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A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry

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■ Preemergent herbicides and their metabolites, particularly atrazine, deethylatrazine, and metolachlor, persisted from 1989 to 1990 in the majority of rivers and streams in the midwestern United States. In spring, after the application of herbicides, the concentrations of atrazine, alachlor, and simazine were frequently 3–10 times greater than the U.S. Environmental Protection Agency maximum contaminant level (MCL). The concentration of herbicides exceeded the MCLs both singly and in combination. Two major degradation products of atrazine (deisopropylatrazine and deethylatrazine) also were found in many of the streams. The order of persistence of the herbicides and their metabolites in surface water was atrazine > deethylatrazine > metolachlor > alachlor > deisopropylatrazine > cyanazine. Storm runoff collected at several sites exceeded the MCL multiple times during the summer months as a function of stream discharge, with increased concentrations during times of increased streamflow. It is proposed that metabolites of atrazine may be used as indicators of surface-water movement into adjacent alluvial aquifers.

Introduction

Agricultural practices may cause widespread degradation of water quality in the midwestern United States (*1*, *2*). Approximately three-fourths of all preemergent herbicides used in the United States are applied to row crops in a 12-state area, which is a major part of the "Corn and Soybean Belt" (*3*). Because many herbicides are partially water soluble, they may leach into groundwater and surface water (*4*), as well as be transported aerially and occur in precipitation (*5*, *6*). Monitoring studies in the Midwest have shown widespread detection of herbicides in groundwater (*7*) and in surface water (*8*–*10*). Runoff from fields immediately after herbicide application results in substantial increases in herbicide concentrations in streams, which are reflected in increased concentrations in large rivers, such as the Mississippi (*11*). Furthermore, conventional water-treatment practices do not remove these soluble herbicides (*12*, *13*), which then affect drinking-water quality. Herbicides also may have deleterious effects on aquatic vegetation (*14*–*17*).

In spite of these documented problems, the use of herbicides has become a standard practice for profitable row-crop farming in the United States, and elimination of herbicide use could create economic hardship for many farmers (*18*). Thus, it is important to understand the effects of herbicides on water quality. By water quality we mean the value of water as a resource for human and animal consumption, the ecological value of water, and the aesthetics of clean water (*19*). More data are needed to understand how herbicides affect water quality on a regional scale and throughout the hydrologic cycle. New analytical methods, such as immunoassay (*20*–*22*), enable analyses to be accomplished quickly and inexpensively. Furthermore, the results of these analyses may be mapped to understand herbicide distribution and transport. Geographic information systems (GIS) are new computer tools that make this mapping feasible. We combine these new analytical methods and mapping tools in a study of herbicide distribution and transport in the midwestern United States.

Our objective was to examine the effect of herbicides on regional surface-water quality, a scale at which little documentation exists (*8*). More specific objectives were to (1) test immunoassay with confirmation by gas chromatography/mass spectrometry (GC/MS) as an analytical tool for studying herbicide transport in the "Corn Belt", (*2*) compare herbicide concentrations in streams and rivers at a regional scale to Federal drinking-water standards, (*3*) examine the annual persistence of herbicides and their metabolites in surface water, and (*4*) assess whether metabolites of atrazine may be used as indicators of surface-water and groundwater interaction.

Sampling and Study Area

Water samples were collected at 149 reconnaissance sites in 122 hydrologic basins in a 10-state area (Figure 1A), which is a major part of the Corn and Soybean Belt. The states included Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin. A stratified random-sampling procedure ensured adequate geographic distribution. The number of sites per state was proportional to corn and soybean production, and sites were chosen randomly by county. Water samples were collected during March and April (preplanting), May and June (postplanting), and October and November (harvest) of 1989 at U.S. Geological Survey streamflow-gaging stations. Fifty sites were resampled with a stratified random procedure for both pre- and postapplication in 1990 to verify the 1989 results. Drainage areas of the selected basins range from 260 to more than 160 000 km^2, and collectively the basins drain more than 500 000 km^2 of the Midwest (Figure 1A).

All water samples were collected by depth-integrating techniques at three to five locations across each stream. The samples were collected and composited in large glass

