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Occurrence and Behavior of the Herbicide Prometon in the Hydrologic System

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Prometon, a triazine herbicide, is used for total vegetation control on industrial sites, on noncrop areas on farms, in and under asphalt, and to a small extent by homeowners. Prometon has often been detected in surface water and groundwater in studies reported in the literature, but its presence is seldom discussed, partly because of its infrequent inclusion on lists of herbicides used in either agricultural or urban areas. In recent large-scale studies by the U.S. Geological Survey, prometon has been the most commonly detected herbicide in surface water and groundwater in urban areas and the third and fourth most commonly detected herbicide in groundwater and surface water, respectively, in agricultural areas. It also has been detected in rain. The frequent detection of prometon in the environment is discussed in relation to its use practices and predicted environmental behavior. Prometon is compared to atrazine, a structurally similar agricultural triazine herbicide that is one of the most studied and most commonly detected herbicides found in the hydrologic environment. The environmental data presented here demonstrate the wide-scale occurrence of prometon in all components of the hydrologic system, particularly in the surface water and groundwater of urban areas.

Introduction

The use of herbicides has increased substantially during the past few decades. Agricultural use of herbicides in the United States increased from 53 000 to 219 000 t active ingredient (ai) from 1966 to 1993 (*1, 2*). Although most herbicides have agricultural uses, an estimated 22% of herbicide use in the United States is in nonagricultural areas (*2*) such as forests, lawns and gardens, and along rights-of-way. Most herbicides are registered only for agricultural use, a few are registered only for nonagricultural use, and others are registered for both. For most herbicides, a small percentage of the amount applied has been observed to move into the hydrologic system (surface water, groundwater, and the atmosphere) through a variety of processes, including runoff, leaching, and volatilization (*3*−*5*).

Little is known about the occurrence and ecosystem effects of herbicides in urban areas. The few published studies (*3*−*5*) show that herbicides are found in the atmosphere (rain and air), surface water, and groundwater of many urban areas. Capel and co-workers (*6*−*8*) have observed both agricultural- and urban-use herbicides in rain and stormwater runoff in Minneapolis, MN.

The common occurrence of prometon in both surface water (*9*) and groundwater (*10*) is one of the most noticeable observations from the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. Prometon was the most frequently detected herbicide at urban sites and the third (groundwater) and fourth (surface water) most frequently detected herbicide at agricultural sites. This finding was particularly unexpected for agricultural areas because prometon has essentially no registered agricultural use in the United States. The NAWQA Program is not the only study that has included prometon in its sampling design. Other studies have analyzed for prometon in various geographic and hydrologic environments (*11*−*32*). For the most part, prometon was detected frequently in these studies, consistent with NAWQA findings, but was seldom discussed in these studies. In fact, there is little information in the open literature about the environmental behavior and fate of prometon. Singh et al. (*33*), who examined the mobility of prometon and atrazine in a soil column, published the only process-oriented study found in a computerized literature search.

The purpose of this paper is to examine the occurrence, sources, properties, and behavior of prometon in the hydrologic system. The environmental observations in surface water and groundwater reported here are from the NAWQA Program and represent samples from 20 diverse areas (study units) across the United States. The data on prometon detections in rain are from Minnesota only because this is the only large temporal and spatial data set available. Throughout this paper, prometon will be compared to atrazine, a structurally similar triazine herbicide that is one of the most commonly detected pesticides in the hydrologic environment (*9, 10*). This comparison helps put the properties, behavior, and environmental observations of prometon into a useful perspective.

Background on Prometon

The primary use of prometon, first used in 1959 (*34, 35*), is for "total vegetation control on industrial sites, noncrop areas around the farm, and for use in and under asphalt" (*36*). It is also registered for use by homeowners. The product literature suggests that prometon be used in areas where complete control of all vegetation is desired and that it usually inhibits plant growth for 1 year or more. Prometon is used "to extend the useful life of asphalt pavement by preventing weeds from emerging through it ... [prometon] may be applied to the ground before laying asphalt, or it may be mixed with cutback asphalt" (*36*). Typical areas for suggested use include roadways, parking lots, highway shoulders and median strips, guardrails, along airport runways, and industrial sites. Because prometon will control virtually all vegetation, it has limited use in agriculture (for instance with certain nut trees) and around the home. It is used as both a pre- and post-emergent herbicide and can be mixed with oil for fast top kill. Depending on the specific purpose, application rates are generally between 10 and 60 lb ai/acre. This is 10−30 times higher than the application rate for atrazine (Table 1), but the treated areas generally are much smaller. Because the primary registered uses of prometon do not include agricultural, home, and garden use, prometon seldom appears on lists of herbicides in use (*37, 38*).

The principle mode of action for triazine herbicides, including prometon and atrazine, is to disrupt the light reaction of photosynthesis. Specifically, electrons are prevented from entering the electron transport system of the chloroplast (*39*). Prometon is absorbed through the root and shoot system and transported through the xylem.

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TABLE 1. Characteristics of Prometon and Atrazine

characteristic[a]	prometon	atrazine
	Product Characteristics	
uses	noncropland–bare ground, in and under asphalt	cropland–corn, sorghum turf (in SE only)
mode of action	photosynthetic inhibition	photosynthetic inhibition
application rate (lb/acre ai)[b]	10–60	1–2
trade name	Pramitol	Aatrex
	Chemical Characteristics	
CAS Registry No.	1610-18-0	1912-24-9
molecular formula	$C_{10}H_{19}N_5O$	$C_8H_{14}ClN_5$
molecular weight (Da)	225.3	215.7
melting point (°C)	89–91	175–177
density (g/mL, 20 °C)	1.088	
water solubility (mg/L, 20–25 °C)	720	33
vapor pressure (mPa, 25°C)	1.028	0.038
Henry's law constant (Pa-m^3/mol, 25 °C)	3.2×10^{-4}	2.5×10^{-4}
acid dissociation constant (20 °C)	4.33	1.68
octanol–water partition coeff (log units)	2.69	2.68
	Environmental Characteristics	
soil sorption (K_D)	0.38–2.90	0.2–2.46
soil sorption (K_{OC})	95 (32–218)	147 (38–288)
bioconcentration factor (calculated)	15	86
hydrolysis rate (L/day)	stable	stable
photolysis rate, soil (L/day)	0.015[c]	0.015[c]
photolysis rate, water (L/day)	stable	0.002[d]
aerobic soil half-life (days)	932	146
anaerobic soil half-life (days)	557	77
field dissipation half-life (days)	1300 (264–3084)	173 (13–402)
runoff (dissolved) potential[e]	large	large
leaching potential[e]	large	large
	Toxicological Characteristics[f]	
EC_{50}, 120 h, green algae (*Selenastrum capricomutun*) (mg/L)	0.098	0.12
EC_{50}, 48 h, water flea (*Daphnia magna*) (mg/L)	25.8	6.9
LC_{50}, 96 h, bluegill sunfish (mg/L)	41.5	54.5
LC_{50}, 96 h, rainbow trout (mg/L)	19.6	4.5
carcinogenicity	no information	group C: possible human carcinogen
	Regulatory Characteristics[g]	
lifetime health advisory (mg/L)	100	3.0
maximum concentration level (mg/L)	no standard	3.0

[a] Chemical and environmental characteristics from ref *40* unless noted otherwise. [b] ai, active ingredient. [c] Artificial light. [d] Natural light. [e] Ref *41*. [f] Ref *42*. [g] Ref *43*.

Although little is published on the environmental behavior and fate of prometon, its behavior can be partly inferred from registration data, physical/chemical properties (Table 1), and information included on the product label (*36*). On the basis of these sources of information, general observations can be made of its mobility in soil, environmental lifetime, and behavior in the hydrologic system.

Prometon has a water solubility of 720 mg/L, which is about 20 times greater than that of atrazine. The degree of sorption to soil for both prometon and atrazine is similar, both on a mass basis and on an organic carbon-normalized basis (Table 1). Singh et al. (*33*) in their study of transport of these two compounds in soil found similar average sorption coefficients for prometon (0.23 and 0.36 in column and in batch studies, respectively) and atrazine (0.31 and 0.27 in column and batch studies, respectively). On the basis of the available information, it seems that prometon and atrazine have similar mobility in soil and can be expected to have similar tendencies with respect to runoff to surface waters and leaching to groundwaters.

The USDA has rated the dissolved-phase runoff and leaching potentials of both prometon and atrazine as "large" (*41*). One of the considerations entering into the USDA's ratings of runoff and leaching potentials is the chemical's environmental lifetime. A chemical must have a relatively long environmental lifetime for its runoff or leaching potential to be rated as "large" in this index. Table 1 compares the rates of transformation of prometon and atrazine for the most common environmental loss mechanisms. Both compounds have little loss from hydrolysis or photolysis reactions. The most important transformation mechanism for both compounds is biodegradation. The rate of biodegradation is dependent on several environmental factors, but the values reported suggest that the environmental lifetime of prometon is longer than that of atrazine. Field studies have shown that the dissipation half-life of prometon in soil is on the order of hundreds to thousands of days, perhaps an order of magnitude greater than the dissipation half-life of atrazine. This is consistent with the statement on prometon's label that "when applied to soil, this product usually inhibits plant growth for a year or more" (*36*).

Previous studies have shown that prometon is present in surface water, groundwater, and rainfall (*11*–*32*). Although there is no direct information on the behavior and fate of prometon in these hydrologic systems, general predictions can be made on the basis of the information in Table 1. There are no efficient loss mechanisms for prometon from the hydrologic system. Biodegradation, although very slow, is the most important loss mechanism in soil and will probably also be the most important loss mechanism in water.

TABLE 2. Results of a Simple Steady-State Fugacity Model (*44*) for Behavior and Fate of Prometon and Atrazine[a] in a Fallow Field

fate profile	prometon (%)[b]	atrazine (%)[b]
moderate soil slope		
volatilization to the atmosphere	0.0.	0.0
storage in soil plus leaching	96	82.
runoff to surface water	0.3	0.3
loss in soil due to degradation	3	18
steep (30%) soil slope		
volatilization to the atmosphere	0.0	0.0
storage in soil plus leaching	94	80
runoff to surface water	3	2.6
loss in soil due to degradation	3	17

[a] Chemical properties from Table 1. Environmental properties for model: temperature, 25 °C; organic carbon fraction of soil, 0.02; soil bulk density, 1.5 mg/L; annual rainfall, 0.7 m/yr. [b] Percentages do not add up to 100 due to rounding.

Another potential loss mechanism from surface water is volatilization into the atmosphere, but the low Henry's law constant of prometon (Table 1) suggests that transfer of prometon from surface water to the atmosphere will be minimal. The same is true for atrazine. On the basis of its water solubility and measured sorption coefficients, prometon has little tendency to sorb to aquatic particles or to bioaccumulate in aquatic biota. Again, the same behavior has been observed for atrazine (*3*).

The overall environmental behavior and fate of prometon can be predicted using a simple steady-state fugacity model for pesticides applied to a fallow field developed by Neeley and Oliver (*44*). This model uses chemical properties, structure−activity relationships, and the physical characterization of a unit environment to predict runoff to surface water, storage in soil plus leaching, loss in the soil due to degradation, and volatilization to the atmosphere. The comparison between the two compounds is informative, even though the absolute accuracy of the predictions may be questioned. The model was run for both prometon and atrazine under identical conditions, using two different values for soil slope (Table 2). The fate profiles for the two chemicals are generally similar, but there are important differences. A much smaller percentage of prometon as compared to atrazine is predicted to undergo degradation in the soil, which is consistent with prometon's longer biodegradation half-life (Table 1). For both compounds, runoff from the soil is predicted to be a small percentage of total loss. The amount lost in runoff is strongly influenced by the slope of the soil, as would be expected. The percentage predicted for loss of atrazine in runoff from moderately sloped soils generally agrees with runoff percentages observed by Larson et al. (*45*). Neither compound is predicted to have any loss to the atmosphere via volatilization because of their low Henry's law constants. Contrary to this prediction, atrazine is known to volatilize to a small degree and has been frequently observed in rain and air samples by numerous investigators (*6*; see review in ref *5*). The largest fraction of both chemicals is predicted to remain in storage in soil and perhaps undergo leaching. Based on environmental observations (*4*), only a small fraction of either compounds is ever leached through the soil column to groundwater. Overall, this modeling exercise suggests that the environmental behavior and fate profile of prometon should be quite similar to atrazine, with the exception that prometon will exist in the environment for a considerably longer period of time.

Methods

Sample Collection. *Surface Water*. Surface water samples were collected as part of the NAWQA Program of the USGS (*46*). Water samples were generally collected using the equal-width increment (EWI) method using a Teflon bottle. The 1-L sample for pesticide analysis was obtained from the composite of the EWI subsamples through a Teflon cone-splitter into a prebaked, amber glass bottle. The pesticide sample was either stored on ice and shipped overnight to the laboratory for extraction or extracted in the field.

Samples were collected from 48 surface water basins across the United States; 37 are small, predominately agricultural basins (median = 335 km^2) and 11 are small, predominately urban/suburban basins (median = 61 km^2). The samples were collected throughout 1993 and 1994, but samples were collected with greater frequency during the period following local pesticide application (1−2 times per week) than during other periods of the year (1−2 samples per month). At most sites, between 20 and 50 samples were collected per year. Although the urban and agricultural basins were chosen to represent one general land use/land cover, this was never completely achieved. In the agricultural basins, there usually was more than one type of row crop grown. In the urban basins, there was almost always some agricultural land. For a more complete summary of the basins and the surface water pesticide data, see Larson et al. (*9*).

Groundwater. Shallow groundwater samples were collected as part of the NAWQA Program of the USGS (*47*). The water was generally collected using a low discharge, submersible pump that contained wetted parts of mostly stainless steel and Teflon. The well was purged until the field parameters (pH, temperature, specific electrical conductance, dissolved oxygen, and turbidity) were stable or until a volume equal to 3−5 times the casing or wellbore volumes was pumped from the well. The water sample for pesticide analysis was collected directly into a prebaked, amber glass bottle. The pesticide sample was either extracted in the field or stored on ice and shipped overnight to the laboratory for extraction.

The shallow groundwater samples were collected according to two sampling designs as part of the NAWQA Program. One sampling design was based on a random distribution of wells throughout a major aquifer underlying each study unit. The second design was a targeted sampling of a specific land use, such as a residential or corn-growing area. In this paper, results from these two sampling designs have been combined into one data set, and the wells have been classified as urban (and suburban), agricultural (rowcrop and pasture), or other. Only the urban and agricultural classifications are discussed in detail in this paper.

Rain. The rain samples were collected only in Minnesota. The samples were collected as part of an ongoing study of pesticides in rain sponsored by the Minnesota Department of Agriculture and the NAWQA Program. Details of the collection procedure are given in Capel et al. (*6*). Briefly, the rain was collected in an AeroChem Metrics sampler that was modified with a Teflon-lined collection vessel, pump, and solid-phase extraction disk for real-time pesticide isolation from the rainwater. The rain samples were weekly composites collected from about May 1 to October 1 of each year. Rain was collected in two to four agricultural areas (depending on the year) and one urban area (Minneapolis).

Sample Analysis. The various water samples were all analyzed in virtually the same manner, following the method of Zaugg et al. (*48*). The water sample was spiked with a surrogate compound (terbuthylazine) and filtered through prebaked glass fiber filters. The pesticides were isolated from the filtered water by octadecyl solid-phase extraction (SPE) cartridges (surface water and groundwater) or disks (rain). The SPE devices were dried, and the pesticides were removed with 9:1 hexane:2-propanol (vol:vol). The solvent volume then was reduced, and internal standards were added. Final analysis was done by capillary gas chromatography with a mass selective detector operated in the selected ion moni-

TABLE 3. Rank of Detection Frequency of Targeted Herbicides in Surface Water, Groundwater, and Rain

	surface water[a]		groundwater[b]		precipitation	
	agricultural	urban	agricultural	urban	agricultural[c]	urban[d]
alachlor	5	7	6	-[e]	2	2
atrazine	1	3	1	2	1	1
cyanazine	6	8	8	6	3	4
EPTC	7	–	9	-	8	6
DCPA	9	9	-	-	-	-
metolachlor	2	4	3	5	6	5
metribuzin	10	-	5	5	5	3
prometon	4	1	4	1	12	12
simazine	3	2	2	3	11	7
tebuthiuron	8	5	7	4	-	-

[a] NAWQA surface water data set, 1993−1994 (*9*) (48 sites, 1839 samples). [b] NAWQA groundwater data set, 1993−1994 (*10*) (1034 sites, 1034 samples). [c] Combined data from two sites in southern Minnesota, 1994 (*6*) (45 samples). [d] Minneapolis, MN, 1994 (*6*) (27 samples). [e] - indicates not included in the top 10 most frequently detected herbicides in these data sets.

toring mode. There were about 40 target pesticides analyzed simultaneously by this method, but only data for prometon and atrazine are reported in this paper. The ion with mass-to-charge ratio (m/z) of 210 was used for quantification of prometon, and the 183 and 225 ions were used for confirmation. The ion with the m/z of 200 was used for quantification of atrazine, and the 173 and 138 ions were used for confirmation. All chromatographic peaks that met predetermined criteria for retention time and relative ion abundances were quantified. Herbicide concentrations were reported to as low as 0.001 μg/L. A reporting limit of 0.01 μg/L for both compounds is used as the basis for many of the comparisons in this paper. Recoveries of atrazine and prometon from laboratory reagent water were 89 ± 6 and 77 ± 3%, respectively (*48*). The reported concentrations were not corrected for surrogate recovery.

Calculations. For surface water, the daily load was calculated as the product of concentration and river discharge (flow) for each day. Daily mean discharge values were available for all surface water sampling points. Concentrations of the herbicides on nonsampling days were estimated by linear interpolation between their concentrations measured on the adjacent sampling days (*45*). The daily loads were then summed to give the total load over a specific time period. All samples in which a herbicide concentration was reported as not detected were assigned a value of zero for the load calculations. The yield (g km^{-2} yr^{-1}) was calculated by dividing the load by the critical area of the watershed. For urban watersheds, the critical area included the combined urban, suburban, and industrial/commercial areas. For agricultural watersheds, the critical area included only areas planted in row crops.

Results and Discussion

Surface Water. In NAWQA surface water samples collected during 1993 and 1994, prometon is the most frequently detected herbicide in urban areas and the fourth most frequently detected herbicide in agricultural areas (Table 3). Detection frequencies of prometon and atrazine are very similar in the selected urban streams (Figure 1A and Table 4). Most of the atrazine in these streams is thought to come from upstream agricultural areas, although some of the atrazine could come from urban uses in the southeastern part of the country. (Atrazine is registered for home use only in Florida, Georgia, Alabama, Mississippi, Louisiana, and Texas.) The prometon presumably comes from the local urban area, as the frequency of occurrence and general concentrations of prometon in streams draining agricultural areas are lower than in streams draining urban areas (Figure 1A). Concentrations of prometon are above 0.1 μg/L in approximately 19% of samples in urban areas and in approximately 4% of samples in agricultural areas, whereas concentrations of atrazine are frequently above this level in both urban and agricultural areas (approximately 33%).

TABLE 4. Frequency of Detection (in %) of Prometon and Atrazine in Surface Water and Groundwater and Rain[a]

		prometon	atrazine
surface water[b]	agricultural	39	80
	urban	85	86
groundwater[b]	agricultural	11	44
	urban	25	19
rain[c]	agricultural	23	85
	urban	11	95

[a] This table reports an uncensored data set with concentrations as low as 0.001 μg/L. It is known that there are a (uncertain) number of false negatives below the concentration of 0.01 μg/L (the minimum level used in Figure 1). This table presents a low estimate of the frequency of occurrence in these hydrologic compartments. [b] National data from NAWQA study units, 1993−1995 (see Figure 1 for sample details). [c] Minnesota data, 1993−1995 (see Figure 1 for sample details).

Many herbicides, particularly atrazine, show a distinct seasonal pattern in surface waters in agricultural areas (*3, 49, 50*). This is due to the seasonal application of atrazine as a preemergent herbicide to bare soil and the subsequent runoff resulting from spring rains or irrigation. As the growing season progresses, surface water concentrations decrease because less atrazine is available in the surface soil for transport in runoff. Concentrations of atrazine in surface waters are generally lowest during late autumn, winter, and early spring. The cycle is then repeated during the next growing season. Prometon concentrations in streams do not have this consistent seasonal pattern. Prometon is observed in almost all samples throughout the year, and for the sites near Norwalk and Harrisburg, the concentrations in winter are generally no lower than at other times of the year.

The differences in the seasonal patterns of atrazine and prometon result from their different uses and application practices. In most parts of the country, atrazine is used primarily as a surface-applied, preemergent herbicide on corn and sorghum, with its major application during the spring to bare soil. This dominant application practice results in a strong seasonal cycle of atrazine concentrations in surface waters. Prometon, on the other hand, has a variety of uses and applications. Its use as a preemergent herbicide to control vegetation on bare ground around buildings, fences, and along rights-of-way can yield maximum concentrations during spring as a result of rain-induced runoff, similar to atrazine. But unlike atrazine, prometon may be applied at any time of the year for these same purposes, and maximum concentrations may occur at any time in surface waters depending on local precipitation patterns. The use of

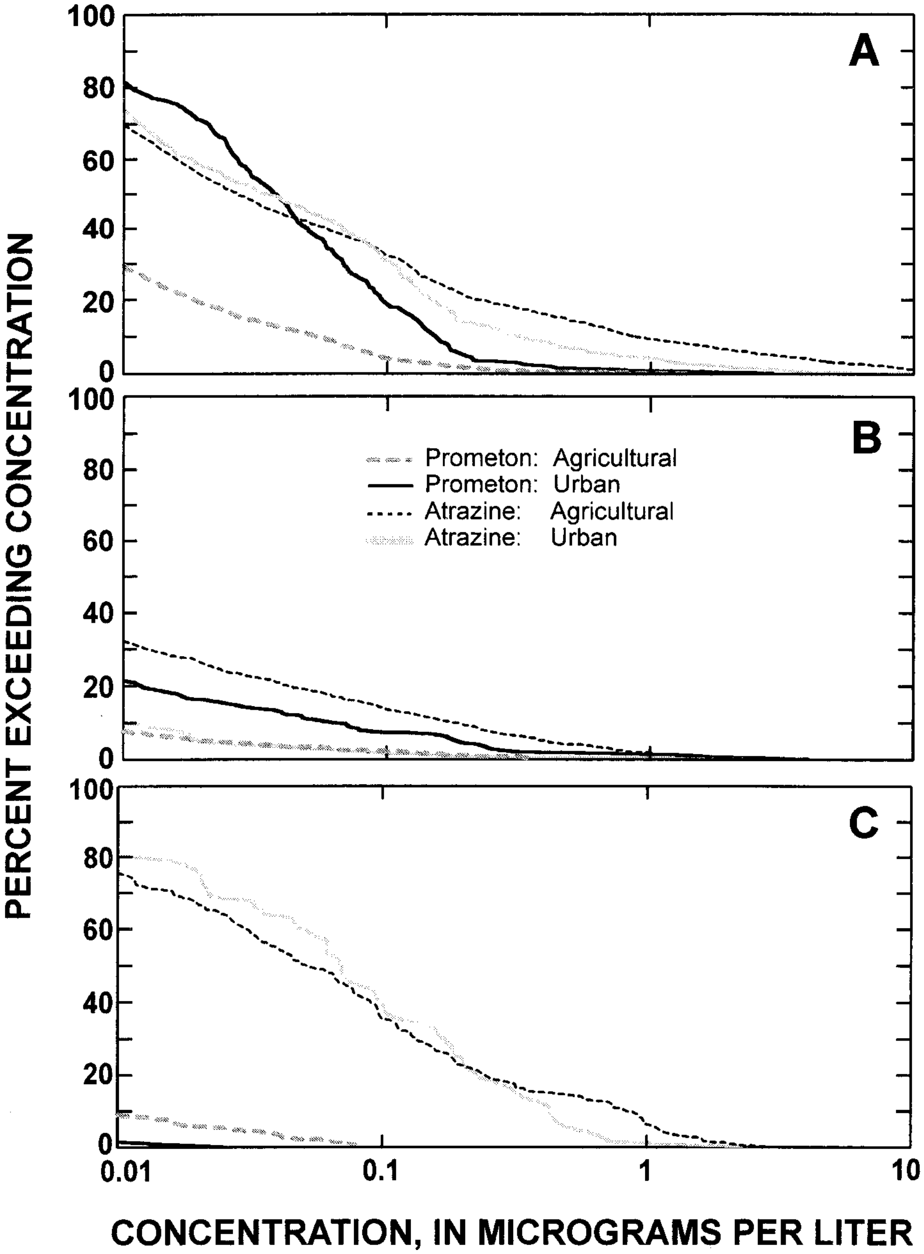

FIGURE 1. Concentration distribution of prometon and atrazine in (A) streams, (B) groundwater, and (C) rain. Stream samples were collected at 37 agricultural sites (1348 samples) and 11 urban sites (491 samples), 1993–1995. Shallow groundwater samples were collected at 813 agricultural sites (813 samples) and 221 urban sites (221 samples), 1993–1995. Rain samples were collected at five agricultural sites (220 samples) and one urban site (84 samples) in Minnesota, 1993–1995. The value on the *y*-axis shows the percentage of samples in which the indicated concentration is exceeded.

prometon in conjunction with asphalt (roads, parking lots, and so forth) probably provides a small but continual source of prometon to surface water. As the asphalt wears and cracks, prometon in or under it becomes exposed to rainwater; some prometon may find its way to surface water drainage. In basins with a high density of paved areas and seasonal freeze/thaw cycles (enhancing asphalt wear), this may be the major source of prometon, particularly during the winter.

The yields (annual loads divided by the critical area (agricultural or urban) of a watershed, g km^{-2} yr^{-1}) of prometon and atrazine are used for comparing different watersheds (Table 5). For atrazine in agricultural areas, the relative magnitude of the yields agrees with intuitive expectations. That is, in high atrazine-use areas (corn and sorghum growing regions such as Indiana, eastern Pennsylvania and Maryland, and central Texas), the yield of atrazine is much greater than in low atrazine-use areas (northern Florida, Colorado, and northern Georgia). The yields of atrazine in urban basins demonstrate the influence of the agricultural land in these basins. The yields of prometon in agricultural basins are substantially lower than the yields of atrazine, except for the Pennsylvania sites. The comparison of the yields of prometon and atrazine in the urban basins is not as clear. In the 11 urban basins, the yield of prometon is greater in four, about equal in three, and lower in four. The yields of prometon are always greater in urban areas than in nearby agricultural areas, probably as a result of the greater density of roads and other potential sources of prometon. It is interesting to note that three of the four urban areas with the lowest yields of prometon are the southeastern sites (near Atlanta, Dallas, and Tallahassee). Because use data are not available for prometon, it can only be speculated that this is due to either low use or the predominant use practices of prometon in this area of the country.

TABLE 5: Yields (g km^{-2} yr^{-1}) of Prometon and Atrazine in Selected Urban and Nearby Agricultural Watersheds

	prometon		atrazine	
	agri-cultural	urban	agri-cultural	urban
Colorado (near Denver)	1.7	21	11	8.9
Connecticut (near Norwalk)		21		4.4
Florida (near Tallahassee)	0.24	0.61	2.9	51
Georgia (near Atlanta)	0.75	3.2	13	14
Indiana (near Indianapolis)	8.7	58	490	490
Nevada (near Las Vegas)		15		0.18
New York (near Albany)	0	4.1	65	2.1
Oregon (near Portland)	0.030	16	180	11
Pennsylvania (near Harrisburg)	96	110	100	100
Texas (near Dallas)	2.4	4.4	420	55
near Washington, DC	4.6	54	131	5.4
median	1.7	21	100	11
mean	13	28	160	68

Groundwater. In groundwater, the relation between prometon and atrazine is similar to that observed in surface water. Prometon is the most frequently detected herbicide in the selected urban areas (Table 3), and the third most frequently detected herbicide in agricultural areas. The overall frequency of occurrence of both compounds in both urban and agricultural areas was lower in groundwater than in surface water (Table 4). There was no simple linear relation between concentrations of prometon and atrazine in individual samples ($r^2 < 0.001$ for both urban and agricultural samples). Figure 1B shows the distribution of concentrations of both prometon and atrazine in groundwater in agricultural and urban areas. As would be expected, atrazine occurs more frequently and at higher concentrations in groundwater in agricultural areas than in urban areas because atrazine use in urban areas is limited. Prometon occurs more frequently and at higher concentrations in groundwater in urban areas than in agricultural areas, probably because more is used (per unit area) in urban than in rural areas. Using these same data, Kolpin et al. (*10*) have shown that the frequency of prometon detection in groundwater is significantly related to the amount of urban land within 1 km of the sampled well. Concentrations of prometon and atrazine are similar in urban areas.

Rain. The rain data are more geographically restricted than both the surface water and groundwater data, but it is the only long-term data set available for prometon. The agricultural sites consisted of two to four sites in southern and central Minnesota. The urban site was in a residential neighborhood of Minneapolis, MN. Prometon occurs in rain less frequently than in surface water and at about the same frequency as it does in groundwater (Table 4), although these numbers are not directly comparable. In the data reported here, detection frequencies in rain are primarily a measure of temporal distribution; whereas, the detection frequencies in groundwater are primarily a synoptic measure of spatial distribution. Detection frequencies in surface water are a measure of both spatial and temporal distribution. Atrazine is the herbicide most frequently detected in rain (in both urban and agricultural areas), but prometon ranks 12 out of the 20 target herbicides in terms of detection frequency (Table 3). No simple linear relation between concentrations of prometon and atrazine was evident in individual samples ($r^2 < 0.001$ for both urban and agricultural samples). Figure 1C shows the distribution of concentrations of prometon and atrazine in rain in agricultural and urban areas. Two observations can be made from this graph. First, prometon was detected much less frequently in rain than was atrazine in both agricultural and urban settings. Second, while nearly 40% of atrazine concentrations were >0.1 μg/L, concentrations of prometon in rain were always <0.1 μg/L.

The results for prometon and atrazine in rain can be explained by the relative amounts used and application practices of the two compounds. Atrazine was one of the highest use herbicides during the study period throughout much of the country (*37*). It is often applied as a preemergent herbicide on the surface of bare soil. In contrast, prometon has considerably less use (*2*), although the actual amount is unknown and is commonly applied in or under asphalt (*36*). This type of application minimizes the amount of prometon that can volatilize into the atmosphere. It can be surmised that considerably less prometon than atrazine enters the atmosphere, resulting in fewer observations of prometon in rain, and at generally lower concentrations as compared to atrazine.

Implications. The physical−chemical properties of prometon (relatively high water solubility and vapor pressure, moderate Henry's law constant, and relatively slow transformation rates in soil, Table 1) suggest that it can become widely distributed throughout the environment. The presence of prometon in surface waters, groundwaters, and rain described here and in previous studies (*11*−*32*) is in agreement with predictions of wide-scale environmental distribution. The rates of transformation of prometon in surface waters or groundwaters have not been measured but are probably slower than those reported for soils (Table 1). This suggests that once prometon reaches lakes, oceans, or groundwater, it may be present for time periods on the scale of years.

There is relatively little is known about the toxicity of prometon to humans and aquatic organisms (Table 1). On the basis of these few values for aquatic organisms and the observed concentrations of prometon in surface waters, there seems to be little threat of acute toxicity to aquatic organisms. Unlike most agricultural herbicides, prometon often has a continuous, albeit low-level, presence in surface waters. This may have implications for chronic health effects on aquatic organisms, but this is unknown. The U.S. EPA has established a lifetime health advisory level (HAL) for drinking water of 100 μg/L for prometon as compared to an HAL of 3 μg/L for atrazine (*43*). The HAL for prometon is much higher than any of the reported surface water and groundwater concentrations of prometon. Concentrations of atrazine above 3 μg/L were observed in about 4% of NAWQA surface water samples and occurred primarily during seasonal peaks (*9*, *10*). In laboratory studies, atrazine and several other herbicides have been linked to potential disruption of endocrine systems in animals (*51*), but prometon has not been evaluated for these effects.

Finally, and perhaps most significant to environmental scientists, prometon can be viewed as one example of perhaps many chemicals that have common but largely undocumented environmental use. Prometon often has been added to the list of target analytes (*12*−*32*), not because of any specific interest, but rather because it was relatively simple to analyze in multi-residue methods. Its presence throughout the hydrologic environment and its relatively high frequency of detection as compared to other herbicides (Table 3) was unexpected. It is likely that there are many other pesticides, disinfectants, and other organic chemicals that have yet to be targeted in environmental studies and are currently cycling through the hydrologic system.

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