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Title: Fate and Transport of Herbicides and Their Transformation Products in the Potomac River Basin, Virginia, USA

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ABSTRACT

FATE AND TRANSPORT OF HERBICIDES AND THEIR TRANSFORMATION PRODUCTS IN THE POTOMAC RIVER BASIN, VIRGINIA, USA

This study is comprised of three projects designed to characterize the fate and transport of S-triazine herbicides (e.g., atrazine), chloroacetanilide herbicides (e.g., metolachlor) and the transformation products (TPs) of those herbicides in surface waters of the Potomac River watershed in Virginia. The projects include instrumental-method development, field-method development and long-term implementation of those methods in a twelve month study on the North Fork of the Shenandoah River.

The goal of project 1 was to develop a robust method of analyzing surface water samples for the target analytes using solid-phase extraction (SPE) cartridges and a single quadrupole LC-MS system. Estimated method detection limits averaged 0.3 ± 0.1 ng L⁻¹. Spike recoveries ranged from $94.2\% \pm 4.8\%$ for S-triazines and their TPs

and $95.9\% \pm 19\%$ for chloroacetanilides and their TPs, thus qualifying the method for instrumental analysis.

The goal of project 2 was to develop field sampling protocols by examining the temporal changes in the seasonally applied herbicides over a seven month period and relating those changes to spatial variables in the upper Shenandoah River basin and in Cedar Run, both tributaries to the Potomac River. TP concentrations increased rapidly following the application period. Substantial differences in TP to atrazine ratios distinguished the Shenandoah River from the Cedar Run basin. Principal component analysis showed that concentration did not correlate well with river flow (discharge).

The goal of the third project was to characterize the major biogeochemical processes in a river system located in the western section of Virginia. Surface water samples were obtained during 14 sampling trips over a 12 month period beginning on 29 March 2008 and culminating on 28 February 2009 from 4 sites along the North Fork of the Shenandoah River in Virginia. Detection frequencies were 100% for five of the target analytes. The desethylatrazine to atrazine concentration ratio (DAR) increased linearly over the study period with a value of ~ 0.4 at the spring flush period to ~ 2.5 at the end of the study. Transformation rates for S-triazines ranged from 0.025 to 0.031 d^{-1} . The removal rates for total herbicide concentrations ranged from 0.019 to 0.050 d^{-1} . Steady-state concentrations for 3 of the 4 sites were above 100 $ng L^{-1}$.

The instrumental and field methods developed in this study proved effective and a long term study using those methods successfully characterized the primary processes affecting the fate and transport of these herbicides in an important surface water system.