Watershed monitoring to address contamination source issues and remediation of the contaminant impairments

P.L. Barnes* and P.K. Kalita**

*Department of Biological and Agricultural Engineering, Kansas State University, Manhattan, Kansas 66506, USA (E-mail: lbarnes@ksu.edu)

**Department of Agricultural Engineering, University of Illinois-Urbana-Champaign, Urbana, Illinois 61801, USA (E-mail: pkalita@uiuc.edu)

Abstract  The Big Blue River Basin is located in southeastern Nebraska and northeastern Kansas and consists of surface water in the Big Blue River, Little Blue River, Black Vermillion River, and various tributaries draining 24,968 km². Approximately 75% of the land area in the basin are cultivated cropland. The Big Blue River flows into Tuttle Creek Reservoir near Manhattan, Kansas. Releases from the lake are used to maintain streamflow in the Kansas River during low flow periods, contributing 27% of the mean flow rate of the Kansas River at its confluence with the Missouri River. Tuttle Creek Reservoir and the Kansas River are used as sources of public drinking water and meet many of the municipal drinking water supply needs of the urban population in Kansas from Junction City to Kansas City. Elevated concentrations of pesticides in the Big Blue River Basin are of growing concern in Kansas and Nebraska as concentrations may be exceeding public drinking water standards and water quality criteria for the protection of aquatic life. Pesticides cause significant problems for municipal water treatment plants in Kansas, as they are not appreciably removed during conventional water treatment processes unless activated carbon filtering is used. Pesticides have been detected during all months of the year with concentrations ranging up to 200 µg/l. If high concentration in water is associated with high flow conditions then large mass losses of pesticides can flow into the water supplies in this basin. This paper will investigate the use of a monitoring program to assess the non-point source of this atrazine contamination. Several practices will be examined that have shown ability to remediate or prevent these impairments.

Keywords  Best management practices; maximum contaminant level; non-point pollution; total maximum daily loading

Introduction

Atrazine herbicide (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been used widely in Kansas and Nebraska since the 1960s for selective control of broadleaf and grass weeds in corn (Zea mays L.) and grain sorghum (Sorghum vulgare (L.) Moench). Another factor along with atrazine effectiveness is the low cost on a per-hectare basis. It provides effective weed control when applied to fields under a wide range of practices that includes conventional tillage with limited residue cover as well as fields with residue levels near complete cover with no tillage. Added benefits include application flexibility which might include the herbicide applied at an early pre-plant, pre-plant incorporated, crop pre-emergence, or post-emergence. The impact of atrazine use in agriculture on water quality is a growing public concern.

Concerns about pesticides in the environment has caused the United States Congress in 1977 to amend the 1972 Federal Water Pollution Control Act into what is know as the Clean Water Act (CWA). This act sets the basic structure for regulating discharges of pollutants to waters of the United States. The law gave the Environmental Protection Agency (EPA) the authority to set effluent standards on an industry basis (technology-based) and continued the requirements to set water quality standards for all contaminants in surface waters. The CWA makes it unlawful for any person to discharge any pollutant from a point source into
navigable water unless permitted by the Act. The 1977 amendments focused on toxic pollutants. In 1987, the CWA was reauthorized and again focused on toxic substances and authorized citizen lawsuit provisions. Since then, the EPA, states, and others have been attempting to implement the Act’s many programs and additions mandated in the law. Changes allowing citizen lawsuits have led to many court cases challenging the EPA and the state’s progress on these programs.

During 1992, the EPA established a new drinking water standard for atrazine, which prior to that date had been proposed to be 150 g/l. This new standard called the maximum contaminant level (MCL) was set at 3 g/l. The MCL is calculated based on an annual average of available monitoring data. Limited monitoring data in Kansas indicated that a majority of the state surface water in streams and lakes exceeded the new MCL. The Kansas legislature developed legislation to address this water quality concern. The Kansas Department of Agriculture (KDOA) was ordered to develop pesticide management areas (PMAs) when notified by the EPA or the Kansas Department of Health and Environment (KDHE) that a pesticide posed a serious threat to the public health, safety and welfare or to the natural resources of the state. Such areas are developed upon examination of precipitation, topography, soils and depths to groundwater and are designated as permitted, modified or prohibited in the use of certain types of pesticides. The PMA has several components that include a technical advisory committee to establish boundaries and management plans for the proposed area. Other components include detailed monitoring used to identify sources of the contamination and an educational extension program to develop management programs to reduce or eliminate the source of the contamination. An audit of the monitoring data during 1998, showed that only six Kansas lakes continued to show impairment from atrazine.

Section 303(d) of the CWA calls for each state to identify those waters within its boundaries for which effluent limitations are not stringent enough to implement any water quality standard applicable to such waters. The state also priority ranks those waters, accounting for the severity of the pollution and the uses to be made of the waters. For those identified waters, the state is to establish the total maximum daily load (TMDL) for those pollutants causing the non-attainment of the water quality standards. Such loads are to be established at a level necessary to implement the applicable water quality standard with seasonal variations and a margin of safety, which accounts for uncertainty concerning the relationship between effluent limitations and water quality.

On 1 November 1995, the Kansas Natural Resource Council and the Sierra Club filed a complaint against the EPA, compelling it to enforce Section 303(d) of the CWA by establishing TMDLs for impaired water bodies in Kansas. Each pollutant source contributing to the deviation from the water quality standards will be identified and their relative contribution to the impaired situation will be determined. Based on the flow-load analysis, judgments can be made on the degree of point and non-point sources contributing to the current condition. The number of sources, their geographic location along the segment or within the watershed, the type of source, the magnitude of their potential pollutant loading and their degree of influence on water quality will be identified. For non-point sources, information will be gathered on the land uses within the watershed, such as topography and soil features. Other information will include likely contributing areas producing runoff, percent of impervious area within the watershed producing storm water discharges, stream-aquifer interaction, existing management practices in place and the limits of those practices to influence hydrologic extremes, and types of water use present along the streams and lakes.

The Big Blue River Basin is located in southeastern Nebraska and northeastern Kansas and consists of surface water in the Big Blue River, Little Blue River, Black Vermillion River, and various tributaries draining 25,900 km². Approximately 75% of the land area in
the basin are cultivated cropland. The Big Blue River flows into Tuttle Creek Reservoir near Manhattan, Kansas. Releases from the lake are used to maintain streamflow in the Kansas River during low flow periods, contributing 27% of the mean flow rate of the Kansas River at its confluence with the Missouri River (Dugan et al., 1991). The largest population centers in Kansas are supplied by surface water from the Kansas River. The CWA monitoring for this water supply has consistently exceeded the drinking water standard for atrazine. This monitoring requires at least an annual quarterly sample to be taken for these drinking water supplies. These data would indicate that in most cases quarterly monitoring does not accurately represent conditions in the water supply.

This paper will investigate the use of a monitoring program to assess the non-point sources of this atrazine contamination. Several practices will be examined that have shown ability to remediate or prevent these impairments.

**Monitoring methods**

The objectives of this study will provide information that can be used to:

- determine seasonal and annual concentrations of atrazine;
- determine seasonal and annual loading of atrazine;
- rank locations in the watersheds based on their contribution to the TMDL. The project objectives will be met by collecting and analysing water samples from ten stream sites in the Big Blue River Basin. Table 1 describes these sampling locations.

Elevated concentrations of atrazine in the Big Blue River Basin are of growing concern in Kansas and Nebraska as concentrations have been shown to exceed the public drinking water standards and water quality criteria for the protection of aquatic life. Atrazine causes significant problems for municipal water treatment plants in Kansas as it is not appreciably removed during conventional water treatment processes unless activated carbon filtering is used (Miltner et al., 1989). Atrazine has been detected during all months of the year in the Big Blue Basin with concentrations ranging from 0.1 to 166 g/l in Nebraska from 1987 to 1992 (Frankforter, 1994). More recently, in the Recharge Lake watershed near York, Nebraska, atrazine concentrations as high as 854 g/l were detected following a May 1995 runoff event (Upper Big Blue NRD, 1995).

Sample collection included a protocol of grab sampling when stream flows were at or below normal base flows. Grab samples were collected at each site on a stratified fixed-frequency basis. Grab samples were collected instead of width-depth integrated samples because grab samples greatly reduce sample time and effort and were considered equivalent to depth-width samples in representing stream water quality conditions if the stream can be assumed to be well-mixed. Grab samples were collected on a weekly basis from April through
September during the runoff season, when atrazine concentration variability is the highest, and on a monthly basis from October through March, when concentration variability is low.

Automated runoff samplers collected additional samples when stream flows were above base flow conditions. These samplers were set to take discrete samples at uniform times during the runoff hydrograph. To determine the mean atrazine concentration for a particular runoff event, selected discrete samples of runoff that were collected by the automated sampler were composited into a single discharge-weighted sample. Discrete samples were selected to adequately define variations in flow rate and atrazine concentration. The method of computing the discharge-weighted value of each discrete sample to be included in the composite sample was based on the mid-interval method (Porterfield, 1977). Each sampling site was located at an existing United States Geological Survey (USGS) gage station or will have continuous flow meters equipped with the samplers.

**Management practice methods**

The objective of this part of the study will provide information that can be used to evaluate management practice success in reducing seasonal and annual concentrations and loading of atrazine.

The movement of atrazine from crop fields is determined by the chemical properties of the herbicide and mechanisms that lead to its transport. Water quality concerns involve primarily atrazine transport by runoff to surface water and leaching to groundwater. The most important chemical characteristics that influence atrazine loss from fields are adsorption and persistence. Solubility of atrazine also plays a role in atrazine losses.

Weakly adsorbed pesticides tend to leave the field in the water and not with soil particles lost in soil erosion. Atrazine is soluble in water and weakly adsorbed in soils, which leads to its loss in water leaving the field and not with eroding soil particles. It has been felt for a number of years that if soil erosion could be reduced, herbicide loss would also be reduced, but that is not the case for atrazine (Baker and Laflen, 1979; Hall et al., 1972; Olson et al., 1998). Because atrazine moves with runoff water leaving the field, the closer the rainfall occurs following atrazine application, the greater the atrazine loss. May through July are the months that have the greatest potential for runoff losses in the Big Blue Basin.

The term persistence refers to how long it takes for a herbicide to break down from chemical decomposition or microbial degradation. The longer a herbicide persists, the longer a herbicide can control weeds. However, the longer a herbicide is present in the environment, the greater the chance it will runoff with surface water or leach into the groundwater. Atrazine has a half-life of approximately 60 days (Olson et al., 1998), which means that half the atrazine applied in April or May will be available to the peak runoff periods in the Blue River Basin. These factors are being considered as the primary causes for atrazine concentration in Nebraska and Kansas drinking water. This paper will examine practices which avoid these factors. Application timing, herbicide incorporation, and the use of vegetative buffers are practices that farmers in the Big Blue Basin are using to reduce surface water impairments.

**Monitoring results**

During 1998, the sampling stations (Table 1) had an average of 42 samples taken per station. The daily atrazine concentration was calculated by interpolating between discrete sampled concentrations. If the daily concentrations are averaged for the year the annual average concentration for atrazine at Station 1 is 2.84 g/l, which is slightly below the drinking water MCL.

These concentration peaks occur during the same time frame that represented the peak stream flows. If the daily flowrate is multiplied by the average daily concentration, then multiplied by a factor (0.005383), the result gives the daily atrazine load in kg.
The data from all the monitoring stations in the Big Blue River Basin are presented in Table 2. The data for the Big Blue River is near or above the drinking water MCL. These data would also suggest that the majority of the atrazine loading is coming out of the Big Blue River part of the basin. The Big Blue River at Marysville, Kansas represents 49% of the drainage area, but produces 80% of the atrazine loading. If we examine the load per area for the Big Blue River, Station 4 at Marysville, Kansas, exceeds the upper stations along the Big Blue River by as much as 1.5 times. Another surprise can be seen if the outflow versus inflow atrazine loading for Station 10, Tuttle Creek Reservoir, is considered. The total inflow atrazine load is 11,509 kg while the outflow is reduced to 4506 kg. This would indicate that Tuttle Creek Reservoir reduces the atrazine loading into the Kansas River by 61%.

The calculation of the total maximum daily load (TMDL) compares daily flow at the measured concentration versus the MCL concentration of 3 \( \text{mg/l} \). This comparison shows that the TMDL is exceeded during the late May through June runoff period. When working with farm practices, this is the atrazine application period that needs revised practices.

**Management results**

If atrazine losses are examined for each of the sampling stations, it is found that over 90% of loading occurs during the months of May and June.

A number of studies have been performed to examine the application timing of atrazine to avoid the loss window. Farm surveys have shown that most farmers in the Big Blue Basin apply their atrazine in or near the May-June period that is showing the greatest loss potential. Application times examined included fall application, early spring application, and post application. Fall application should be made after harvest during the months of October or November before the ground is frozen. Early spring application should be made in the spring after the soil has thawed and before the primary runoff periods in May and June. The post application would be made after the crop has emerged and before the crop reaches labeled crop height. Post application is made at a quarter of the labeled atrazine rate and requires a chemical weed burn down at planting time which has a higher cost. Alternative application timing can reduce atrazine runoff losses by 60-90%.

Chemical incorporation is another practice that farmers have used to apply their herbicides. The problem with this practice is that as the tillage tool incorporates the herbicide it also incorporates the residue cover needed to reduce soil erosion. If tillage is used prior to planting corn or grain sorghum atrazine losses can be reduced by 90%.

Vegetative buffer strips along the edge of fields are zones that can contain various forms of vegetation such as grass and trees. The purpose of these buffers is to reduce the runoff losses.

**Table 2** Blue River Basin sampling locations and atrazine annual mass loss (1998)

<table>
<thead>
<tr>
<th>Station number</th>
<th>Location</th>
<th>Atrazine mass loss (kg)</th>
<th>MCL</th>
<th>Percentage of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Crete, Nebraska (Big Blue River)</td>
<td>3819</td>
<td>2.84</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>Beatrice, Nebraska (Big Blue River)</td>
<td>5333</td>
<td>3.78</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>Barneston, Nebraska (Big Blue River)</td>
<td>7491</td>
<td>4.20</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>Marysville, Nebraska (Big Blue River)</td>
<td>9241</td>
<td>4.55</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Deweese, Nebraska (Little Blue River)</td>
<td>256</td>
<td>1.46</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Fairbury, Nebraska (Little Blue River)</td>
<td>473</td>
<td>1.96</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>Hollenberg, Kansas (Little Blue River)</td>
<td>791</td>
<td>1.88</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>Barnes, Kansas (Little Blue River)</td>
<td>1665</td>
<td>2.31</td>
<td>14</td>
</tr>
<tr>
<td>9</td>
<td>Frankfort, Kansas (Black Vermillion River)</td>
<td>603</td>
<td>2.24</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>Manhattan, Kansas (Tuttle Creek Reservoir)</td>
<td>4506</td>
<td>1.27</td>
<td>39</td>
</tr>
</tbody>
</table>
flow rate from the field to allow deposition of sediments and nutrients contained on the sediments (Dillaha et al., 1986, 1988; Cooper and Gilliam, 1987). Limited data is available on the effectiveness of these buffers to reduce herbicides in the runoff water (Arora et al., 1995). It is important to realize that the vegetation in the buffer does not remove the pesticide from the water passing through the buffer. It is the proportion of the herbicide-containing water that infiltrates into the buffer that reduces the herbicide runoff. Vegetative buffers used in the Big Blue Basin have reduced atrazine loss in runoff from fields by 30%.

Conclusions
This monitoring research suggests that additional management practices are needed in a portion of the Big Blue River Basin. Reducing runoff leaving fields with vegetative buffers combined with proper timing and application method can bring these parts of the basin into compliance with the current water quality standards.

Acknowledgements
This work was supported by the Kansas Agricultural Experiment Station, Kansas State University, Manhattan, Kansas 66506, Contribution No. 01-424-J.

References