# Reply to "Comments on 'Pore-Scale Visualization of Colloid Transport and Retention in Partly Saturated Porous Media'"

Wan and Tokunaga's (2005) comments give us an opportunity to relate our recent findings to our initial paper (Crist et al., 2004). The main purpose of our first paper (Crist et al., 2004) was "to describe a novel pore-scale visualization technique" and "help reconcile some inconsistencies among earlier studies," in particular by demonstrating the need to refine the widely held assumption used to explain observed breakthrough curves, namely that colloids are retained at air–water (AW) interfaces in unsaturated media. Contrary to the statement of Wan and Tokunaga (2005), attempting "to provide pore-scale insights into mechanisms responsible for controlling colloid transport in unsaturated porous media" was not the aim of the initial Crist et al. (2004) paper. We discussed insights into retention mechanisms in a subsequent paper (Crist et al., 2005) under conditions in which evaporation effects on colloid retention were greatly reduced by using steady-state flow. Furthermore, the length of the unsaturated zone in this subsequent paper was increased by using larger diameter sand particles and employing a steeper chamber slope. We are therefore disappointed that Wan and Tokunaga restricted their comments "for brevity" mainly to our 2004 paper.

It is of interest that we did not observe the colloid straining conceptualizations that Wan and Tokunaga (2005) depicted in their Fig. 2b ("with evaporation," where colloids form a wide band at air–water–solid (AWS) interfaces in pendular rings) unless colloid diameter and water film thickness were approximately the same. With some slight adjustments, we observed phenomena similar to their Fig. 2a, with one difference: while Wan and Tokunaga (1997, p. 2418) envisioned that "colloids are constrained to rolling along the grain surfaces..." below critical saturation, in our case colloids were stagnant after they attached at the AWS interface, indicating a slightly different mechanism. Note that by "AWS interface" we refer to the location where the meniscus *either* meets the dry grain surface *or* diminishes in thickness to a thin water film covering the grain surface. In our recent work (Zevi et al., 2005) we have proposed the term *air–water meniscus–solid interface* (abbreviated $AW_mS$) for this concept, denoting the region where the water *meniscus* ends by thinning to a thin film, which more correctly represents the interfaces observed in unsaturated media. Our equipment at the time of the Crist et al. (2004) experiments could not observe thin films. Wan and Tokunaga's (2005) reasons for distinguishing whether a thin film exists at the AWS interface are not clear to us at this time, although it could prove to be important in the future.

We are also puzzled by Wan and Tokunaga's (2005) comment that the "magnitude of [our] observations [of colloid retention at the AWS] are not likely to occur anywhere except within the most superficial few centimeters of soils." In this initial paper we did not claim (nor understand) that it was an important mechanism, noting that we "fully expected" not to find "the rings" of colloids in vertical columns. Only at the end of the paper did we suggest that retention at the AWS interface could reconcile the contrasting results of their earlier work, in which they found negatively charged colloids at the

AW interface (Wan et al., 1994a, 1994b), but did not find them in air bubbles in their Wan and Tokunaga (2002) paper. In our subsequent work with both better experimental controls and fewer evaporation effects, we proved that the tentative findings of retention at the AWS in Crist et al. (2004) were both real and significant.

The comment of Wan and Tokunaga (2005) also claims that evaporation increases the advection of colloids to AWS contact lines where they are subsequently deposited. In this reply we show that although evaporation has an effect (as was noted in the original paper [Crist et al., 2004]; e.g., the legend of Fig. 6) in terms of increasing the color intensity of the visible bands at the AWS surfaces, it is clearly not the only process that influences colloid retention at the AWS interface. In the flowing water experiments described in Crist et al. (2005), the same pattern of immobilization of colloids near the AWS interface was clearly seen under conditions where any effect of evaporation would be negligible. The videos accompanying that paper visually document the high flux of water across grain surfaces and within pendular rings, and demonstrate that retention did not occur at the AW interface, but only at or near what we termed the AWS interface.

Since the initial set of experiments reported in Crist et al. (2004), we have continued experimentation with better visualization equipment, including a more powerful bright field microscope and a longer chamber to avoid problems that arise from the presence of capillary fringes in the field of visualization (Zevi et al., 2005). In this new set of experiments, we similarly found colloid attachment to the AWS (termed $AW_mS$ in that paper) interface. More importantly, colloid attachment occurred *as soon as the colloids were added* and before there was any opportunity for evaporation to exert an effect.

To further determine the relative significance of evaporation, we repeated the Crist et al. (2004) experiment in a larger chamber using a bright field microscope, but this time with a cover plate on the chamber to prevent evaporation. The microscope halogen light source produced less heat in the chamber than was the case with the light source used in Crist et al. (2004). The image in Fig. 1 (which is of only moderate quality due to the optical effects of the cover) clearly shows that colloids are attached at the AWS ($AW_mS$) interface. Wan and Tokunaga's (2005) argument, if we understand it correctly, is that the movement of colloids to the AWS interface is driven only by evaporation. In contrast, Fig. 1 shows that colloid retention rapidly occurs at the AWS interface in the absence of evaporation. Bands in this case are less numerous than in Crist et al. (2004).

We feel that the Wan and Tokunaga (2005) experiments on evaporation of a static 1-μL droplet of a colloidal suspension are a poor analog for our observations on colloid retention at a much larger scale and with flowing water that would continually replenish any small amount of water that might be lost to evaporation. In their experiment, the contact line recedes during evaporation, resulting in the deposition of colloids at the contact line as shown in their Fig. 3. In our flowing water experiments, the contact line is not receding because of the constant inflow of water. In these situations (Crist et al., 2005, and Fig. 1) evaporation can only be important if it creates a significant velocity vector perpendicular to the direction of flow. Comparing our input colloidal suspension flux of 2 cm³ min⁻¹ with the evaporative flux typically in the order of a few millimeters per day we find that the input flux is one to two orders greater than the evaporation flux. Obviously, the evaporation rate would be even more negligible

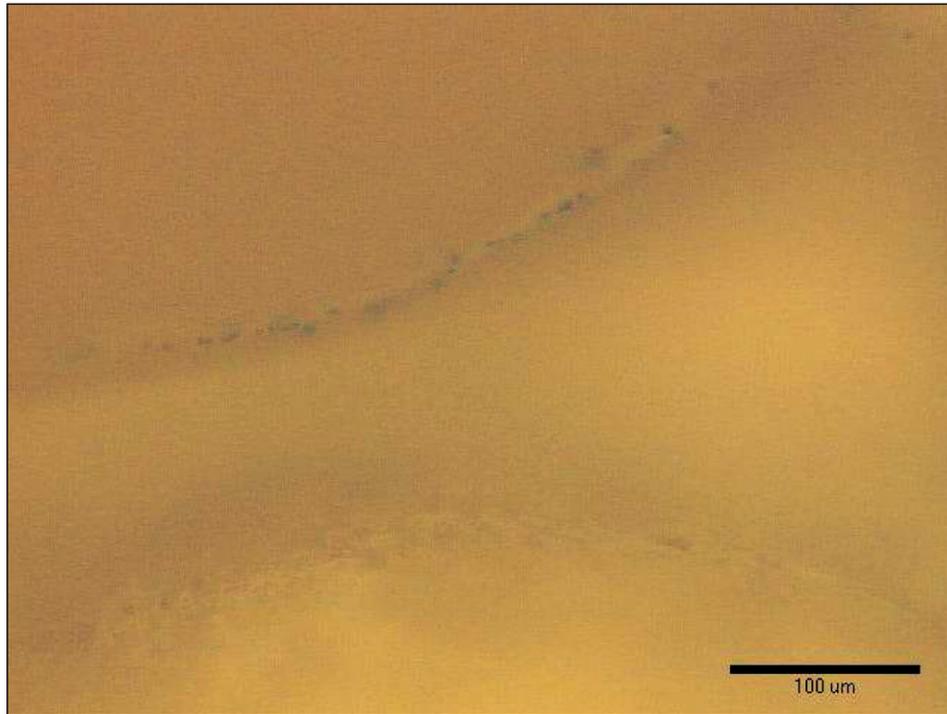**Abbreviations:** AW, air–water; AWS, air–water–solid; $AW_mS$, air–water meniscus–solid interface.

**Fig. 1. Image of colloid retention at the air–water–solid interface in a closed chamber using a bright field microscope (Olympus BX 50) with a 10× objective (Olympus U Plan APO, numerical aperture 0.4), and a zoom factor of 2. Image size is 499 by 374 µm. The microscope is equipped with a high-resolution CCD camera. Light from a built-in halogen illuminator was aimed toward a lens beneath the stage and through the infiltration chamber. The image was taken at a location 5 cm below the column inlet 23 min after colloids were added (flow rate of 1.5 mm min⁻¹, initial concentration of $6.6 \times 10^6$ colloids mL⁻¹).**

with the cover over the chamber, as shown in Fig. 1. This makes it implausible to invoke evaporation as the only significant driving force to explain the observed colloid deposition at the AWS interface.

Wan and Wilson's (1994a, 1994b) ground-breaking experiments should be credited for stimulating the discussion of colloid retention mechanisms in unsaturated media. That these early findings are being refined with better visualization equipment does not reduce the significance of their contributions. The aim of our 2004 manuscript was to facilitate this process by introducing a novel three-dimensional visualization system by employing translucent silica sand. We suggest, however, that readers who want to follow the advice of Wan and Tokunaga (2005) to "perform independent tests of their own" follow the procedures detailed in our recently published paper (Crist et al., 2005), or even better those in our most recent work (Zevi et al., 2005; contact us directly for additional experimental details when needed). These visualization tests can then also reveal under what conditions the conceptual model of film straining of Wan and Tokunaga (1997, depicted in Fig. 2) would be valid. We are not aware of any direct visual evidence of these interesting model conceptualizations.

## Acknowledgments

TAMMO S. STEENHUIS, JOHN F. MCCARTHY, JOHN T. CRIST,
YUNIATI ZEVI, PHILIPPE C. BAVEYE, JAMES A. THROOP,
ROSEMARIE L. FEHRMAN, ANNETTE DATHE,
AND BRIAN K. RICHARDS
*Biological and Environmental Engineering*
*Riley Robb Hall*
*Cornell University*
*Ithaca, NY 14853*
*tss1@cornell.edu*

## References

Crist, J.T., J.F. McCarthy, Y. Zevi, P.C. Baveye, J.A. Throop, and T.S. Steenhuis. 2004. Pore-scale visualization of colloid transport and retention in partly saturated porous media. Available at www.vadosezonejournal.org. Vadose Zone J. 3:444–450.

Crist, J.T., Y. Zevi, J.F. McCarthy, J.A. Throop, and T.S. Steenhuis. 2005. Transport and retention mechanisms of colloids in partially saturated porous media. Available at www.vadosezonejournal.org. Vadose Zone J. 4:184–195.

Wan, J., and T.K. Tokunaga. 2005. Comments on "Pore-scale visualization of colloid transport and retention in partly saturated porous media". Available at www.vadosezonejournal.org. Vadose Zone J. 4:954–956 (this issue).

Wan, J., and T.K. Tokunaga. 2002. Partitioning of clay colloids at air–water interfaces. J. Colloid Interface Sci. 247:54–61.

Wan, J.M., and T.K. Tokunaga. 1997. Film straining of colloids in unsaturated porous media: Conceptual model and experimental Environ. Sci. Technol. 31:2413–2420.

Wan, J., and J.L. Wilson. 1994a. Colloid transport in unsaturated porous-media. Water Resour. Res. 30:857–864.

Wan, J., and J.L. Wilson. 1994b. Visualization of the role of the gas-water interface on the fate and transport of colloids in porous-media. Water Resour. Res. 30:11–23.

Zevi, Y., A. Dathe, J.F. McCarthy, B.K. Richards, and T.S. Steenhuis. 2005. Distribution of colloid particles onto interfaces in partially saturated sand. Environ. Sci. Technol. (In press.)