Report for 2002WA19G: Using environmental tracers to improve prediction of nonpoint pollutant loadings from fields to streams at multiple watershed scales

Publications

- Conference Proceedings:
    - Allen-King, R., 2003, Ground and Surface Water Contributions to Chemical Mass Discharge: Field to Basin Scales, Keynote Address, "in" Abstracts, 4th Symposium on the Hydrogeology of Washington State, April 8-10 2003, Tacoma, Washington, p. 1. http://www.ecy.wa.gov/events/hg/PastSymposia/abstracts2003.pdf
    - Simmons, Amy N., Richelle M. Allen-King, C. Kent Keller, and Jeffrey L. Smith, 2003, Dissolved pesticide mass discharge in a semi-arid dryland agricultural watershed at the field and basin scale. Proceedings of the Fourth Symposium on the Hydrogeology of Washington State, April 8-10, 2003, Tacoma, Washington, p. 78. http://www.ecy.wa.gov/events/hg/abstracts_talks.htm
    - Suzuki, Kosuke, C. Kent Keller, and J. Vervoort, 2004. Weathering in and calcium losses from semi-arid agricultural landscapes: Insight from strontium isotope ratios, in EOS Transactions, American Geophysical Union 85(47), F873.
    - Wannamaker, Caroline N., Angela J. Goodwin, C. Kent Keller, Richelle Allen-King, and Jeffrey L. Smith, 2004. Edge of field nitrate loss and oxygen-18 dynamics in a dryland agriculture setting, in EOS Transactions, American Geophysical Union 85(47), F912.
    - Wannamaker, Caroline N., C. Kent Keller, Richelle M. Allen-King, and Jeffrey L. Smith. 2005. Edge of field nitrate loss in a dryland agricultural setting, "in" Abstracts, 5th Washington Hydrogeology Symposium, 12-14 April 2005, Tacoma, Washington, p. 92. http://www.ecy.wa.gov/events/hg/PastSymposia/abstracts2005.pdf
- Other Publications:
    - Keller, C.Kent, 2003, Using environmental tracers to understand agrichemical transport pathways to Palouse

surface water, Invited Presentation to WSU Water Quality Research and Extension Colloquium, April 24, 2003, Washington State University, Pullman, WA.
    - Simmons, A.N., Lauren L. Bissey, Richelle M. Allen-King, C.Kent Keller, and Jeffrey L. Smith, 2003, Estimated dissolved agricultural mass discharges using environmental tracers in a semi-arid dryland agricultural watershed (Abstract), "in" Abstracts with Programs, Geological Society of America Annual Meeting, November 2-5, 2003, Seattle, Washington, Abstracts with Programs 34(7), Paper No. 130-12, p. 316.
    - Keller, C.Kent. 2005. Hydrology of nitrate in Missouri Flat Creek Watershed, invited presentation to Washington State University Conference of Extension Personnel, Washington State University, Pullman, Washington, 2005.
    - Keller, C. Kent. 2005. Hydrology of nitrate in Missouri Flat Creek watershed, presentation to WSU Water Quality Research and Extension Colloquium, State of Washington Water Research Center and Cooperative Extension Water Quality Management Group, March 3, 2005.
    - Keller, C. Kent. 2005. Hydrologic elements of the N budget at Cunningham Farm, presented at WSU Field Day, Cunningham Agronomy Farm, 20 June 2005.
- Dissertations:
    - Simmons, Amy N., 2003, Dissolved Pesticide Mass Discharge in a Semi-arid Dryland Agricultural Watershed at the Field and Basin Scale, M.S. Dissertation, Department of Geology, Washington State University, Pullman, Washington, 165 pp.
    - Suzuki, Kosuke. 2005. Calcium losses from a semi-arid agricultural field: Insight from strontium isotopes, M.S. thesis, Department of Geology, Washington State University, Pullman, Washington, 62 pp.
    - Wannamaker, Caroline. 2005. Edge of field nitrate occurrence and loss in a semi-arid dryland agriculture setting, M.S. thesis, Department of Geology, Washington State University, Pullman, Washington, 174 pp.
    - Goodwin, Angela J. 2006. Oxygen-18 in surface and soil waters in a dryland agricultural setting, eastern Washington: Flow processes and mean residence times at various watershed scales. M.S. Thesis, Department of Geology, Washington State University, Pullman, Washington, 132 pp.
- Unclassified:

- Keller, C. Kent. 2005. N Pollution: Palouse perspective, hydrogeologic view, presented at WSU Soil Science Research Seminar, 12 September 2005.
- Keller, C. Kent. 2005. Nitrate in agricultural runoff on the Palouse, presented at FarWest Agribusiness Association Annual Palouse Agronomy Training, December 14 2005, Coeur d'Alene, Idaho.

Report Follows

PROBLEM AND RESEARCH OBJECTIVES

Post-WWII fertilization practices have loaded terrestrial and coastal ocean waters with N to unprecedented extents. In the US, tens of thousands of river and shore reaches are considered impaired by the EPA, and many of these impairments are believed to be attributable to agricultural non-point sources. This means that it is important to understand how agricultural practices are related to streamwater N loading, in various climate/cropping associations.

This study considers how field-scale processes influence delivery of nitrogen (primarily as dissolved nitrate, NO_3) to streams. We have hypothesized that in our semiarid dryland farming region, stream NO_3 discharge, from field and small catchment to basin scales, is principally controlled by the response of field-scale flow and transport processes to drainage regime and strongly seasonal hydrology. We are testing this hypothesis by expanding our ongoing study of field-scale processes to include undrained settings, and developing a spatially- and temporally-detailed ^{18}O data set which can be used, in parallel with geochemical data sets, for simultaneous isotope and geochemical hydrograph separations at multiple watershed scales. The isotope data are needed to identify water sources ("new" vs "old"). Used in combination with pathway information from the geochemical tracers, they will help us understand how temporal evolution of soil NO_3 distributions is related to transport times to streams.

METHODOLOGY

Our two field locations are near Pullman, WA, within the Missouri Flat Creek watershed of the South Fork of the Palouse River. The Missouri Flat Creek drainage has a long record of study by USGS and WSU scientists. The fields are subject to typical farming practices and crop rotation, receiving N fertilizer during fall and spring planting, and they represent typical bottom-slope, streamflow-generating locations. The undrained field exhibits intermittent winter-spring surface runoff while the tile-drained field does not. These fields represent the principal settings we assume to control streamflow generation and NO_3 discharges.

The tile-drained location was instrumented in 2001 with suction lysimeters (operated at 0.5 bar) and zero-tension pan lysimeters. These samplers were installed horiontally in triplicate at 0.2, 0.5, and 1.0 m depths from a trench (to permit location of sampler intakes beneath undisturbed field soil). They allow us to sample subsurface-pathway events (pans) as well as resident porewater over a range of saturation conditions (suction). In addition, depth profiles of 5 thermistors and 5 TDR moisture probes were installed via the trench wall. Data from these instruments are logged continuously by the weather station (with precip gauge/sampler) located nearby. With this array, we monitor subsurface conditions above a tile drain which drains approximately 10 ha and outlets 10 m distant. The undrained location has soil-water samplers in parallel with the tile-drained location.

Pressure transducers and dataloggers have been deployed and rating curves developed that measure water discharge from nested 660–7000 ha watersheds.

Conventional analytical methods are used to determine our principal geochemical tracer, electrical conductivity (EC). Each EC result is adjusted to eliminate the effect of NO_3 on that

result, so that EC may be taken as an index of weathering progress. Nitrate itself is determined colorimetrically. Oxygen-18 (O-18) is determined by Delta S dual-inlet MS with continuous-flow GasBench autosampler/equilibrator in the Geoanalytical Lab at Washington State Unversity. Its abundance is reported in conventional "δ" per mil notation relative to VSMOW. Strontium stable isotope ratios were determined on column-purified samples redissolved in nitric acid, by Finnigan Neptune MC-ICP-MS in the Geoanalytical Lab.

PRINCIPAL FINDINGS AND SIGNIFICANCE

Again during this reporting period all datasets were extended. Much student and PI effort was devoted to interpretation and writing. Three theses were defended during the current reporting period. This project has now generated four MS theses.

Analysis of TDR, flow and NO_3 concentration data shows that at all gaging stations, NO_3 levels rise immediately upon soil profile wetup and streamflow initiation in the wet season. This implies the existence of a reservoir of dissolved NO_3 which is present both throughout soil profiles (to depths of tile drains) and pervasively across the MFC watershed. However the transport history of that nitrate, in particular the rate of its movement through and extent of its reaction with soil and biota, could not be estimated in that analysis. In other words, we could not answer the questions "How long has that nitrate been in the soil system? When was it applied as fertilizer?"

Most of this period's analysis was devoted to using O-18 data to constrain the mean residence times (MRT) of the waters which carry dissolved NO_3 through soils. These times then provide minimum NO_3 residence times and maximum NO_3 transport rates, assuming NO_3 moves conservatively with soil water. The operating principle, in this application of O-18 as environmental tracer, is to track seasonal variations of its abundance through the watershed of interest, examining how the timing of the variations changes between precipitation source and gauging-station outflow.

The global gauging-station dataset (Figure 1) shows definite O-18 "troughs" occurring during three of the five flow seasons analyzed. The 2002-2003 water year (no "trough" evident) was relatively warm such that volume-weighted precipitation O-18 levels were two per mil greater than during the following, relatively cold water year 2003-2004 when a deep "trough" developed. The magnitude of this trough (and of the others) is approximately that of the decrease in precipitation O-18, relative to the previous year. The implication is that a water-year's outflow carries carries the O-18 imprint of precipitation which falls that same water year, i.e. water MRT in the catchments of interest are on the order of months or less, rather than a year or more. We tested this idea using simple lumped-parameter convolution-integral simulations of catchment O-18 response to precipitation input. The best simulations were based on response functions with MRT set at 4-7 months, which is consistent with the qualitative interpretation.

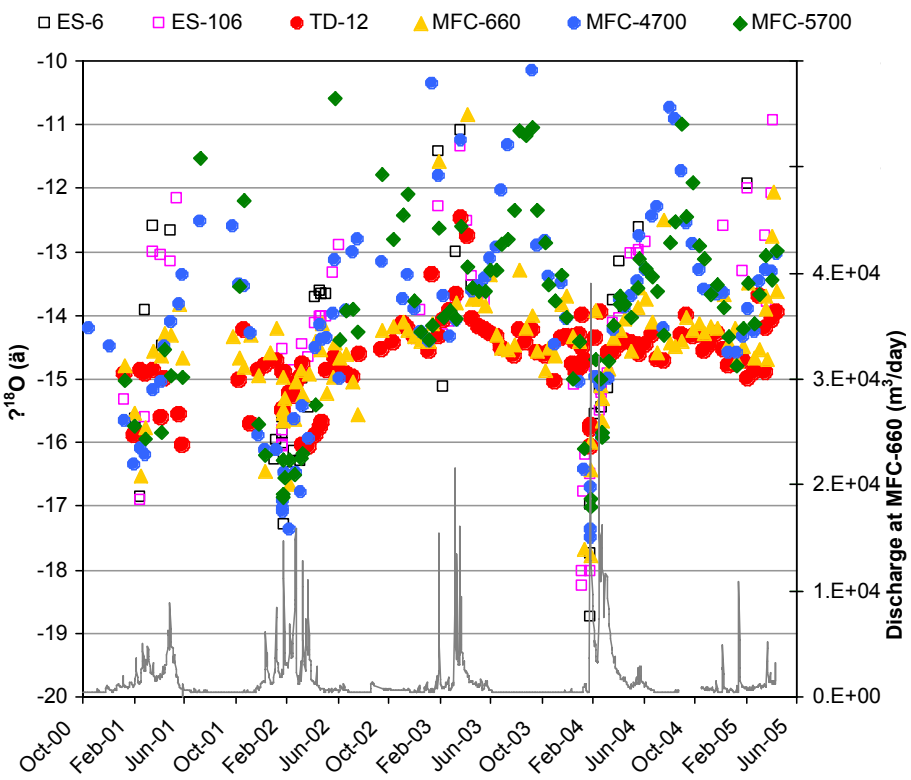

Figure 1. δ ^{18}O values for all gauging stations, plotted vs. discharge at one station. Numbers in legend refer to estimated catchment areas in hectares, e.g. the tile drain "TD-12" drains 12 ha. ES stations are within fields.

Especially at the largest gauging scales, upward excursions of O-18 values occurred during dry-season, low-flow periods (Figure 1). These values and the accompanying EC values for the same samples are higher than what we observe in any of our soil waters or groundwaters. We therefore attribute these dry-season dynamics to instream processes, probably dominated by evaporation.

Tile-drain runoff from the drained location (TD-12, Figure 2) exhibited steadier O-18 behavior than at any other gauging station, and was much steadier than runoff generated in an ephemeral rill from the nearby undrained location (ES-6, Figure 3). In the latter setting soil-water O-18 dynamics, as shown by the lysimeters, were more effectively propagated to runoff than in the tile-drained setting. This comparison shows that the O-18 dynamics at larger gauging scales (Figure 1) require a substantial component of runoff like that generated at ES-6, i.e. much of the runoff from our fields follows relatively shallow, short flow paths characteristic of our undrained location. This is consistent with findings of our earlier hydrograph-separation studies.

We now know with reasonable confidence that water movement through the study catchments could transport NO_3 , from point of fall field application to where we find it in stream runoff, in a single season. We do not yet know whether that is in fact the characteristic fate of most of the NO_3 in our systems, because the mass which is discharged to runoff may have undergone reactions – particularly biological uptake and re-release – in the subsurface. We plan

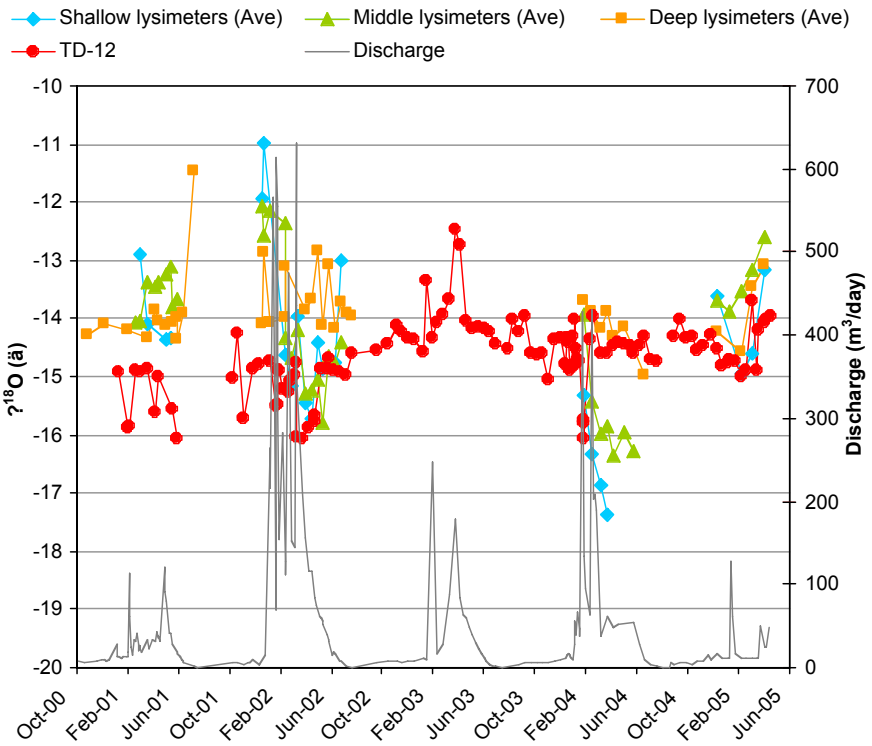

Figure 2. δ ^{18}O values for the drained location. TD-12 data are from Figure 1; Depths of soil-water lysimetric samplers are 25 cm (shallow), 40 cm (middle), and 85 cm (deep). "Ave" indicates average of replicated samplers yielding water on a given date.

We plan to investigate this issue by observation of the isotopic composition of the oxygen and nitrogen of the NO_3 itself. That work is beyond the scope of this project.

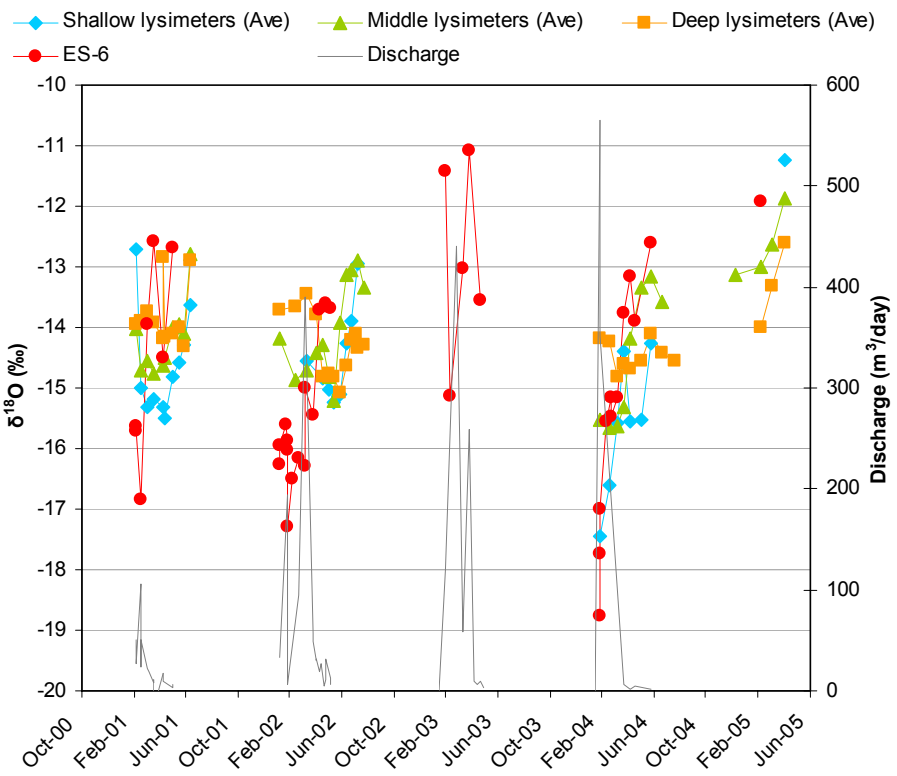

Figure 3. δ ^{18}O values for the drained location. TD-12 data are from Figure 1; Depths of soil-water lysimetric samplers are 25 cm (shallow), 40 cm (middle), and 85 cm (deep). "Ave" indicates average of replicated samplers yielding water on a given date.