

# PLAN OF STUDY TO DETERMINE THE EFFECT OF CHANGES IN HERBICIDE USE ON HERBICIDE CONCENTRATIONS IN MIDWESTERN STREAMS, 1989-94

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## ABSTRACT

An approach was developed to determine if recent changes in the use of herbicides has affected herbicide concentrations in Midwestern streams. This approach also provides a plan to determine if the abnormally high rainfall and flooding in 1993 has an effect on nitrate concentrations in 1994 in streams that flooded in 1993. The approach involves sampling 53 stream sites, 50 of which were sampled in 1989 and 1990 as part of a reconnaissance to determine the geographic and seasonal distribution of herbicides in 10 Midwestern States. Sites will be sampled twice, once prior to application of herbicides, in March or early April, and once during the first runoff event after application of herbicides. Samples will be analyzed for 11 herbicide and 2 atrazine metabolites by gas chromatography/mass spectrometry. Samples will also be analyzed for ESA (an alachlor metabolite), two cyanazine metabolites, and nutrients.

Changes to the manufacturers' label have decreased the maximum recommended application rate for atrazine on corn and sorghum by about 50 percent since the 1989-90 study. Conversely, the use of other herbicides, such as cyanazine, has increased by more than 25 percent since 1989. Statistical procedures such as Wilcoxon signed rank tests for paired samples will be used to determine if the distributions of herbicide and nitrate concentrations in 1994 are different from those measured in 1989 and 1990.

## INTRODUCTION

In 1989 the U.S. Geological Survey (USGS) Toxic Substances Hydrology Program conducted a reconnaissance of about 150 streams in 10 Midwestern States to determine the geographic and seasonal distribution of herbicides. These streams were sampled three times: (1) before application, (2) during the first major runoff event after application, and (3) during low flow in the fall. Results from the study showed that large amounts of atrazine, cyanazine, alachlor, and metolachlor were flushed into streams during the first post-application runoff event (Thurman and others, 1991, 1992; Goolsby and Battaglin, 1993). Both atrazine and cyanazine temporarily exceeded health-based limits in about one-half of the streams. The atrazine maximum contaminant level (MCL) is 3  $\mu\text{g}/\text{L}$  (micrograms per liter); the cyanazine health advisory (HA) is 1  $\mu\text{g}/\text{L}$ . In addition, alachlor temporarily exceeded the alachlor MCL of 2  $\mu\text{g}/\text{L}$  in about 35 percent of the streams. Although the concentrations of some herbicides exceeded MCLs in some of the post-application samples, this does not necessarily constitute a violation of the Safe Drinking Water Act (SDWA). A violation occurs only if the average annual concentration exceeds the MCL or if the herbicide concentration in a single sample is more than four times the MCL. Thus, samples with atrazine concentrations exceeding 12  $\mu\text{g}/\text{L}$  or alachlor concentrations exceeding 8  $\mu\text{g}/\text{L}$  may represent violations of the SDWA if the water is used for public supply. About 25 percent of the samples collected during the post-application period had atrazine concentrations larger than four times the MCL and about 15 percent had alachlor concentrations larger than four times the MCL (fig. 1). Cyanazine has a nonenforceable HA of 1  $\mu\text{g}/\text{L}$ ; the