Watershed Protection Development Review

Total Triazine Levels in Austin Area Springs

By Scott E. Hiers, Environmental Scientist

Abstract

Atrazine, a triazine herbicide, is used extensively in the United States for the control of weeds and is the most frequently detected herbicide in ground water nationwide. In response to its detection at Barton Springs, the City of Austin's Watershed Protection and Development Review Department initiated an atrazine-monitoring study. Phase 1 of the study consists of the screening of 54 Austin area springs for total triazine compounds. A low-cost rapid enzyme-linked immunosorbent assay (ELISA) screening indicated that 55% of spring samples had total triazine concentrations of between 0.035 and 0.881 µg/l, relatively low compared to the Maximum Contaminant Level (MCL) of 3 µg/l. Variability of the concentration of triazine compounds was examined by sampling selected springs during various antecedent weather conditions. The data indicate that antecedent weather condition and rainfall affect triazine compound concentrations to differing degrees depending upon the spring. However, at least two springs, Backdoor and Stillhouse Springs, showed relatively consistent triazine concentrations on all sampling dates. In addition, two springs, Upper Barton and Spicewood Springs, respond similarly to a similar size rainfall event.

Introduction

Atrazine, a triazine herbicide, is an active ingredient in many weed-feed formulations extensively used in the United States to control broadleaf and grassy weeds. Atrazine was detected at Barton Springs by the US Geological Survey (USGS) in 2000 and 2001, and reported in Water Resources Data Texas - Water Year 2000 (USGS, 2000). The USGS reported atrazine concentrations of 0.07 µg/l to 0.555 µg/l in baseflow and stormflow, respectively. In view of this finding and the fact that there is high potential for atrazine to contaminate groundwater, an Austin atrazine-monitoring study was developed. The goal of the monitoring program is to determine if atrazine is present and at what concentrations and if the atrazine concentrations are varying significantly among major aquifer in the Austin area such as Edwards, Glen Rose, and alluvial aquifers as indicated by springs discharging from these aquifers.

Project Design and Methods

The atrazine-monitoring program is divided into two phases. Phase 1 employed a low-cost and rapid enzyme-linked immunosorbent assay (ELISA) screening of 54 springs in the Austin area for total triazine herbicides. The ELISA test does not differentiate between atrazine and other triazine compounds; however, the total triazine screening results are semi-quantitative with enough accuracy to provide reliable total triazine levels for identifying potential atrazine-contaminated springs sites for Phase 2 monitoring. Table 1 shows the method detection limit (MDL) and limit of quantitation (LOQ) for the compounds that the assay does detect.

The MDL is the lowest concentration of the compound that can be detected in the assay. The LOQ is an approximate concentration of the compound required to yield a positive result at the lowest standard used in the assay 0.035 µg/l (or 35 ppt). MDL for total triazine is 0.010 µg/l (or 10ppt).

Table 1
Triazine MDL and LOQ

Compound	**MDL** (ppt)	**LOQ** (ppt)
Atrazine	15	35.00
Propazine	5	14.48
Prometryn	13	378.64
Prometon	15	378.64
Ametryn	19	967.27
Terbutylazine	19	809.80
Simiazine	19	323.00
Desethyl Atrazine	27	138.40
Terbutryn	27	10102.30
Cyanazine	36	8066.00
Desisopropyl Atrazine	156	20363.60
6-Hydroxy Atrazine	158	>15900.00

(Strategic Diagnostic Inc, 1997)

The Phase 1 monitoring has been completed. An evaluation of the quality control data indicates that the accuracy of the results was within the test method design. However, the precision, the measure of variation between replicates, was weak. Therefore, the total triazine screening results should be treated as semi-quantitative.

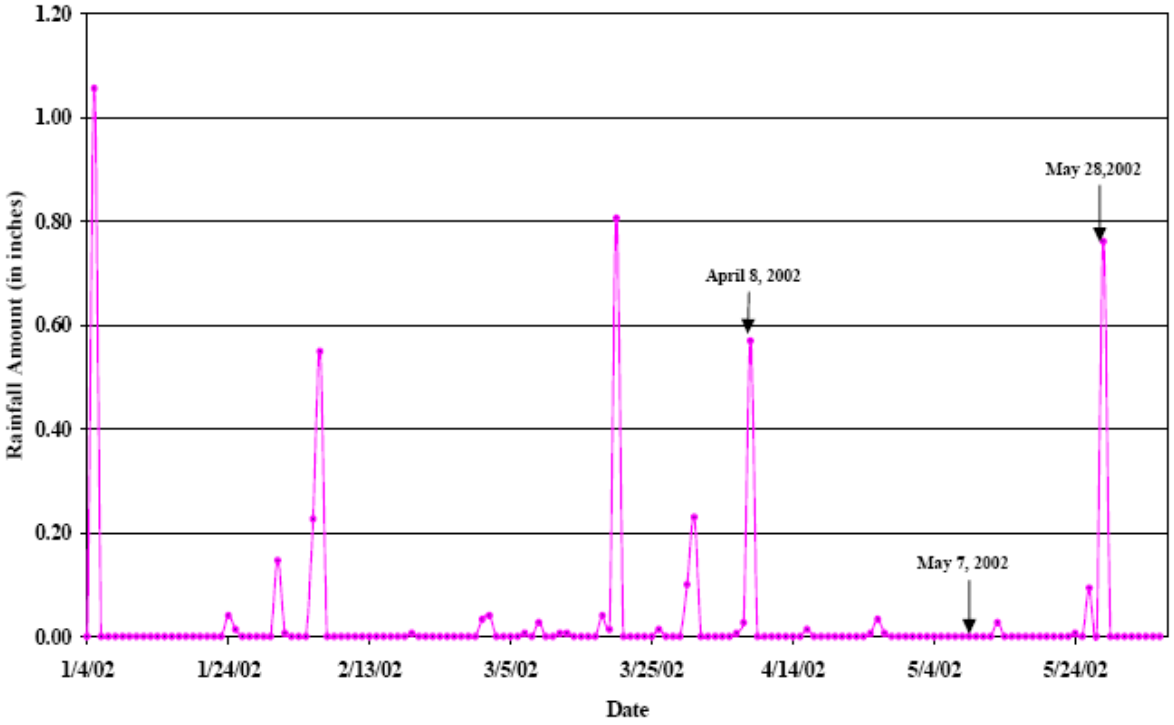
Phase 2 monitoring will consist of a quantitative assessment of atrazine concentrations at 10 representative spring sites. Samples will be analyzed at an EPA certified lab using a quantitative analytical method such as High Performance Liquid Chromatography (HPLC) or Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The spring sites selected for Phase 2 monitoring will be determined by the aquifer type, total triazine screening concentration, and estimated springshed size.

Results

On April 8, 2002, groundwater samples were collected from 34 springs in the Austin area, 12 to 18 hours after a 0.60-inch of rainfall. Rainfall varied from 0.55 to 0.87 inches across the area. Daily rainfall data were obtained by using the City of Austin Flood Early Warning System (FEWS). Seven representative gages, scattered throughout the Austin area, were used to track and calculate 30-day cumulative rainfall amounts. Samples were collected during a moderately wet period during which the average 30-day cumulative rainfall amount was about 1.3 inches. Average daily rainfall in Austin over the sampling period is shown in Figure 1.

Figure 1

Austin's Average Daily Rainfall Amount from January 1st, 2002 to June 5th, 2002



The water chemistry results, including the field parameters, for April 8, 2000, are presented in Table 2. Total triazine concentrations above the MDL and below the LOQ are estimated values and are denoted by a J-flag to the left of the reported value. The total triazine concentrations above the LOQ ranged from 0.035 to 0.881µg/l. Fifty percent of the sample results are above the LOQ and 76 percent of the results are above MCL for total triazine. None of the total triazine concentrations are at levels of concern when compared to U.S. Environmental Protection Agency's (USEPA) Safe Drinking Water Act (SDWA) atrazine Maximum Contaminant Level (MCL) for drinking water and Drinking Water Level of Concern (DWLOC) of 3 µg/l and 296 µg/l, respectively. Since atrazine and simiazine are the only triazine compounds with a SDWA standard, atrazine with the lowest standard which is used above, the total triazine would be expected to be above the atrazine level making the above-mentioned comparison to screening results conservative from a water-protection standpoint.

Table 2. Atrazine and Related Triazine Compounds Sceening Results 4/8/02

Method: SDI RaPID Assay HS Atrazine Test Kit A00151

Analyzed by: Scott Hiers, Sylvia Pope and Ellen Giesmar

Site No.	Site Name		Atrazine/ Triazine Compounds		pH	Cond.	Turbidity	Collection Time	Collection Date	Atrazine Analysis Date	pH, Cond., & Turb. Analysis Date	Lab ID
			ppt*		Std. Units	uS/cm	NTU's					
1355	Avery Deer		881.72	H	***6.98***	542	2.8	13:00	4/8/2002	4/9/2002	4/8/2002	28
582	Spicewood		758.40	H	***6.87***	745	3.1	9:50	4/8/2002	4/9/2002	4/8/2002	25
31	Tanglewood		345.87	H	***7.13***	796	3.1	13:00	4/8/2002	4/9/2002	4/8/2002	23
30	Fire Oak		311.04	H	***7.00***	842	6.5	12:50	4/8/2002	4/9/2002	4/8/2002	21
175	Loop 360		306.82	H	***7.50***	925	4.6	10:45	4/8/2002	4/9/2002	4/8/2002	26
25	Barrow		199.45	H	***7.02***	1087	1.4	10:30	4/8/2002	4/9/2002	4/8/2002	20
1187	Elephant Ear		101.17	H	***7.64***	940	3.6	14:45	4/8/2002	4/9/2002	4/8/2002	38
183	Upper Barton		98.03	H	***7.03***	657	4.2	16:40	4/8/2002	4/9/2002	4/8/2002	30
164	Lost Creek Package		98.03	H	***7.21***	1027	2.4	10:18	4/8/2002	4/9/2002	4/8/2002	35
441	Hearth		89.17	H	***6.69***	850	2.2	12:35	4/8/2002	4/9/2002	4/8/2002	33
761	Spring Hollow		79.06	H	***6.98***	798	3.0	13:30	4/8/2002	4/9/2002	4/8/2002	31
24	Stillhouse		62.80	H	***7.10***	1098	19.1	10:10	4/8/2002	4/9/2002	4/8/2002	17
9	Cold		52.75	H	***7.29***	624	3.5	15:15	4/8/2002	4/9/2002	4/8/2002	39
160	Backdoor		48.32	H	***7.16***	761	3.4	12:30	4/8/2002	4/9/2002	4/8/2002	41
423	Seider		45.61	H	***7.47***	484	5.8	8:50	4/9/2002	4/9/2002	4/8/2002	14
1874	Emily Solan		42.92	H	***6.74***	749	2.1	13:30	4/8/2002	4/9/2002	4/8/2002	37
425	Pecan	J	***32.66***	H	***7.63***	841	2.5	15:00	4/8/2002	4/9/2002	4/8/2002	34
35	Barton	J	***25.37***	H	***7.05***	631	2.7	16:00	4/8/2002	4/9/2002	4/8/2002	20
428	Eliza	J	***24.66***	H	***7.13***	635	4.0	16:23	4/8/2002	4/9/2002	4/8/2002	43
664	Long Bank	J	***24.42***	H	***7.30***	832	2.2	12:58	4/8/2002	4/9/2002	4/8/2002	15
422	Old Mill	J	***24.19***	H	***7.12***	728	3.0	17:00	4/8/2002	4/9/2002	4/8/2002	42
661	Roy Rizer	J	***23.95***	H	***6.90***	992	2.2	12:45	4/8/2002	4/9/2002	4/8/2002	36
36	Great Hills	J	***21.40***	H	***7.29***	2260	6.4	11:15	4/8/2002	4/9/2002	4/8/2002	19
983	El Mercado	J	***15.54***	H	***6.60***	1306	3.8	8:40	4/9/2002	4/9/2002	4/8/2002	13
104	Leif Johnson	J	***15.10***	H	***6.79***	950	2.3	10:50	4/8/2002	4/9/2002	4/8/2002	29
939	Big Boulder	J	***11.87***	H	***7.65***	1312	5.9	10:30	4/9/2002	4/9/2002	4/8/2002	11
434	Brinkley-Anderson		nd	H	***7.72***	671	2.5	15:30	4/8/2002	4/9/2002	4/8/2002	24
504	Tubb		nd	H	***7.25***	666	2.7	14:55	4/8/2002	4/9/2002	4/8/2002	32
34	Pit		nd	H	***7.28***	540	2.8	14:05	4/8/2002	4/9/2002	4/8/2002	22
577	Grotto		nd	H	.	.	.	14:20	4/8/2002	4/9/2002	4/8/2002	10
578	Scenic Bluff		nd	H	***7.06***	1078	3.2	13:55	4/8/2002	4/9/2002	4/8/2002	40
23	Bull Creek Dam		nd	H	***6.90***	921	1.9	11:00	4/8/2002	4/9/2002	4/8/2002	27
161	Lost Creek		nd	H	***6.85***	736	2.0	9:50	4/8/2002	4/9/2002	4/8/2002	16
366	Brodie Oaks		nd	H	***7.02***	926	27.4	11:15	4/8/2002	4/9/2002	4/8/2002	12

0.6-inches of rainfall in 12 to 18 hour. Average 30-day cumulative rainfall is 1.38 inches.

J = Estimated Value
H = Holding Time Violation

Comments:The sample vials (20ml VOC vials) for Big Boulder, Seider and El Mercado that were collected on 4/8/02 had air bubbles - Sites were resampled for Atrazine on 4/9/02. The ph. Cond. and Turbidity measurements listed above are from the samples collected on 4/8/02.

* = part per trillion (or nanogram per Liter ng/L) of atrazine and related triazine compounds.

On May 7, 2002, 30-days after the initial sampling, nine of the springs sampled on April 8, 2002 were re-sampled, along with 20 additional springs. Dry conditions existed prior to sample collection with only about 0.04 inches of isolated rainfall occurring on April 26, 2002, and no significant rain within 29 days prior to sampling. Results for the May 7, 2002 sampling are presented in Table 3. Total triazine levels are substantial lower than the levels observed on April 8, 2002. Total triazine above the LOQ concentrations ranged from 0.035 to 0.135µg/l accounting for 38 percent of the sampled springs. Sixty-five percent of the sites had total triazine concentration above MDL. All the results are well below any safe water drinking act levels of concern.

Table 3. Atrazine and Related Triazine Compounds Sceening Results 5/7/02

Method: SDI RaPID Assay HS Atrazine Test Kit A00151

Analyzed by: Scott Hiers and Sylvia Pope

Site No.	Site Name	Atrazine/ Triazine Compounds		pH	Cond.	Turbidity	Collection Time	Collection Date	Atrazine Analysis Date	pH, Cond., & Turb. Analysis Date	Lab ID	
		ppt*		Std. Units	uS/cm	NTU's						
582	Spicewood Springs	135.38	H	***6.86***	1063	1.6	12:00	5/7/2002	5/8/2002	5/7/2002	33	62
1189	Cuernavaca Spring	70.00	H	***6.76***	659	5.0	17:50	5/7/2002	5/8/2002	5/8/2002	37	
1384	Cow Trough Spring	60.62	H	***7.72***	848	6.1	10:43	5/7/2002	5/8/2002	5/7/2002	27	
1774	Indian Spring	52.86	H	***6.97***	1174	4.1	13:30	5/7/2002	5/8/2002	5/7/2002	23	
1956	Ivanhoe X Spring	50.74	H	***7.89***	558	1.0	13:45	5/7/2002	5/8/2002	5/7/2002	36	
193	Gentle Spring	48.45	H	***6.72***	1287	4.0	14:55	5/7/2002	5/8/2002	5/7/2002	35	
1355	Avery Deer	45.59	H	***6.93***	619	1.2	12:15	5/7/2002	5/8/2002	5/7/2002	17	
1934	Davis Spring @ Robison Ranch	41.60	H	***7.42***	821	0.6	13:34	5/7/2002	5/8/2002	5/7/2002	26	44
1383	Blunn Creek Preserve Spring	40.59	H	***7.79***	934	11.0	10:23	5/7/2002	5/8/2002	5/7/2002	29	45
1078	Fern Gully	39.79	H	***6.68***	659	1.6	10:40	5/7/2002	5/8/2002	5/7/2002	19	46
445	Balcones Dist. Park Spr.	37.08	H	***6.92***	846	7.0	14:06	5/7/2002	5/8/2002	5/7/2002	25	47
160	Backdoor	J **28.82**		7.05	840	.	11:15	5/6/2002	5/8/2002	5/7/2002	13	48
1954	Carrington Spring	J **28.01**	H	***6.75***	680	7.3	10:45	5/7/2002	5/8/2002	5/7/2002	30	49
796	TNS Spring	J **27.69**	H	***6.80***	907	3.6	15:00	5/7/2002	5/8/2002	5/7/2002	24	50
1190	Seven Oaks	J **26.13**	H	***6.84***	1060	4.1	18:00	5/7/2002	5/8/2002	5/8/2002	38	51
24	Stillhouse Hollow	J **20.80**	H	***7.01***	1094	0.5	12:15	5/6/2002	5/8/2002	5/7/2002	11	52
1935	Brandt Spring	J **18.07**	H	***7.40***	630	1.6	12:00	5/7/2002	5/8/2002	5/7/2002	28	53
1955	Avery S17	J **15.20**	H	***6.62***	859	2.2	11:20	5/7/2002	5/8/2002	5/7/2002	21	54
1456	Spillar Spring 2	J **13.87**	H	***7.24***	632	11.0	15:55	5/7/2002	5/8/2002	5/7/2002	31	55
1957	Ivanhoe Spring 2	**nd**	H	***6.99***	615	1.1	13:15	5/7/2002	5/8/2002	5/7/2002	34	56
1353	Hill Marsh Spring	**nd**	H	***7.23***	757	4.6	11:40	5/7/2002	5/8/2002	5/7/2002	22	57
1352	Avery Springhouse	**nd**	H	***6.67***	655	0.8	11:10	5/7/2002	5/8/2002	5/7/2002	20	58
183	Upper Barton	**nd**		6.67	659	5.0	12:40	5/6/2002	5/8/2002	5/7/2002	14	59
1455	Spillar Spring 1	**nd**	H	***6.77***	722	1.6	16:05	5/7/2002	5/8/2002	5/7/2002	32	60
422	Old Mill	**nd**		6.89	733	2.3	10:45	5/6/2002	5/8/2002	5/7/2002	15	61
428	Eliza	**nd**		6.80	638	3.2	11:15	5/7/2002	5/8/2002	5/7/2002	16	63
35	Barton	**nd**		6.80	640	2.1	12:00	5/6/2002	5/8/2002	5/7/2002	12	64
9	Cold	**nd**		7.11	678	.	12:30	5/6/2002	5/8/2002	5/7/2002	10	
166	Schlumberger 1	**nd**	H	***7.54***	609	5.1	10:00	5/7/2002	5/8/2002	5/7/2002	18	
1956	Ivanhoe X Spring - Duplicate	**28.65**		.	.	.	13:45	5/7/2002	5/8/2002	5/7/2002	39	
1355	Avery Deer Spring - Duplicate	**73.55**		.	.	.	12:15	5/7/2002	5/8/2002	5/7/2002	40	

No significant rain in 30-days

J = Estimated Value
H = Holding Time Violation

* = part per trillion (or nanogram per Liter ng/L) of Total Triazine compounds.

On May 28, 2002, after about a 1-inch rainfall, 12 springs were re-sampled to determine if a rainfall event similar to the April 8, 2002 amount would produces similar to those observed on April 8. The average 30-day cumulative rainfall prior to May 28, 2002 was about 0.15 inches. This is an 88 percent drop in 30-day cumulative rainfall amount from the previous sample dates and an unusually dry May, overall. Results from the May 28 sampling are presented in Table 4.

Table 4. Atrazine and Related Triazine Compounds Sceening Results 5/28/02

Method: SDI RaPID Assay HS Atrazine Test Kit A00151

Analyzed by: Scott Hiers

Site No.	Site Name	Atrazine/ Triazine Compounds		pH	Cond.	Turbidity	Collection Time	Collection Date	Atrazine Analysis Date	pH, Cond., & Turb. Analysis Date	Lab ID
		ppt*		Std. Units	uS/cm	NTU's					
582	Spicewood Springs	317.07	H	***6.41***	726	.	10:00	5/28/2002	5/29/2002	5/29/2002	10
31	Tanglewood	134.09	H	***6.70***	676	.	11:00	5/28/2002	5/29/2002	5/29/2002	20
1187	Elephant Eat	86.60	H	***7.11***	1005	.	9:40	5/28/2002	5/29/2002	5/29/2002	14
25	Barrow	74.62	H	***7.14***	975	.	10:35	5/28/2002	5/29/2002	5/29/2002	19
160	Backdoor	J ***34.07***	H	***6.69***	771	.	14:05	5/28/2002	5/29/2002	5/29/2002	11
175	Loop 360	J ***32.50***	H	***7.52***	840	.	13:25	5/28/2002	5/29/2002	5/29/2002	21
183	Upper Barton	J ***24.73***	H	***6.66***	637	.	14:45	5/28/2002	5/29/2002	5/29/2002	12
1355	Avery Deer	J ***22.48***	H	***6.63***	604	.	11:50	5/28/2002	5/29/2002	5/29/2002	15
24	Stillhouse Hollow	J ***21.52***	H	***6.78***	1047	.	10:20	5/28/2002	5/29/2002	5/29/2002	13
422	Old Mill	nd	H	***6.88***	704	.	15:10	5/28/2002	5/29/2002	5/29/2002	17
35	Barton Spring	nd	H	***6.70***	640	.	15:25	5/28/2002	5/29/2002	5/29/2002	16
428	Eliza	nd	H	***6.84***	627	.	14:55	5/28/2002	5/29/2002	5/29/2002	18

Last rainfall 4-28-02 between 00:45 and 01:30. 0.75 and 1.25inches. Samples collected 8 to 14 hr after storm.

J = Estimated Value
H = Holding Time Violation

* = part per trillion (or nanogram per Liter ng/L) of Total Triazine compounds.

Thirteen sites were re-sampled once or twice during the Phase 1 monitoring. A comparison of the total triazine levels at the re-sampled spring site is presented in Table 5. The relative percent difference between the April 8 and May 28 sampling events is shown. The Relative Percent Difference (RPD) is the difference between the two values divided by the average of the two values and multiplied by 100. The smaller the RPD result, the smaller the change in values. Generally, the triazine concentrations are lower than those observed on April 8. Based on the semi-quantitative triazine results and relative low RPD values for five of the springs: Spicewood, Stillhouse, Elephant Ear, Barrow and Backdoor, the total triazine levels between the April 8 and May 28 are similar. However, the remaining eight sites have triazine levels considerably lower than those observed on April 8. The differences between the two observed atrazine concentrations are attributed to the difficulty with collecting samples at the peak rainfall event concentration and the difference in soil moisture content. The dry conditions prior to May 28 most likely resulted in smaller amounts of the rainfall recharging the groundwater and transporting pollutants into the spring's source aquifer. Other unknown factors include when and where the triazines are being applied in the springshed and the time of migration from application sites to spring sites.

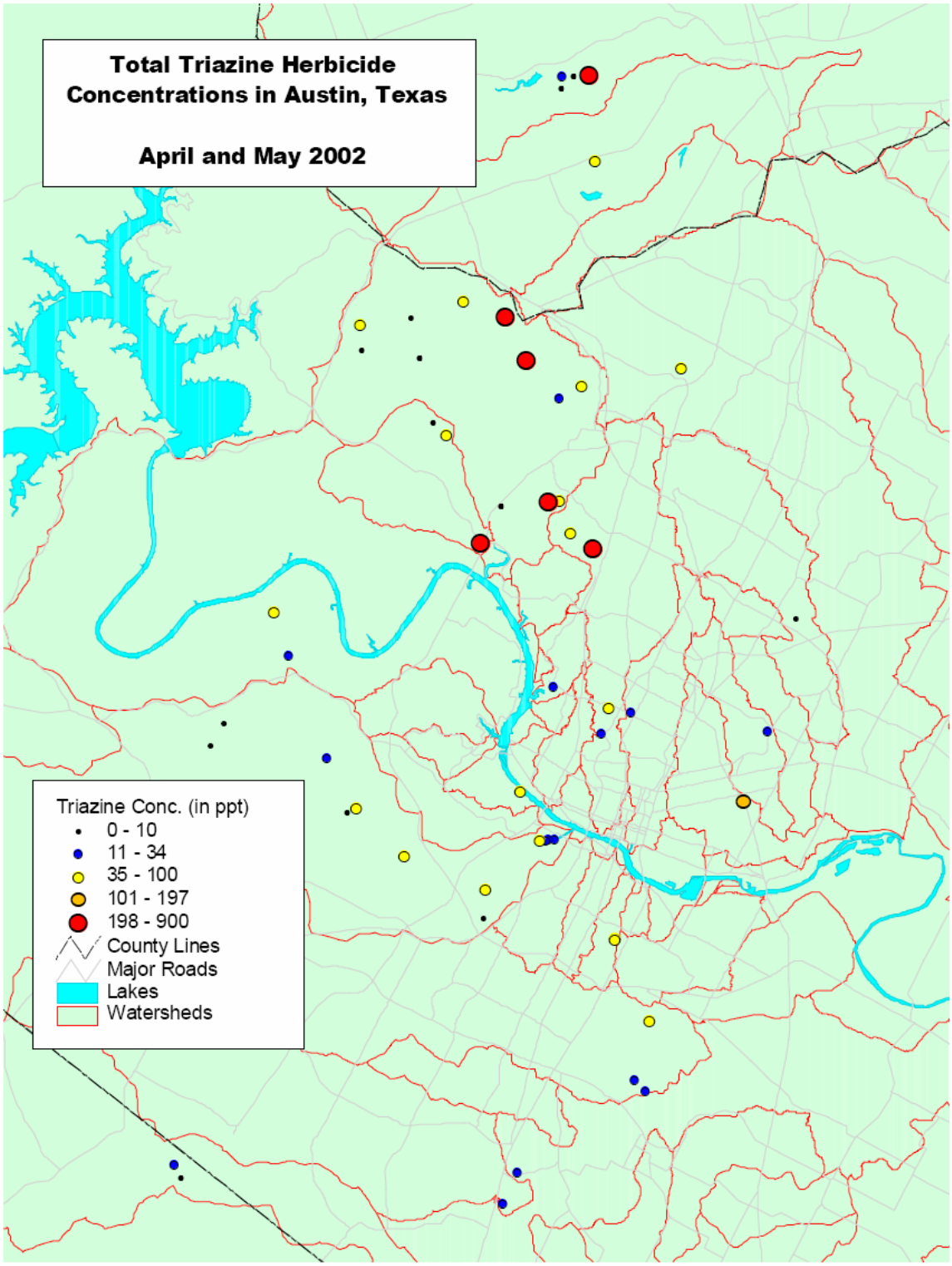
Table 5. Total Triazine Concentrations (in parts per trillion) at Phase 1 Springs Re-sampled During the Study.

Spring/Date	**April 8, 2002** Rainfall Event	**May 7, 2002** Dry	**May 28, 2002** Rainfall Event	**Relative % Difference** between April 8th and May 28th Results
Tanglewood	758	-	134	140
Elephant	101	-	87	**15**
Barrow	199	-	75	**91**
Stillhouse	63	21	22	**96**
Loop 360	307	-	33	161
Avery Deer	882	46	23	190
Spicewood	758	135	317	**82**
Backdoor	48	29	34	**34**
Upper Barton	98	nd	25	119
Barton Springs	25	nd	nd	-
Old Mill	24	nd	nd	-
Eliza	25	nd	nd	-
Cold	53	nd	-	-

Conclusions

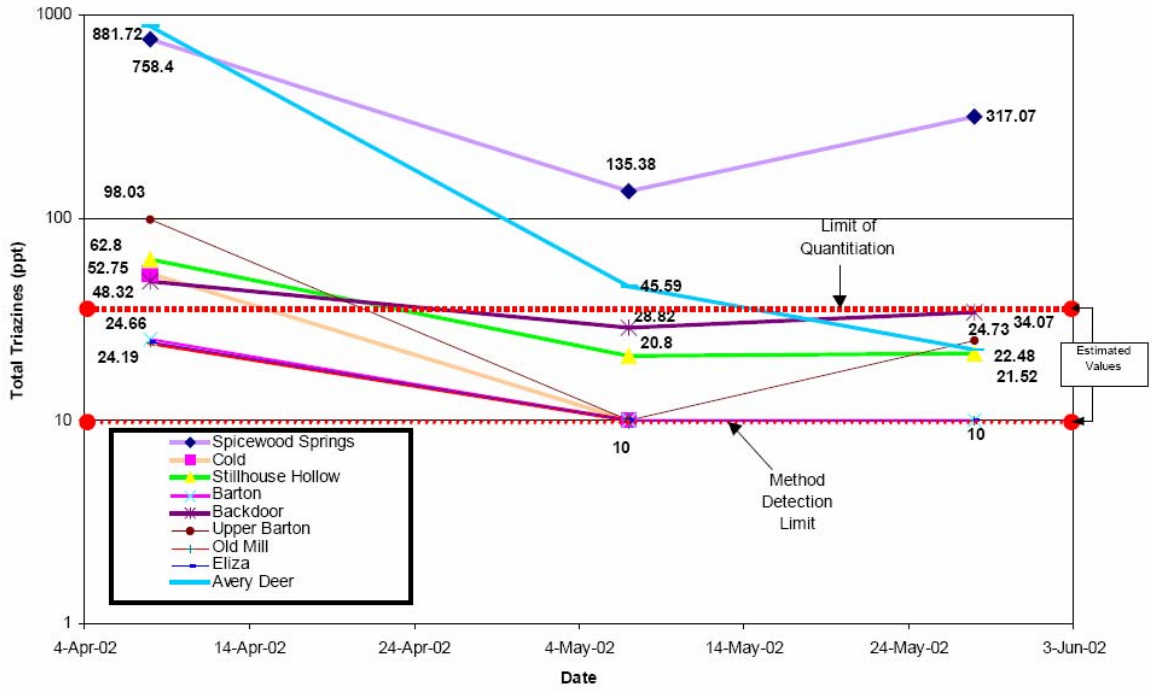
Results from Phase 1 monitoring indicated that 55 percent of the sampled springs had triazine concentrations above the LOQ (<0.035µg/l), extremely low but quantifiable levels. The distribution of the total triazine levels shows that all the relatively high concentrations (above 100 ng/l) were observed north of the Colorado River, mostly in springs from the Northern Edwards Aquifer, a karst aquifer (Figure 2).

Figure 2


Total Triazine Herbicide Concentrations in Austin, Texas
April and May 2002
Triazine Conc. (in ppt)
0 - 10
11 - 34
35 - 100
101 - 197
198 - 900
County Lines
Major Roads
Lakes
Watersheds

The variability in concentrations of the triazine compounds was examined by repetitively re-sampling 13 springs (Figure 3). The data appear to indicate that antecedent weather conditions and rainfall affect triazine compounds concentration to differing degrees depending upon the spring. Based on the semi-quantitative triazine results and relative low RPD values for five of the springs (Spicewood, Stillhouse, Elephant Ear, Barrow and Backdoor), the total triazine levels between the April 8 and May 28 sampling events are similar. Two of the five springs; Backdoor and Stillhouse, showed very little change in triazine concentration between dry and wet conditions. This suggests that the triazine compounds are present and are at persistent levels at these karst springs. The remaining springs showed notable drops in total triazine levels over the 51-day period. Triazine concentration at two springs, Upper Barton and Spicewood, respond similarly to a similar size rainfall event as the one initial sampled on April 8.

Figure 3: Total Triazine Screening Results at Austin Springs



Phase 2 monitoring is scheduled to start after the Spring of 2003. Information collected during Phase 1 monitoring will be used to select up to 10 spring sites for more accurate and precise quantitative analysis of spring during a 5-year period. The data quality objectives are to determine if atrazine concentrations in Austin area aquifers are increasing over time to levels of environmental concern, and to identifying which springs and aquifers are at greater risk of atrazine contamination.

References

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Strategic Diagnostics Inc., 1997, RaPID Assay® HS Atrazine Test Kit A00151 Procedure, 9 p.