

Enhanced Removal of Dissolved Manganese in Hyporheic Zones: Centimeter-Scale Causes and Kilometer-Scale Consequences

By Judson W. Harvey, Christopher C. Fuller, and Martha H. Conklin

ABSTRACT

Characterizing both the causes and consequences of enhanced oxidation of dissolved manganese (Mn) in the hyporheic zone required measurements with spatial resolution varying across five orders of magnitude. Our measurements at Pinal Creek basin, AZ ranged in scale from that of the fundamental interactions between surface and ground water (centimeters) to the scale of the perennial stream that receives ground-water discharge from the entire drainage basin (kilometers). Mean rate constants for the removal of dissolved manganese agreed closely between three scales of resolution in the field, ranging from centimeter-scale field measurements acquired *in situ* in hyporheic zones to kilometer-scale estimates determined using stream tracers. The laboratory estimate of the Mn removal-rate constant was approximately 30% lower than field estimates. *In situ* and laboratory rate constants had relatively large coefficients of variation (107% and 84%, respectively), which may be too large to be used reliably in transport simulations. Stream-tracer experiments provided estimates of the rate constant with lower uncertainties; 56% when averaged at the reach-scale (approximately 500 meters) and 26% when averaged at the basin-scale (3 kilometers). Because of the lower uncertainties the stream-tracer approach appeared to provide the most reliable basin-scale simulation of the effects of enhanced Mn-removal in hyporheic zones. The stream-tracer characterization alone, however, could not determine that removal of manganese was pH-dependent, or even that the reaction occurred in hyporheic zones (as opposed to slow-moving zones in surface water). Laboratory and *in situ* measurements within hyporheic zones provided the crucial evidence to support interpretations about the causal processes. Our experience at Pinal Creek basin leads us to conclude that a multi-scale approach is a necessity for characterizing enhanced biogeochemical reactions in hyporheic zones.

INTRODUCTION

Hydrologic exchange of streamwater and ground water back and forth across channel beds of rivers and streams enhances chemical transformations in shallow groundwater beneath the streambed (hyporheic zone). The hyporheic zone is defined hydrologically by flow paths that route streamwater temporarily through the subsurface and chemically by subsurface water that can be shown to receive greater than 10% of its water from the surface (Triska and others, 1993). Steep chemical gradients in dissolved oxygen, dissolved organic carbon, and pH in hyporheic zones enhance biogeochemically mediated transformations of solutes, such as nitrification and denitrification (Grimm and Fisher, 1984; Triska and others, 1993), oxidation

of metals (Benner and others, 1995), and biodegradation of volatile organic compounds (Heekyung and others, 1995). Hyporheic flow paths are typically small in their spatial dimensions, but if chemical reaction rates are fast enough, and if enough exchange occurs between flowing water and sediment, then the effects can accumulate downstream and affect water quality (Harvey and Fuller, 1998).

This paper considers three types of measurements at different spatial scales of resolution. Our previous comparisons across spatial scales (Harvey and Fuller, 1998) are updated here with new findings by Marble and others (this volume) and Fuller and Harvey (this volume). The purpose was twofold: (1) to verify previous conclusions that were based on a limited

data set, and (2) to assess the relative merits of the three modes of investigation in informing us about causes and consequences of enhanced chemical reactions in hyporheic zones. The three measurement types are:

(1) laboratory-batch experiments that quantify solute-sediment interactions at the millimeter-scale, i.e. the scale of individual sediment grains, (2) *in-situ* measurements in hyporheic flow paths at the scale of centimeters beneath the streambed, and (3) stream-tracer experiments that quantify removal rates at the scale of experimental subreaches in the perennial stream (approximately 500 meters) or at the scale of the perennial stream that receives ground-water discharge from the entire drainage basin (3 kilometers).

A number of physical and chemical measurements of the hyporheic zone have been made as part of our investigations, including the hyporheic-zone depth, hydrologic residence time in the hyporheic zone, net removal-rate constant for dissolved manganese (Mn), and percent removal of Mn in hyporheic flow paths. Previously, we found good agreement across scales of measurement based on a relatively limited data set (Harvey and Fuller, 1998). In this paper, we update with new data the means and standard deviations for manganese removal-rate constants and compare them among the three measurement types. Field methods, analyses, and modeling calculations for reach-scale and *in-situ* measurements are presented in Harvey and Fuller (1998) and Fuller and Harvey (this volume). Laboratory methods and analyses are given by Marble and others (this volume) and Harvey and Fuller (1998).

COMPARISON OF REMOVAL-RATE CONSTANTS ACROSS SCALES

All available data from field work in 1994, 1995, and 1997 were used to compute a mean and standard deviation for *in situ* rate constants (cm-scale). The summary statistics shown in Figure 1 were determined for sub-reaches (500-m scale) by averaging results from 9 experimental sub-reaches from stream-tracer injections in 1994 and 1995. The basin-scale estimates were computed by averaging the mean

rate constant from the four subreaches in 1994 with the mean for the five subreaches in 1995. The laboratory estimates were computed using data from the subset of experiments conducted between pH 6 and 6.9, which matches the range of pH's that were measured *in situ*.

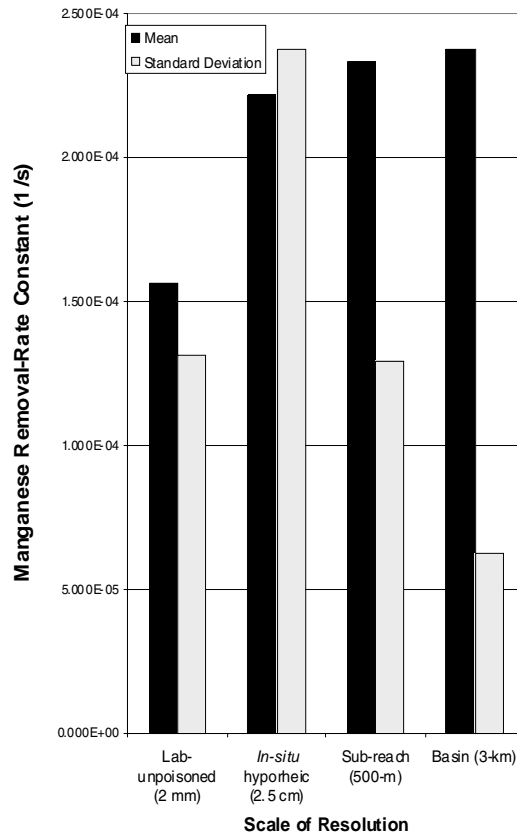


Figure 1. Means and standard deviations for Mn removal-rate constants estimated at different spatial scales. Summary statistics are based on sample sizes of 8, 11, 9, and 2 for laboratory, *in-situ*, sub-reach, and basin-scale estimates, respectively.

The mean rate constants for field estimates (e.g. *in situ*, sub-reach, and basin-scale) varied little (4% coefficient of variation), however the estimate from the laboratory was approximately 30% lower. Standard deviations varied widely across all scales over approximately a factor of four. We chose the coefficient of variation (standard deviation divided by the mean) as a measure of uncertainty. The *in situ* estimate of the removal-rate constant was most uncertain with a coefficient of variation of 107%. Estimates made at the kilometer-scale based using the stream-tracer approach were least

uncertain, with a coefficient of variation equal to 26%. The coefficient of variation for laboratory and sub-reaches had intermediate values of 84% and 56%, respectively.

CAUSES OF ENHANCED OXIDATION OF DISSOLVED MANGANESE IN HYPORHEIC FLOW PATHS

Evidence for the influence of microbial activity and pH is illustrated in Figure 2, which summarizes all of the data from Marble (1998), Marble and others (this volume), Fuller and Harvey (this volume), and Harvey and Fuller (1998). Laboratory experiments were controlled for the effects of microbial activity and pH demonstrated that manganese oxidation rates are highly sensitive to the presence of an active microbial colony and to pH.

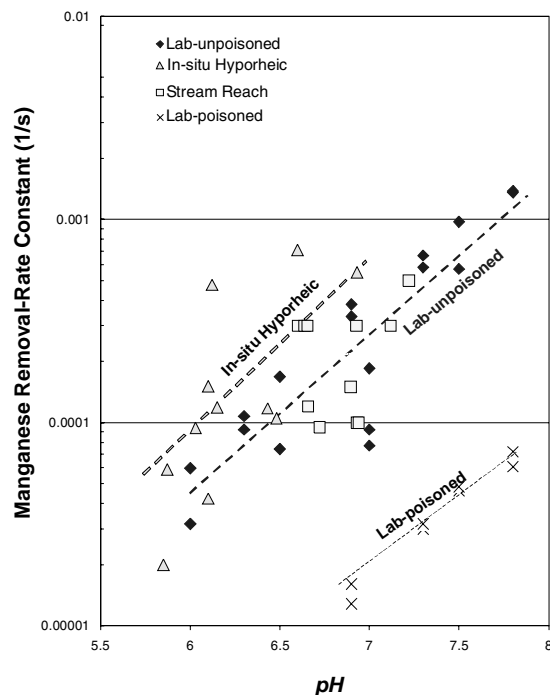


Figure 2. Laboratory measurements and *in-situ* estimates of rate constants indicate a positive relationship with pH, but reach-scale estimates do not.

Figure 2 shows that for a given pH, the rate constants are approximately an order of magnitude lower in samples that were poisoned to reduce or eliminate microbial activity. A

statistically significant positive correlation ($p = 10^{-6}$) between unpoisoned laboratory rate constants and pH was also apparent. A similar positive correlation with pH was apparent for the removal-rate constants determined within hyporheic flow paths, although that relation was only barely significant at $p = 0.05$ (using a typical statistical criterion for significance that p is less than or equal to 0.05). No correlation with pH was apparent for removal-rate constants determined by stream-tracer experiments. The lack of a pH relation for reach-scale removal rates stems at least in part from using stream pH as a proxy for a reach-averaged pH in the hyporheic zone.

CONSEQUENCES FOR REACH-SCALE WATER QUALITY

The data requirements for characterizing spatially-variable processes in hyporheic zones using small-scale sampling are massive. As a result, *in-situ* field sampling and laboratory measurements of Mn removal-rate constants might not be reliable to determine cumulative effects in the drainage basin. Stream-tracer experiments offer a possible means to average over small-scale spatial variability to estimate cumulative effects (Kimball and others, 1994). The principal advantage of the stream-tracer approach is that average characteristics of mass transport and chemical reactions are determined at spatial scales that are appropriate for water-quality modeling (hundreds of meters to tens of kilometers). A major disadvantage of the stream-tracer approach, however, is the empirical nature of the parameters. For example, the ‘storage-exchange’ parameters of the stream-tracer approach describe a zone of temporary retention of stream water on the basis of fitted-parameter values that best match in-stream bromide tracer experiments.

To justify an interpretation that storage zones inferred by tracer methods represent hyporheic zones, it is necessary to directly compare stream-tracer results with *in situ* measurements within hyporheic zones. Figure 3 compares measured depths of the hyporheic zone with inferred depths from modeling.

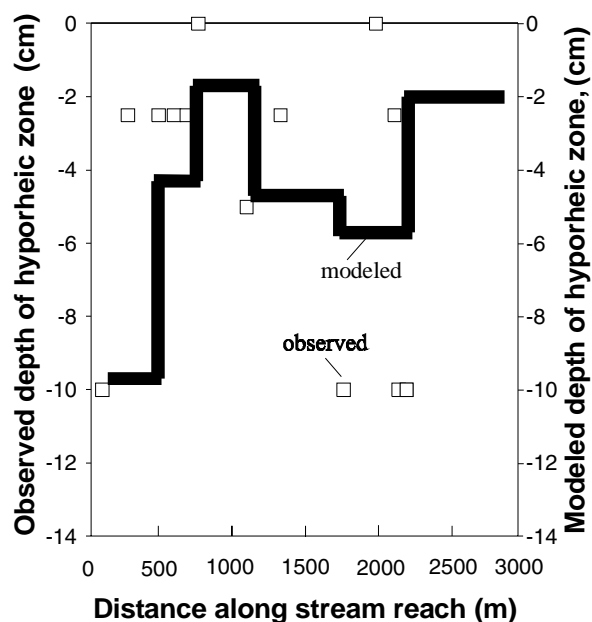


Figure 3. Comparison of *in-situ* measurements of the depth of the hyporheic zone with depths inferred by modeling transport of a stream tracer.

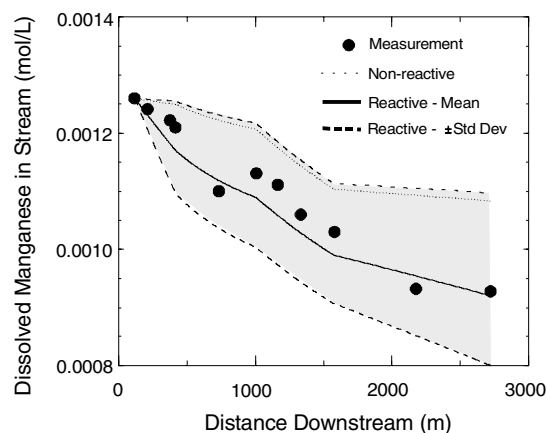
Although site-specific measurements of the depth of the hyporheic zone were much more variable than modeled stream-tracer results, there was a general correspondence between the central tendencies and the downstream trends in the two data sets. These results supported our interpretation that the stream-tracer experiments at Pinal Creek were in fact sensitive to hydrologic exchange with hyporheic zones, rather than stagnant or recirculating areas in surface water.

The use of *in-situ* and basin-scale estimates of rate constants to simulate the cumulative effects of manganese removal in Pinal Creek basin are compared in Figure 4.

Transport of Mn in a 3-km reach of Pinal Creek (about half the length of the perennial stream in the basin) in 1994 is used as the basis for comparison with field data. The model allows for removal of dissolved manganese only in storage (hyporheic) zones for which the physical dimension and hydrologic residence time were determined by modeling bromide injections in the stream. The analysis equations and supporting information are presented in Harvey and Fuller (1998). The ‘non-reactive’ simulation only indicates the effects of dilution by inflow of groundwater with lower Mn concentration. For ‘reactive’ simulations, mean removal-rate

constants were determined either by averaging all of the available *in-situ* rate-constant estimates (Figure 4A), or by averaging rate-constants determined by stream-tracer methods in five sub-reaches in 1995 (Figure 4B). The dashed simulations and shaded represent uncertainties of plus or minus one standard deviation around simulations that used the mean removal-rate constant.

A. Using *In-situ* Estimates of Removal-Rate Constant



B. Using Reach-Scale Estimates of Removal-Rate Constant

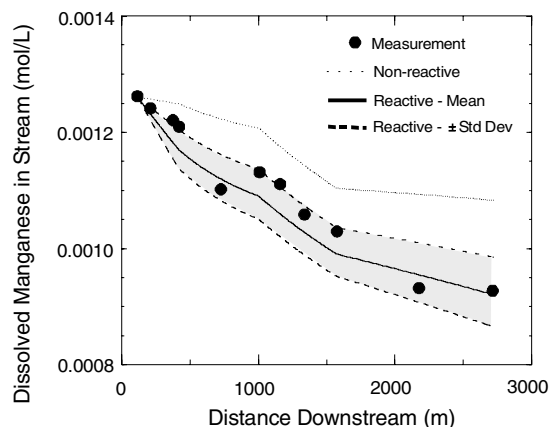


Figure 4. *In-situ* estimates of the removal-rate constant are too variable to reliably simulate basin-scale consequences. Reach-scale estimates of the rate constant reliably simulate the basin-scale effect of enhanced manganese oxidation in the hyporheic zone.

In both panels of Figure 4, measured Mn and simulated Mn were lower in concentration than indicated by the non-reactive simulation, suggesting that removal of dissolved manganese occurs in hyporheic zones. Uncertainty of the

simulation using the *in-situ* rate constant, however, overwhelmed our ability to characterize cumulative effects in the drainage basin. This is apparent in Figure 4A by the large envelope of uncertainty that overlaps the measured data as well as the simulation for non-reactive transport. If judged alone, the modeling result in Figure 4A would cast doubt as to whether a significant loss of mass of manganese even occurs at Pinal Creek. In contrast, the simulation in Figure 4B had a smaller error envelope that only encompassed the measured data. Simulated concentrations in Figure 4B were well below those predicted by the non-reactive transport simulation, suggesting greater confidence that substantial removal of Mn occurred in hyporheic zones. Comparison of simulated non-reactive and reactive Mn concentrations indicated that approximately 14% of the manganese in the 3-km reach was removed by enhanced oxidation in hyporheic zones.

DISCUSSION

Rate constants for removal of manganese differed little between laboratory experiments, *in-situ* field measurements, and measurements based on stream-tracer experimentation. The advantage of laboratory experiments was the isolation of the effects of microbial colonies and pH. Marble and others (this volume) discuss pH and other factors affecting Mn-oxidation reactions. One problem of the batch-laboratory experiments is extrapolating results to sediment-water ratios that more accurately approximate field conditions. Following Harvey and Fuller (1998), we scaled laboratory-rate constants by multiplying them times the ratio between the average sediment concentration (grams/liter) in the streambed at Pinal Creek and the sediment concentration used in laboratory experiments. That adjustment assumes that grain-size variations, which are likely to affect sediment-surface area available for oxidation of manganese, are the same in laboratory experiments and in the streambed. Another possible problem of the laboratory experiments is controlling for variation in activity levels of microbial colonies. For example, Marble and others (this volume) report a significant time lag before removal in Mn begins in sediment samples that were stored before usage

in experiments. Either of those possible problems might explain the lower Mn removal-rate constant compared with *in-situ* and stream-tracer estimates.

In-situ sampling within hyporheic flow paths addresses the problem of realistic field conditions by quantifying rates of removal without disturbing the sediments or natural hydrologic fluxes. But this method has practical limitations, however. *In-situ* sampling has the disadvantage that the measurements are difficult and time consuming to make in the field, which limits sample sizes. In addition there is also the problem that ancillary physical and chemical factors cannot be varied except through careful site selection. The principal advantage of *in-situ* field measurements is that interactions between flow and biogeochemical processes are preserved, which potentially could reveal findings that would be difficult to detect in a laboratory setting.

Stream-tracer experiments provided the the most reliable reach-averaged rate constants for modeling the basin-scale consequences of enhanced chemical reactions in hyporheic zones. Nevertheless, there remains a major disadvantage of the stream-tracer approach for quantifying hyporheic-zone processes. On the basis of stream-tracer experiments alone, we cannot be sure that the removal of reactive solutes actually occurs in hyporheic-zones, or on the leaves of aquatic vegetation in slowly-moving surface water at channel margins or behind channel obstructions. Another problem with stream-tracer methods is that the detection sensitivity for hyporheic zones is not equal across the multiple types of hyporheic zones that may be present in a given system (Harvey and others, 1996). Only direct sampling of hyporheic zones using *in-situ* methods can provide the independent confirmation needed to support physical interpretations at larger spatial scales.

CONCLUSIONS

We compared rates of microbially-enhanced oxidation of manganese in hyporheic zones at Pinal Creek basin in Arizona across spatial scales ranging from that of individual sediment grains in laboratory investigations to the scale of a 3-km reach of the perennial stream.

Marble and others (this volume) illustrated how Laboratory measurements illustrated the biogeochemical factors that influence reaction rates, with pH-dependent activity of manganese-oxidizing bacteria being a primary factor (Marble and others (this volume)). *In-situ* measurements in the field were much more difficult to make and results were more variable than in the laboratory. Consequently, the positive relation of removal-rate constants with pH that was easily detected in the laboratory data was only marginally significant for field data. *In-situ* studies, however, had the advantage of investigating chemical and physical factors and their interactions simultaneously, and the agreement with laboratory rate constants thus lent support to interpretations. At the largest spatial scale, stream-tracer investigations provided reliable estimates of overall removal of manganese in the reach, but interpretations about where reactions occur or what factors control them could not be defended without supporting information from *in-situ* measurements in hyporheic zones. Our experience leads us to conclude that, due to the disparity in scales between the fundamental processes and their consequences, a multi-scale approach is essential to investigating enhanced chemical reactions in hyporheic zones.

REFERENCES

- Benner, S.G., Smart, E.W., and Moore, J.N., 1995, Metal behavior during surface-groundwater interaction, Silver Bow Creek, Montana, *Environmental Science and Technology*, 29, 1789-1795.
- Fuller, C.C., and Harvey, J.W., The effect of trace-metal reactive uptake in the hyporheic zone on reach-scale metal transport in Pinal Creek, Arizona, in Morganwalp, D.W. and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 1—Contamination from Hard Rock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, this volume
- Grimm, N.B., and Fisher, S.G., 1984, Exchange between interstitial and surface water: implications for stream metabolism and nutrient cycling. *Hydrobiologia* 111:219-228.
- Harvey, J.W., and Fuller, C.C., 1998, Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, *Water Resources Research*, 34, 623-636.
- Harvey, J.W., Wagner, B.J., and Bencala, K.E., 1996, Evaluating the reliability of the stream-tracer approach to characterize stream-subsurface water exchange, *Water Resources Research*, 32(8), 2441-2451.
- Heekyung, K., Hemond, H.F., Krumholz, L.R., and Cohen, B.A., 1995, In-situ biodegradation of toluene in a contaminated stream, 1, *Field Studies, Environmental Sciences and Technology*, 29, 108-116.
- Kimball, B.A., Broshears, R.E., Bencala, K.E., and McKnight, D.M., 1994, Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage, *Environmental Science and Technology*, 28, 2065-2073.
- Marble, J.C., Corley, T.L., Conklin, M.H., and Fuller, C.C., , Environmental factors affecting oxidation of manganese in Pinal Creek, Arizona., in Morganwalp, D.W. and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 1—Contamination from Hard Rock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, this volume
- Marble, J.C., 1998, Biotic contribution of Mn(II) removal at Pinal Creek, Globe, Arizona, unpublished M.S. thesis, University of Arizona, Department of Hydrology and Water Resources, Tucson. 91 p.
- Triska, F.J., Duff, J.H., and Avanzino, R.J., 1993, The role of water exchange between a stream channel and its hyporheic zone on nitrogen cycling at the terrestrial-aquatic interface, *Hydrobiologia*, 251, 167-184.

AUTHOR INFORMATION

Judson W. Harvey, U.S. Geological Survey,
Reston, Virginia (jwharvey@usgs.gov)

Christopher C. Fuller, U.S. Geological Survey,
Menlo Park, California

Martha H. Conklin, The University of Arizona,
Tucson, Arizona