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Herbicide Loading to Shallow Groundwater Beneath Nebraska's MSEA

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Triazine and acetamide herbicides' mobility and moderate persistence cause them to be the most frequently reported pesticides in groundwater in agricultural areas. Atrazine and its transformation products together with cyanazine, simazine, alachlor and metolachlor and their transformation products are the herbicides most commonly detected in row-cropped regions. Atrazine is the most widely detected pesticide in the nation's groundwater and the EPA has set 3 µg L^{-1} as the maximum contaminant level (MCL) in drinking water.

The groundwater assessments that are the basis for EPA's strategy of developing state Pesticide Management Plans for atrazine, cyanazine, simazine, alachlor and metolachlor have done little to explain the transport mechanisms of pesticides to shallow groundwater and the temporal variability of concentrations. Especially prevalent in groundwater are the triazine metabolites deethylatrazine and deisopropylatrazine.

The USDA sponsored Management Systems Evaluation Area (MSEA) projects in five Midwestern states in the Corn and Soybean Belt. The Nebraska MSEA focused on the development of methods to mitigate nitrate leaching and the impact of irrigated agriculture on groundwater quality.

The objectives of this paper are to assess pesticide loading on shallow groundwater quality beneath the Nebraska MSEA and to determine the relative effects of precipitation and irrigation management on pesticide transport to the groundwater.

The Nebraska MSEA site was chosen because it is centrally located within 202,000 contiguous ha underlain by a shallow, nitrate- and atrazine-contaminated, sand and gravel aquifer that is the primary source of both drinking and irrigation water. Historically, the atrazine concentrations have been exceptionally high.

Annual precipitation during the six-year study (1991-1996) ranged from 468 mm (1991) to 879 mm (1993). With 585 mm of precipitation the 1993 growing season was the wettest in more than 100 years of record keeping. One week before to two weeks after planting is the most critical period for the potential flush of mobile compounds below the shallow root zone. While the average precipitation during this window was quite low (36 mm) from 1991 to 1994, it tripled to an average of 111 mm during 1995 and 1996. Evapotranspiration (ET) in excess of precipitation during the growing season results in an average seasonal irrigation requirement of 280 mm for corn in the central Platte Valley, although it ranged from 0 to >450 mm during the 30-year period ending in 1996.

The unsaturated zone of the research–demonstration site is a 1.1-m-thick, well-drained silt loam overlying approximately 4.3 m of fine to medium-textured sands. During the six-year investigation, the depth to water in the water table aquifer fluctuated from approximately 3 to approximately 6 m beneath the land surface. The direction of horizontal groundwater flow switched from east–northeast to east in response to anomalously heavy recharge and limited pumping during the 1993 growing season and reverted back to east–northeast after the 1994 growing season. The horizontal groundwater flow rate is 0.55 m d^{-1}. The estimated 0.0 $\pm$ 0.5 year residence time for the shallowest groundwater beneath the Nebraska MSEA supports its origin as seasonal recharge.

The site was subdivided into four 13.4-ha management fields. Three fields were cropped to corn and the fourth to alfalfa. Each spring the cooperating farmer prepared the cornfields by shredding stalks and tilling twice with a tandem disk harrow. Each cornfield received 46-cm banded applications of 1.68 kg atrazine ha^{-1} and 0.75 kg metolachlor ha^{-1} as Bicep between April 29 and May 20. Metolachlor was not used on the site prior to 1991. While each cornfield was subject to identical herbicide application practices, the irrigation practices were different. Irrigation supplements averaged 752, 267 and 198 mm $year^{-1}$ on the conventional-, surge- and center pivot–irrigated corn, respectively, and 246 mm $year^{-1}$ on the center pivot–irrigated alfalfa. The center pivot was equipped with a corner system capable of irrigating the entire field. Applications of herbicide and irrigation water were restricted in the irrigated buffer upgradient of the research–demonstration site to reduce recharge upgradient of the management fields.

Conventional furrow-irrigated corn management field: The landowner managed the conventional field and irrigated through gated pipe into furrows with 12-hour continuous sets. Every furrow was irrigated, and runoff water accumulated behind the end-of-field dike. The field was irrigated weekly barring significant precipitation or very cool temperatures. With the exception of 1996, annual irrigation applications were significantly less than they were prior to the study.

Surge-irrigated corn management field: Surge irrigation provides a more uniform water application than conventional furrow irrigation and, therefore, is considered an improved furrow irrigation technique. To improve water distribution the gently sloping field was graded in fall 1990 with a laser-guided system. Water was delivered to the surge valve, distributed through gated pipe to furrows on both sides of the valve and conveyed through the furrows, and the excess discharged to a ditch at the lower end of the field and eventually to a lined tailwater recovery pit. Irrigations were scheduled by standard water balance techniques. Typical beginning-of-season net applications ranged from 55 to 75 mm. Subsequent applications usually averaged approximately 50 mm.

Center Pivot–Irrigated Corn Management Field: Irrigation via the corner system center pivot followed the same scheduling technique employed on the surge-irrigated cornfield. Typical irrigation applications were approximately 25 mm. After mid-July a soil-water deficit of approximately 25 mm was maintained to provide storage of rainfall, thereby reducing leaching. The deficit was gradually increased in late summer.

Center Pivot–Irrigated Alfalfa Management Field: Water applications were based upon precipitation, evapotranspiration and the need to keep the field dry during hay harvest. Four cuttings of alfalfa were removed annually.

RESULTS AND DISCUSSION

Temporal and areal variability in atrazine concentrations: With the exception of a few short-lived peaks, the average atrazine concentration in the shallow (< 1.5m) groundwater downgradient of the cornfields progressively decreased from approximately 5.5 to < 0.5 µg L^{-1} during the six years of MSEA management. The source of the especially high concentrations in the initial years was atrazine applied prior to the study.

Improved irrigation management during the study appeared to significantly reduce atrazine loading to the shallow groundwater. This improvement may result from a combination of increased soil residence time and concurrent rapid microbial transformation of atrazine.

After heavy rainfall average atrazine concentrations peaked in the shallow groundwater in fall 1993 and summer 1995 and 1996. Since herbicide applications and practices at the cornfields were identical during the study, only rainfall and irrigation practices affect shallow groundwater herbicide loading. All three peaks are the result of atrazine being flushed from the vadose zone in response to precipitation. The 1993 growing season was the wettest in more than 100 years and although atrazine concentrations peaked in the irrigation season, very little water was applied. Spring rains were excessive after atrazine applications in 1995 and 1996.

The differences in atrazine and nitrate loading of shallow groundwater observed at the Nebraska MSEA can explain the very weak correlation of nitrate and atrazine concentrations in regional groundwater studies in the central Platte Valley. While both compounds are present in most wells in the region, they do not infiltrate at the same time. Nitrate loading occurred annually during irrigation season and was controlled by improved water and nutrient management. Peak atrazine loading after herbicide application was unpredictable and occurred only when excessive rains caused rapid infiltration.

Deethylatrazine (DEA) to atrazine molar ratios: The concept of DARs, the ratio of the molar concentrations of DEA and atrazine introduced by researchers in 1991, is useful for evaluating the timing of leaching processes. In groundwater DARs may range from very low values to infinity (DEA present and atrazine below reporting limits). The average DAR in the shallow groundwater downgradient of the cornfields gradually increased from approximately 1 in 1991 to greater than 4 in 1995, retreated to approximately 1.5 in summer 1996 and abruptly increased to greater than 7 at the next sampling in fall 1996. The trend toward higher DARs coincided with improved water management, which favors the retention of atrazine in the biologically active upper soil horizon. The longer residence time enhances metabolism, thereby increasing the DEA available for subsoil transport to the shallow groundwater. Below the soil zone DEA is more mobile than atrazine in sand and gravel, which may partially explain the high DARs. The reversal of the trend toward higher DARs occurred in summer 1996 prior to irrigation and coincided with flushing rains several days after herbicide application. The low DARs suggested that the parent compound was rapidly leached below the biologically active root zone before significant metabolism occurred.

The reversal in DARs and the increase in atrazine concentrations in the summer 1996 samples were greatest downgradient of the two furrow-irrigated corn management fields and suggest that anomalously high amounts of atrazine were preferentially introduced to the aquifer. Ponding of storm runoff in the drainage ditch on the eastern edge of the surge-irrigated field and at the lower end of the conventionally irrigated field within days of herbicide application appears to have exacerbated the leaching of atrazine. In contrast, the average atrazine concentration downgradient of the pivot-irrigated cornfield increased only slightly and there was little, if any, concentration change beneath the irrigated alfalfa field. Both pivot-irrigated fields have minimal propensity for ponding and runoff.

Temporal and areal variability in metolachlor concentrations: Downgradient of the corn management fields, the frequency of metolachlor detections in shallow groundwater increased during the six years, as did average metolachlor concentrations. The driving mechanism for the sharp increase in concentration and frequency of detection appeared to have been the 100-year record rainfall during the 1993 growing season, which increased matrix flow through the overlying soils and also caused atrazine concentrations to peak. Metolachlor leaching was pronounced again in summer 1996, when concentrations rose and were sustained through fall sampling. The 1996 metolachlor peak was broader than the atrazine peak due to inherent differences in mobility. Metolachlor is more retarded than atrazine and is transported more slowly through the vadose zone. As with atrazine concentrations in summer 1996, peaks in metolachlor concentrations in the shallow groundwater downgradient of the furrow-irrigated fields and their absence downgradient of the pivot-irrigated cornfield resulted from focused recharge of ponded runoff from the furrow-irrigated fields shortly after herbicide application. Thus, peak loading occurred prior to irrigation and was related mostly to the ponding of precipitation runoff by drainage control structures that are inherent in furrow irrigation in Nebraska.

Enhanced leaching of metolachlor and atrazine by focused recharge beneath the surge irrigation drainage ditch and the diked lower end of the conventionally irrigated field is further supported by the shallow groundwater data upgradient of the site. Located immediately west of a 1-m deep road ditch that receives runoff from the north half of the pivot-irrigated corn buffer upgradient of the research–demonstration site, ML1 through ML8 are grout-sealed from the surface to the water table to ensure they do not convey surface water to the aquifer. The sharp atrazine and metolachlor concentration peaks in the shallow groundwater of ML1 through ML8 in summer 1995 and 1996 followed the only intense precipitation within two weeks of herbicide application during the study. Data indicate the pesticide-contaminated runoff that filled the road ditch after the intense rains was rapidly flushed through the unsaturated zone, which has only a thin layer of soils. Upgradient atrazine concentrations exceeded those of DEA, causing a reversal in DAR, and provided further indication that much of the shallow groundwater atrazine contamination originated from infiltration of runoff from recently treated fields.

Impacts of irrigation management practices: Although peaks in atrazine and metolachlor concentrations were best controlled on the pivot-irrigated corn field, there were only slight differences in herbicide loading beneath the conventionally furrow-irrigated field and the center pivot–irrigated field during most sampling periods. From 1993 through 1995 there was a similar trend toward lower atrazine concentrations beneath the conventional and pivot-irrigated fields. The slightly greater decrease in atrazine concentration beneath the conventionally irrigated field suggested that the application of larger quantities of irrigation water further diluted the atrazine concentration. Throughout most of the Nebraska MSEA study, DEA concentrations were significantly higher beneath the pivot-irrigated cornfield, suggesting there was less leaching of atrazine and more active microbial transformation than beneath the conventionally irrigated field.

Deisopropylatrazine (DIA) to deethylatrazine molar ratios: Concentrations of DIA, a metabolite of atrazine, simazine and cyanazine, exceeded the reporting limit (0.1 µg L^{-1}) in 86.4% of the 7,848 samples from the water table aquifer. Simazine, which was occasionally used for weed control in the shelterbelt south of the management fields, was reported in only 6.3% of the samples while cyanazine, with no history of use at the site, was detected in less than 0.1% of the samples. Thus, most of the DIA was the product of atrazine metabolism.

The molar ratio of DIA to DEA (D^2R) was used as a tool to better confirm the parent contribution to water bodies. Regression analysis showed the slope of DIA to DEA in a surface drainage basin where atrazine was almost exclusively applied was 0.4 $\pm$ 0.1 while proportionally constant concentrations of DIA and DEA had D^2Rs ranging from about 0.5 to 0.6 during a runoff event in eastern Nebraska. Seasonal average D^2Rs in the shallow groundwater downgradient of the Nebraska MSEA corn management fields were very low and ranged from 0.06 to 0.18. In general, DEA concentrations were 10 times higher than DIA concentrations and there was not a hint of association between the two metabolites. The lower persistence of DIA in soil solution and its lower mobility relative to DEA accounted for low concentrations in the groundwater. The very low values and wide range of D^2Rs in groundwater areas dominated by atrazine usage indicated that, in this groundwater, D^2Rs have limited value for distinguishing triazine herbicide inputs. Proportionally, groundwater DIA concentrations beneath the site represented less than 15% of total triazine residue.

CONCLUSIONS

Major improvements in water management quickly lowered atrazine concentrations in the shallow groundwater downgradient of the three corn management fields and concentrations remained well below the 3 µg L-1 maximum contaminant level except for transient peaks in concentration. The highest levels of pesticide contamination were largely associated with focused recharge of ponded contaminated runoff at the diked end-rows and in the runoff collection ditches at the furrow-irrigated fields and in the road ditch after heavy spring rains closely followed herbicide application. Although not as dramatic as the effect on surface water, the spring flush can negatively affect groundwater quality. The results challenge presently accepted paradigms that assess herbicide vulnerability by focusing solely on soil characteristics, such as soil permeability, organic content and slope. At least in this region, peak herbicide concentrations were associated with infiltration through road ditches that, with the soil stripped almost to the vadose zone sands and the additional head caused by the ponded runoff, acted as infiltration galleries during runoff events in the days following herbicide application. The end rows of the furrow-irrigated fields where the soils were altered or eliminated in the construction of dikes and ditches also became avenues for focused infiltration of pesticides during runoff events in the days after herbicide application.

Sprinkler irrigation technology benefited groundwater quality by reducing the areas for focused recharge of contaminated storm runoff and providing a favorable environment for soil microbial degradation of atrazine. In Nebraska, groundwater beneath areas of pivot-irrigated corn was characterized by lower atrazine concentrations and higher DARs than groundwater in areas dominated by furrow irrigation.

Molar ratios of deethylatrazine to atrazine indicated that during the study atrazine remained in the biologically active soil zone longer than it did prior to MSEA management. Except for one sampling event, more DEA than atrazine was present in the shallow groundwater. Deisopropylatrazine concentrations were very low and appeared inconsequential in proportion to atrazine and DEA concentrations.

Metolachlor, which had no history of use at the site prior to initiation of the project, was detected in the very shallow groundwater at frequencies of approximately 10% in the first year. Frequency of detection tended to increase during the six-year study and reached approximately 50% in 1996. Mechanisms of metolachlor transport appeared to be both matrix flow during anomalously wet years and focused recharge in areas with disturbed or partially removed soils.

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Herbicide Loading to Shallow Groundwater Beneath Nebraska's MSEA

November Self-Study Examination

DETACH HERE

1. The most widely detected pesticide in the nation's groundwater is:

[ ] a. metalachlor.
[ ] b. atrazine.
[ ] c. cyanazine.
[ ] d. alachlor.

2. The EPA has set the maximum containment level in drinking water for atrazine at:

[ ] a. 1 µg L^{-1}.
[ ] b. 2 µg L^{-1}.
[ ] c. 3 µg L^{-1}.
[ ] d. 4 µg L^{-1}.

3. The most critical period for the potential flush of mobile compounds below the shallow root zone is:

[ ] a. one week before to two weeks after planting.
[ ] b. one week before to three weeks after planting.
[ ] c. two weeks before to two weeks after planting.
[ ] d. two weeks before to three weeks after planting.

4. The average atrazine concentration in the shallow groundwater down gradient of the cornfields:

[ ] a. progressively decreased.
[ ] b. progressively increased.
[ ] c. stayed the same.
[ ] d. varied each year.

5. Nitrate loading:

[ ] a. was unpredictable.
[ ] b. occurred only when excessive rains caused rapid leaching.
[ ] c. occurred annually during the irrigation season and was controlled by improved nutrient and water management.
[ ] d. occurred annually during the irrigation season; however, improvements in nutrient and water management could not control the loading.

6. Peak atrazine loading:

[ ] a. was unpredictable and occurred only when excessive rains caused rapid leaching.
[ ] b. occurred annually during the irrigation season and was controlled by improved water management.
[ ] c. differed by soil texture.
[ ] d. did not change with improved irrigation management.

7. Peaks in atrazine and metolachlor concentrations were best controlled on the:

[ ] a. surge-irrigated corn management field.
[ ] b. conventional furrow-irrigated management field.
[ ] c. center pivot-irrigated corn management field.
[ ] d. center pivot-irrigated alfalfa management field.

Over

8. Throughout most of the Nebraska MSEA study, DEA concentrations were significantly higher beneath the pivot-irrigated cornfield than the furrow irrigated fields, suggesting there was less leaching of the atrazine and:

[ ] a. greater sorption by the soil.
[ ] b. greater adsorption by the soil.
[ ] c. more active chemical transformation.
[ ] d. more active microbial transformation.

9. The highest levels of pesticide contamination were largely associated with:

[ ] a. surge-irrigated corn management fields.
[ ] b. focused recharge of ponded contaminated runoff.
[ ] c. high organic matter.
[ ] d. clay textured soils.

10. Sprinkler irrigation technology benefited groundwater quality by:

[ ] a. reducing the areas for focused recharge.
[ ] b. decreasing microbial activity.
[ ] c. increasing atrazine infiltration.
[ ] d. increasing soil organic matter.

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