# Report for 2003WA40B: Non-point Pesticide Transport from Fields to Streams: Testing the Predictive Capability of a Geochemical Tracer Approach

- Water Resources Research Institute Reports:
  - Allen-King, Richelle and C. Kent Keller, 2004, Non-point Pesticide Transport from Fields to Streams: Testing the Predictive Capability of a Geochemical Tracer Approach. State of Washington Water Research Center, Washington State University, Pullman, Washington, State of Washington Water Research Center Report WRR-19, 39pp.
- Conference Proceedings:
  - Simmons, A. N., L. L. Bissey, R. M. Allen-King, C.K. Keller, J. L. Smith, 2003, Estimated dissolved agricultural mass discharges using environmental tracers in a semi-arid dryland agricultural watershed (Abstract), "in" Geological Society of America Abstracts with Programs, 35(6): page 316, Abstract No. 130-12.

Report Follows

**Problem and Research Objectives**

Forecasting from previous research in the Palouse basin indicates that lindane concentrations in surface runoff should decrease significantly following the relatively step-wise decrease in use of this chemical in the 2002 water year. A log-linear decline in surface runoff lindane concentrations characterized by an approximately 129 day half-life in an individual field over two years of study followed a single fall application[*1*]. The overall goal of this project was to measure the response of the stream system to the relatively step-wise change in application practice on total pesticide stream discharge over multiple catchment scales.

**Methodology**

***Field Area Description***

The research was conducted in the Missouri Flat Creek Watershed (MFC), a semi-arid agricultural watershed, near Pullman, Washington at N 46 43'40" latitude and W 117 11'30" longitude. Annual precipitation for the region is 31-58 cm/yr [*2*] with the average near the Cunningham Agronomy Farm (CAF) of 56 cm [*3*]. Undulating hills and basins of wind-blown loess deposited over basalt dominate the topography. The annual mean summer and winter temperatures are 27$^{o}$C and -7$^{o}$C, respectively [*3*]. The soils of the Palouse area, MFC, and CAF are comprised of mostly silt loam type soils [*4*].

Because lindane is applied as a seed treatment, local seed company trends give a good indication of lindane use in the area. Whitman County seed distributors and chemical sales representatives were contacted to obtain information about lindane applied to seeds to be used in the 2002 water year (WY, Fall 2002 and Spring 2003 crops). Whitman County Growers, Inc., indicated that 60-70% of winter wheat sold during fall 2002 was treated with “Cruiser” instead of lindane (G. Hatley, Pers. Comm., Oct. 11, 2002). Columbia Grain International used “Cruiser” on all seeds instead of lindane unless the farmers specifically requested lindane (K. Moser, Pers. Comm., Oct. 11, 2002). However, representatives from the Gustafson, the producer and distributer of lindane and ‘Gaucho’ (one of the replacement chemicals), stated that they had not observed a decline in lindane sales in the Palouse region during fall 2002 (S. Mansker, Oct 28, 2002, pers. comm.; N. Anderson, Nov. 4, 2002, pers. comm.). During the two years prior to fall 2002, most crops planted in the region were treated with lindane prior to planting (Simmons, 2003). While the lindane application information is not completely consistent between the seed distributors versus lindane distributors, the information presented is consistent among the seed distributors suggesting that lindane use likely declined significantly between the 2001 and 2002 WYs.

Traditionally, triallate is applied to 7% of wheat, barley, and pea crops planted annually in Whitman County [*1*]. In Whitman County, triallate was applied to 10% of winter wheat, 85% of spring barley, peas, lentils, and garbanzos for the 2002 WY.

Triallate was applied to almost the entire CAF in October 2000 using an application rate of 1.5lbs/acre[*1*]. Lindane was applied as a seed treatment to all crops (with the exception of winter and spring canola) planted on CAF during the 2000-2001 water years [*1*]. The WSU seed house (which provided some of the wheat seeds at CAF) bought no seeds that were treated with lindane for the 2002 WY (Pers. Comm., Nov. 5, 2002). Pesticide application data confirms that no lindane was used on seeds planted at CAF for the 2002 WY. Pesticide application data also shows that triallate has not been applied to CAF fields since the 2000 WY ([*1*])

***Sampling Locations***

Stream samples were collected at four locations within the MFC drainage and a tile drain. Samples were collected from a tile drained field (location TD-12) and an ephemeral stream at a non-tile drained field (ES-6) within the CAF. The ephemeral stream draining a single field discharges into an ephemeral stream that drains several fields (ES-106). The smallest watershed scale sampling location is called ES-6, and is a naturally occurring ephemeral stream that flows on 6 hectares of CAF that is not tile drained. The tile drain (TD-12) is installed at a depth of approximately one meter on another CAF cropped field. The 660 ha sampling location (MFC-660) gains water from both the instrumented tile-drained and non-tile drained fields, and is located at a culvert that feeds into MFC. The area of the largest watershed scale sampling location (MFC-4700) is 4700 ha and is located on MFC.

***Sample Collection and Analysis***

Tile drain and surface water samples were collected fortnightly during the 2002 WY. Surface water sample collection/filtration methods are consistent with recommended United States Geological Survey (USGS) methods [*5*]. During field collection, pesticide samples are filtered in the field (weather permitting). Samples for triallate and lindane analysis were passed through a through a pre-baked, in-line, glass fiber membrane (0.7 μm pore size) in a stainless steel holder, directly into a 30 ml borosilicate glass vial, and sealed with a PTFE lined silicone septa. Pesticide samples were refrigerated until analysis.

All samples were analyzed for the pesticides triallate and lindane, electrical conductivity (EC), and turbidity. Electrical conductivity and turbidity were measured in the laboratory immediately after sampling using an Orion® temperature compensated probe and a Hach® 2100P portable turbidimeter, respectively. Silica concentrations are going to be determined in the near future. Silica concentrations will be determined by spectrophotometric methods [*6*]. Pesticides were analyzed using solid-phase microextraction (SPME) and gas chromatography with electron capture detection according to previously established methods [*1,7*]. The ascribed non-detectable value of the pesticides of interest is 0.005μg/L. All of our field blanks, with the exception of a triallate value of 0.007μg/L on February 28, 2003 contained no detectable lindane or triallate. All triallate concentrations in all field samples collected on February 28, 2003 were greater than the limit of detection.

We performed six and nine field sample duplicate pesticide analyses for lindane and triallate, respectively. The average percent differences between the pairs were 13.6% and 18.9% for lindane and triallate, respectively. The initial analysis of one sample collected on July 4, 2003 contained no detectable lindane or triallate and 0.007 μg/L and 0.014 μg/L for lindane and triallate, respectively, in the duplicate analysis. The initial reports less than detectable concentrations are ascribed to sample processing error. The detected concentrations are assumed correct because these pesticides were detected in all other surface samples collected on the same date.

**Principal Findings and Significance**

Strong seasonal trends were observed for both triallate and lindane at all drainage scales with greater concentrations observed during the winter and spring, wet seasons, compared to the summer dry period.

At MFC-660 and MFC-4700, the data indicate that the lindane concentration has declined compared to the triallate concentration during the most recent WY compared to prior years. At both of these locations, which integrate over many fields and much of Whitman county, respectively, the mean, median, minimum, maximum and geometric mean of the lindane concentration:triallate concentration ratio for all samples was lower in the 2002 compared to the 2001 WY (Tables 1 and 2). The geometric mean lindane concentration (Table 1) and frequency of lindane detection declined at MFC-660 (60% during the 2002 WR compared to 79% in the 2001 WR) while the mean detected triallate concentration (Table 1) and frequency of triallate detection remained essentially constant over the three water years (detection in 73-75% of samples). The mean lindane concentration and frequency of lindane detection also declined at MFC-4700 (42% during the 2003 WR compared to

84% in the 2002 WR) while the mean detected triallate concentration and frequency of triallate detection remained essentially constant over these same two water years (Table 2).

Contrary to the data at the larger scales of MFC-4700 and MFC-660, the data at ES-106 suggests an increase in lindane concentrations with respect to triallate concentrations. At the ES-106 location, the mean, median, and geometric mean of the lindane concentration:triallate concentration ratio increased from the 2000-2002 WYs (Table 3). The geometric mean lindane and triallate concentrations at ES-106 decreased over the three years but the detection frequency remained relatively constant with both chemicals detected in nearly all of the samples collected. It appears that the difference in the concentration ratio trend in the smaller drainage compared to the larger drainages is associated with a more rapid decline in the triallate concentration compared to the lindane concentration at the ES-106 location. Behavior within the smaller drainages more closely reflects application patterns specific to the fields whereas the larger drainages integrate over many fields.


(1) Simmons, A. N., *Dissolved pesticide mass discharge in a semi-arid dryland agricultural watershed at the field and basin scale,* M.S., 2003, Washington State University, Pullman, WA, pp.

(2) Donaldson, N. C. *Soil survey of Whitman County, Washington*; U.S. Department of Agriculture, 1980.

(3) Geyer, D. J.; Keller, C. K.; Smith, J. L.; Johnstone, D. L. *Journal of Contaminant Hydrology* **1992**, *11*, 127-147.

(4) Allen-King, R. M.; Keller, C. K.; Barber, M. E.; Flury, M.; Smith, J. L. "Surface and Subsurface Transport Pathways of Non-Point Agricultural Pollutants: Analysis of the Problem over Four Decades of Basin Scale," Washington, State of Washington Water Research Center Report No. WRR-12, State of Washington Water Research Center, Washington State University, Pullman, WA, 2002, 84 pp.

(5) Shelton, L. R. *Field guide for collection and processing stream-water samples for the National Water-Quality Assessment Program*; Sacramento, CA U.S. Geological Survey: Denver, CO, 1994.

(6) APHA; (American Public Health Association); AWWA (American Water Works Association); WPCA (Water Pollution Control Federation) *Standard Methods for the Examination of Water and Wastewater*; 15th ed., 1981.

(7) Schaumloffel, J. C.; Allen-King, R. M.; Talmage, D. In *Abstracts Of Papers Of The American Chemical Society*, 2000; Vol. 220, p U83.

Table 1 -Lindane concentration: triallate concentration ratios for 2000-2002 water years at MFC-660. Only samples with detectable lindane or triallate were included in the statistics describing the concentration ratios.

| | 2000 | 2001 | 2002 |
|---|---|---|---|
| m | 15 | 28 | 15 |
| mean (lindane):(triallate) | 0.83 | 1.51 | 0.62 |
| median (lindane):(triallate) | 0.73 | 0.90 | 0.58 |
| minimum (lindane):(triallate) | 0.19 | 0.36 | 0.07 |
| maximum (lindane):(triallate) | 1.74 | 8.80 | 2.15 |
| geometric mean (lindane):(triallate) | 0.73 | 0.99 | 0.44 |
| n | 12 | 23 | 11 |
| geomean detectable (lindane)* | 0.019 | 0.019 | 0.011 |
| m" | 10 | 22 | 9 |
| geomean detectable (triallate)* | 0.024 | 0.020 | 0.021 |
| m" | 11 | 21 | 11 |

m=total number of samples
n=samples with detectable concentrations of lindane or triallate
*Only m' or m" samples with detectable lindane and triallate, respectively, included.

Table 2 -Lindane concentration : triallate concentration ratios for 2000-2002 water years at MFC-4700. Only samples with detectable lindane or triallate were included in the statistics describing the concentration ratios.

| | 2000 | 2001 | 2002 |
|---|---|---|---|
| m | 14 | 25 | 19 |
| mean (lindane):(triallate) | 1.06 | 1.23 | 0.47 |
| median (lindane):(triallate) | 0.87 | 0.96 | 0.41 |
| minimum (lindane):(triallate) | 0.55 | 0.13 | 0.01 |
| maximum (lindane):(triallate) | 2.04 | 5.09 | 1.42 |
| geometric mean (lindane):(triallate) | 0.95 | 0.94 | 0.26 |
| n | 8 | 22 | 12 |
| geomean detectable (lindane)* | 0.017 | 0.021 | 0.012 |
| m" | 7 | 21 | 8 |
| geomean detectable (triallate)* | 0.018 | 0.032 | 0.036 |
| m" | 7 | 17 | 12 |

m=total number of samples
n=samples with detectable concentrations of lindane or triallate.
*Only m' or m" samples with detectable lindane and triallate, respectively, included.

Table 3 -Lindane concentration: triallate concentration ratios for 2000-2002 water years at ES-106. Only samples with detectable lindane or triallate were included in the statistics describing the concentration ratios.

| | 2000 | 2001 | 2002 |
|---|---|---|---|
| m | 7 | 19 | 9 |
| mean (lindane):(triallate) | 0.58 | 0.97 | 1.41 |
| median (lindane):(triallate) | 0.41 | 0.54 | 1.21 |
| minimum (lindane):(triallate) | 0.24 | 0.21 | 0.15 |
| maximum (lindane):(triallate) | 1.28 | 4.75 | 3.56 |
| geometric mean (lindane):(triallate) | 0.48 | 0.69 | 0.97 |
| n | 7 | 19 | 9 |
| geomean detectable (lindane)* | 0.109 | 0.032 | 0.016 |
| m' | 7 | 19 | 9 |
| geomean detectable (triallate)* | 0.228 | 0.047 | 0.019 |
| m'' | 7 | 19 | 8 |

m=total number of samples
n=samples with detectable concentrations of lindane or triallate
*Only m' or m'' samples with detectable lindane and triallate, respectively, included