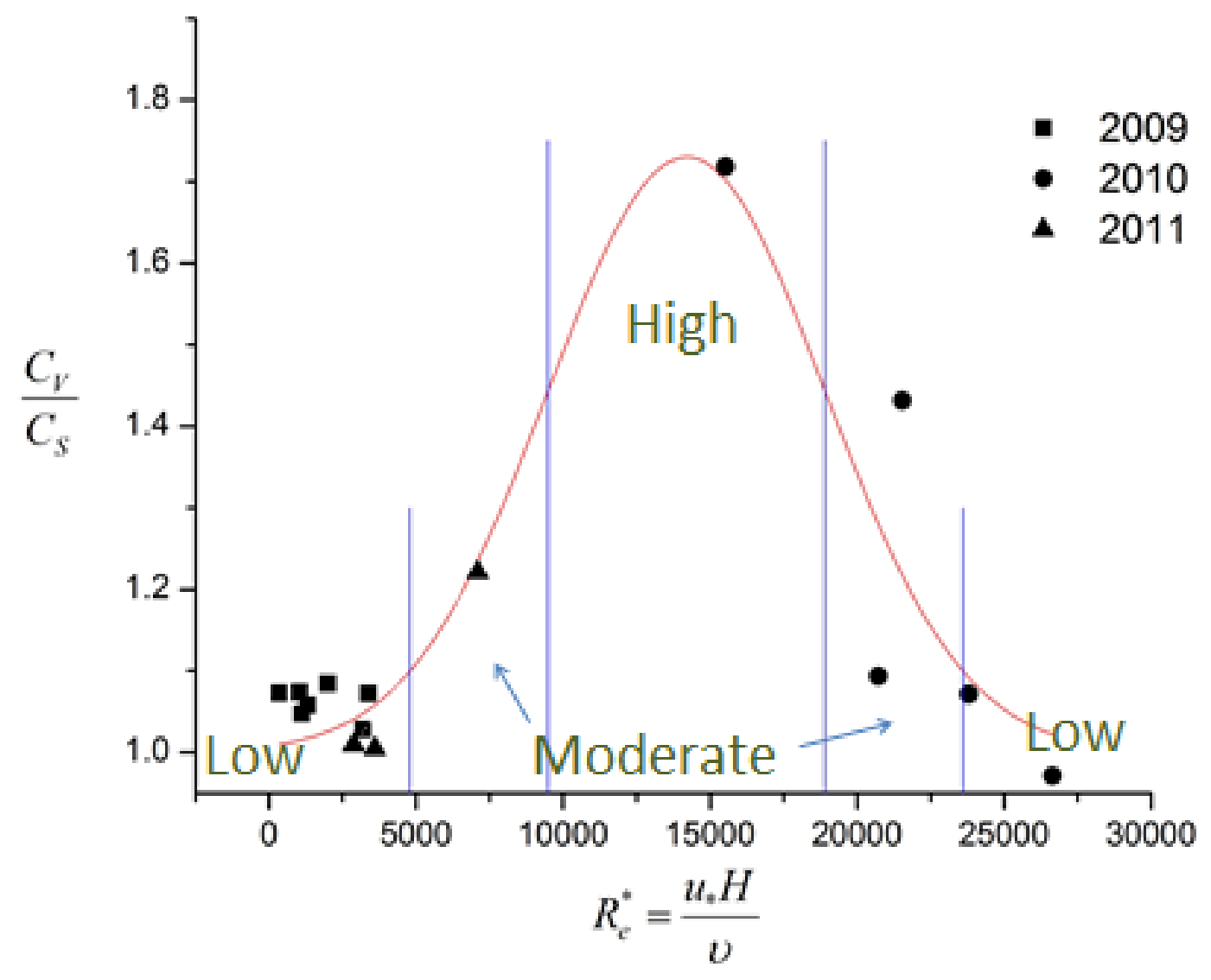

Figure 2: Results of time-series experiments showing the relation between the local boundary Reynolds number and the dimensionless NO_3 concentration. Areas denoting high, moderate, and low NO_3 uptake are labeled.

Spatial variability was exhibited in all variables (NO_3, DO, temperature, velocity) throughout each case. The local boundary Reynolds value proved to be a primary indicator for NO_3 uptake over all hydraulic scenarios. Figure 2 shows data acquired during time-series measurements which demonstrated vertical uptake of NO_3 . Measurements taken near the banks were negated due to additional effects imposed by the boundary. A Gaussian-type equation was fit to the data (red line in Figure 2) and used as a boundary condition for a turbulent 3-D model:

$$\frac{C_V}{C_S} = 1 + 0.67e^{-0.5\left(\frac{R_e^* - 17{,}300}{10{,}220}\right)^2}$$

Sediment coring results (Figure 3) found a positive relationship between the dimensionless NO_3 concentration (C_V/C_S) and potential denitrification as measured by headspace accumulation of N_2O. This demonstrates that as the sediment bacterial community increases its ability to denitrify, it draws down the NO_3 concentration at the sediment-water interface (C_S) and increases the vertical gradient in NO_3.

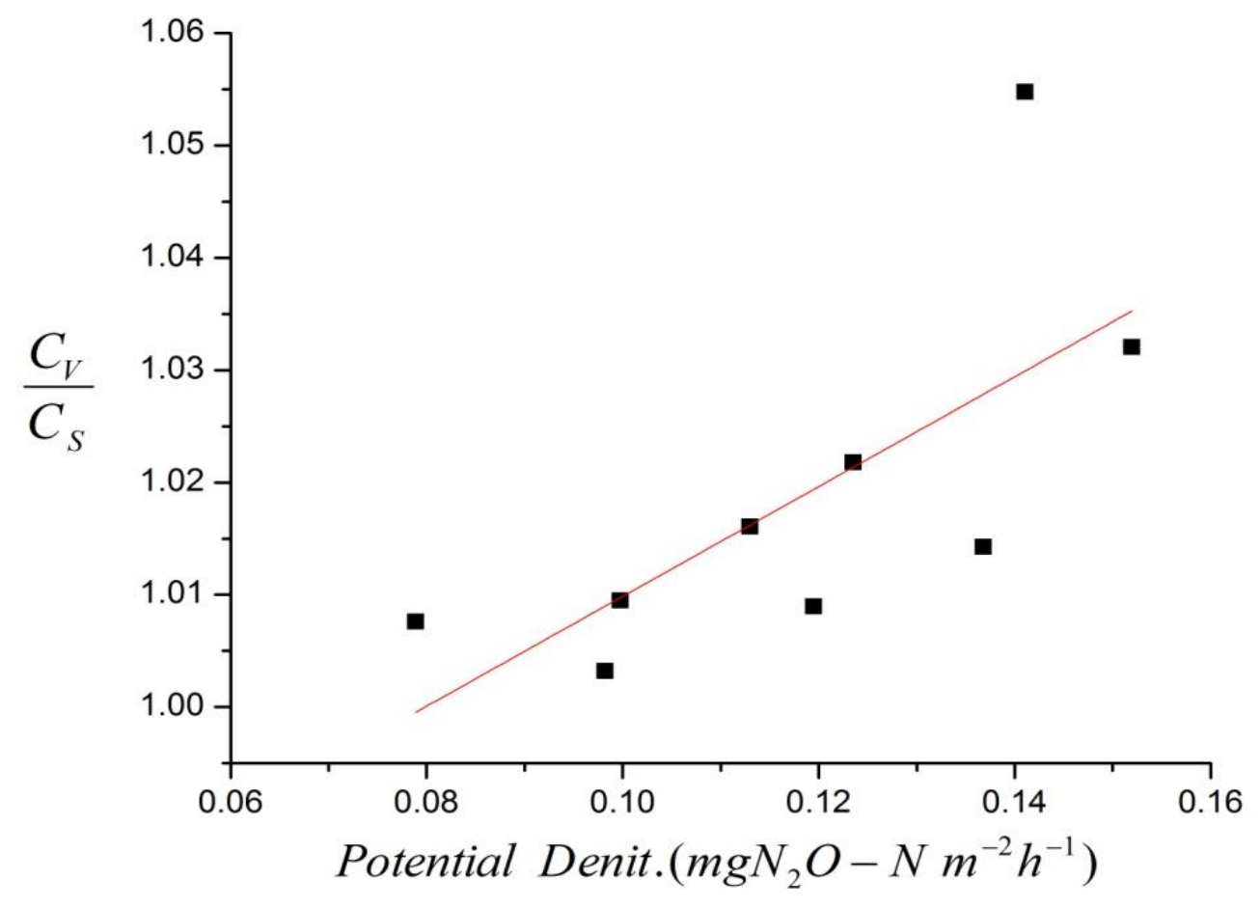

Figure 3: DEA results exhibiting positive relationship between potential denitrification and dimensionless NO_3 concentration ($R^2 = 0.43$, $P < 0.05$).

Modeling Results

Modeling was performed using a turbulent, 3-D Large Eddy Simulation (LES) model which couples morpho- and hydrodynamic processes. The model was run first with a no-flux boundary condition, then run using our proposed boundary condition along the bed and over the hydraulic structures at both low and bankfull flow conditions . Figure 4 shows the results compared to field measurements taken during a low-flow conservative/non-conservative tracer experiment (25 lps). As exhibited in the figure, the model was able to more accurately capture lateral variability in NO_3 concentration when the boundary condition was imposed.

Reach-scale NO_3 loss, as seen in Figure 5, was overestimated as compared to field measurements . This may be due to the constraints of the boundary condition, such that only areas of uptake were taken into account (Figure 2).

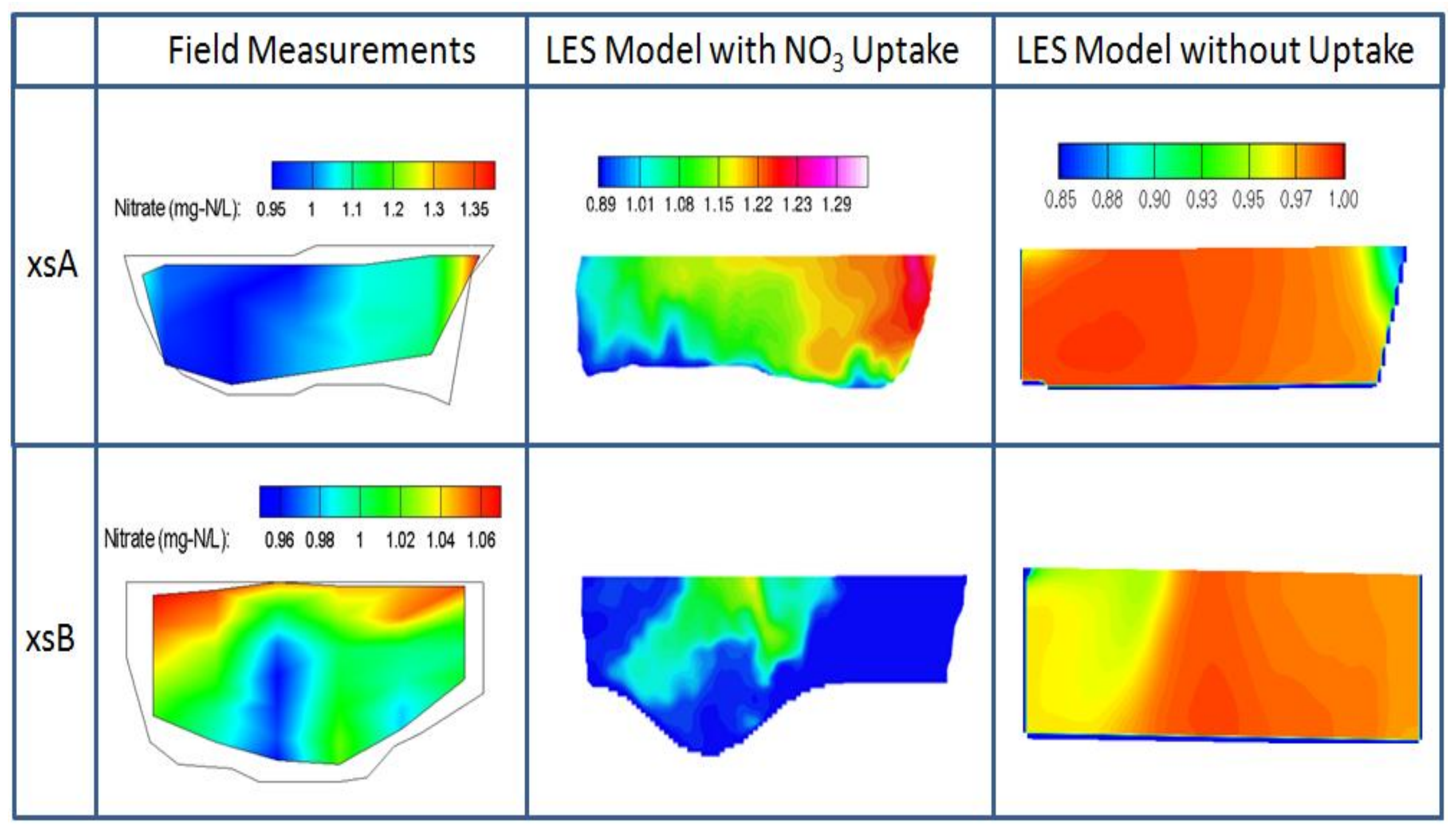

Figure 4: Comparison of Field measurements with LES model results both with and without the proposed boundary condition. Discharge was 25 lps for all cases.

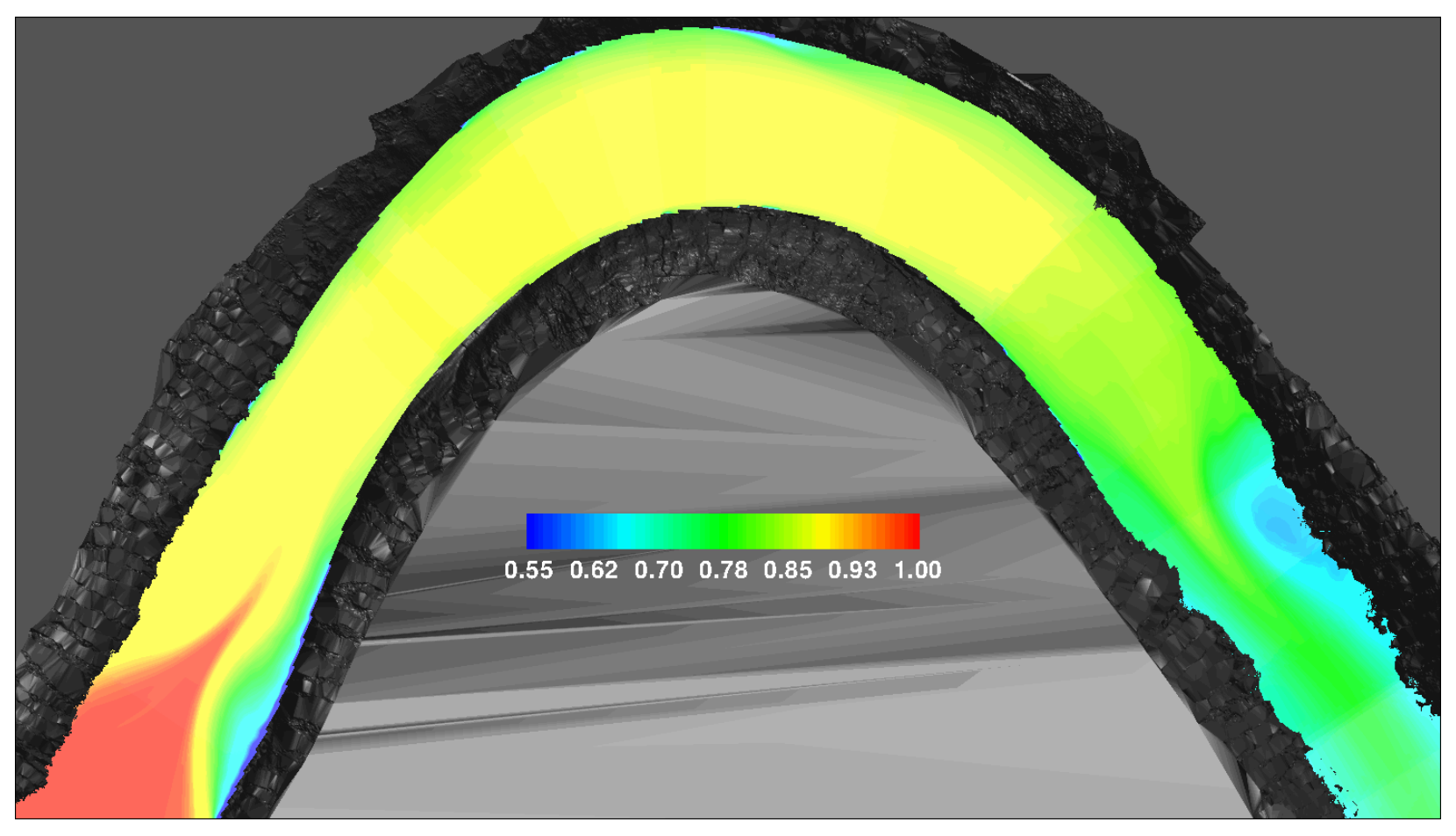

Figure 5: Reach-scale, time-averaged NO_3 distribution at the free-surface at bankfull (284 lps) flow conditions

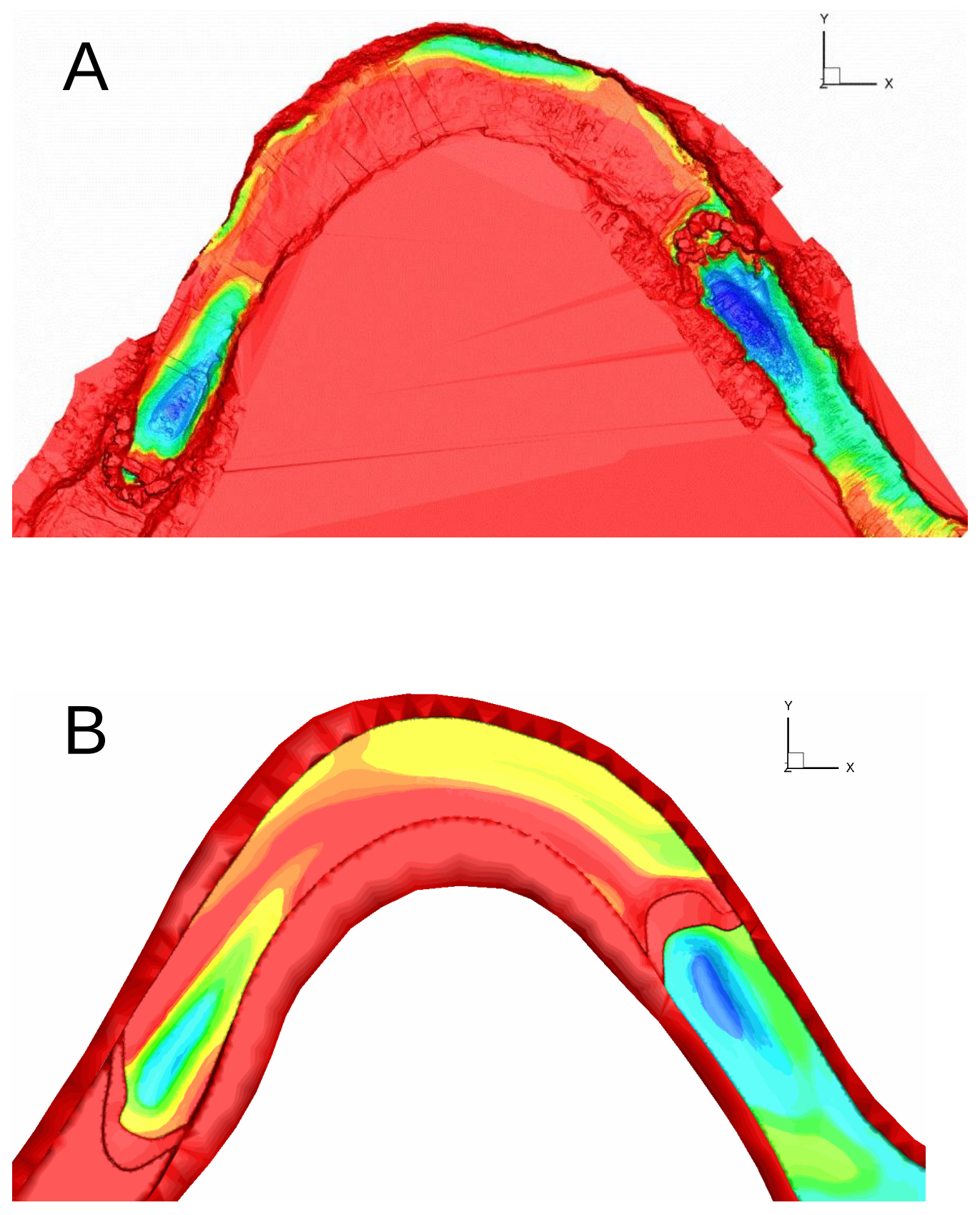

Figure 6: Comparison of A) measured bed topography in the OSL using an ultrasonic transducer placed atop a DAQ cart and B) topography created within the model

Conclusions

- A primary driver for NO_3 uptake from the bulk flow is the momentum flux from the channel to the sediment bed. This was depicted by the local Reynolds value (through shear velocity) at the sediment-water interface.

- Sediment cores confirmed a positive relationship between the vertical gradient in NO_3 concentration and the potential ability of sediments to denitrify. This signifies that NO_3 lost form the bulk flow is likely permanently lost as nitrogen gas, not just retained in the short-term via storage (e.g. hyporheic exchange) or plant assimilation.

- Model analysis is able to better exhibit spatial heterogeneity in NO_3 distribution with the use of the proposed uptake boundary condition.
- Further laboratory work will attempt to connect nitrite reductase (nir) gene abundance in sediment cores with hydraulic and environmental conditions in these experiments. In addition, the proposed boundary condition will be further scrutinized to try to more accurately capture both cross-sectional and reach-scale nutrient uptake.

References and Acknowledgements

BIRON, P. M., ROBSON, C., LAPOINTE, M. F. & GASKIN, S. J. 2004. Comparing different methods of bed shear stress estimates in simple and complex flow fields. *Earth Surface Processes and Landforms,* 29**,** 1403-1415.
CRAIG, L. S., PALMER, M. A., RICHARDSON, D. C., FILOSO, S., BERNHARDT, E. S., BLEDSOE, B. P., DOYLE, M. W., GROFFMAN, P. M., HASSETT, B. A., KAUSHAL, S. S., MAYER, P. M., SMITH, S. M. & WILCOCK, P. R. 2008. Stream restoration strategies for reducing river nitrogen loads. *Frontiers in Ecology and the Environment,* 6**,** 529-538.
GROFFMAN, P. M., ALTABET, M. A., BOHLKE, J. K., BUTTERBACH-BAHL, K., DAVID, M. B., FIRESTONE, M. K., GIBLIN, A. E., KANA, T. M., NIELSEN, L. P. & VOYTEK, M. A. 2006. Methods for measuring denitrification: Diverse approaches to a difficult problem. *Ecological Applications,* 16**,** 2091-2122.
GROFFMAN, P. M., BUTTERBACH-BAHL, K., FULWEILER, R. W., GOLD, A. J., MORSE, J. L., STANDER, E. K., TAGUE, C., TONITTO, C. & VIDON, P. 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry,* 93**,** 49-77.
PARSHEH, M., SOTIROPOULOS, F. & PORTE-AGEL, F. 2010. Estimation of Power Spectra of Acoustic-Doppler Velocimetry Data Contaminated with Intermittent Spikes. *Journal of Hydraulic Engineering-Asce,* 136**,** 368-378.

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