

## Pesticides and Herbicides in Austin Watersheds

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### ABSTRACT

*A review of pesticide and herbicide data in the City of Austin was performed to determine the potential impacts to aquatic life. Data were collected from various agencies and combined with City of Austin Watershed Protection sampling to evaluate sediment and water column concentrations from the beginning of recorded monitoring through the end of 2000. Although the frequency of detecting pesticides is low, one pesticide type or another has been detected in most of the media in Austin water bodies. Organochlorine pesticides still pose a problem, but they have been banned and should decrease over time. Organophosphorus pesticides, although not expected to be found in sediment, have been found, with at least some samples exceeding EPA advisory levels. In addition, diazinon has been seen in stormwater and at Barton Springs. Herbicides are just beginning to be evaluated, but levels in sediments in the Central Park wet pond may warrant further investigation into their significance. The future analyses of pesticides in the Austin area should be targeted, particularly with regard to the difference in the use (banned vs. current) and the characteristics of the pesticides and herbicides themselves. The information garnered from pesticide analyses can provide direction for City watershed protection efforts, particularly for source control.*

### INTRODUCTION

Approximately 1.1 billion pounds of pesticides are currently used each year in the United States (Larson et al., 1997). These chemicals include insecticides, fungicides, and herbicides used to control many different types of weeds, insects, and other pests. Creeks and lakes, and their biological inhabitants, are vulnerable to impacts from spills and from runoff of pesticides from the land's surface.

The high cost of laboratory analysis, and low levels at which pesticides are observed to be a concern, restrict the number of pesticide analyses that can be obtained in a cost-efficient monitoring program. Therefore, sampling by the City of Austin has evolved over the years in response to information needs and funding priorities in efforts to determine the pesticide sources, persistence, and impacts in our watersheds. This report examines historical pesticide data through the year 2000 on a citywide basis. Data were obtained from the City's monitoring program, from a cooperative monitoring program with the U.S. Geological Survey (USGS), and from historical data collected by state agencies.

Pesticide groups with the highest historic and present urban use were examined. Representative parameters within each group of pesticides were selected for data analysis based on the frequency and level of occurrence in the Austin area. From the most persistent group of pesticides, organochlorine (OC) pesticides, discussion focuses on DDT and chlordane; both are representative of currently banned products, which degrade slowly (high half-life) and toxicity, which has been a problem in Austin, as has been documented in previous assessments (City of Austin, 1993). The other two commonly used pesticide types include organophosphorus (OP) pesticides, and herbicides. For these groups, those compounds detected more than once are tabulated. Many individual pesticides analyzed within each type were never detected and include more of those not commonly used. Other detected pesticides that are chemically

similar to the examples examined in detail show the same patterns in affinity for sediment or water and distribution.

## **ORGANOCHLORINE PESTICIDES**

Because of their toxicity and persistence, the majority of OC pesticides (including chlordane and DDT) were banned in the U.S. during the 1970's. Chlordane demonstrates the pattern of sampling media and site type where most organochlorine (OC) pesticides have been found. The frequency of sampling and detection for chlordane in sediments and water was examined for the combined data set. Organochlorines have been of concern in Town Lake since a pesticide spill and major fish kill in 1961; concern increased in 1987, when a fish consumption advisory was issued. Therefore, it is not surprising that the first concentrated sampling undertaken before 1990 was exclusively in sediment in Town Lake. In the early to mid 90's more sediment data were collected in structural stormwater controls (Best Management Practices), urban and non-urban creeks, and area springs. Conversely, much more water samples were obtained early on in urban and non-urban tributaries as well as Town Lake in the 1980's. Baseline well sampling for pesticides was also more common in the 80's and early 90's. Spring sampling was performed consistently over the period of record. Because surface water detection frequencies were low, chlordane data were collected more often in sediment media in the late 90's for all sample types.

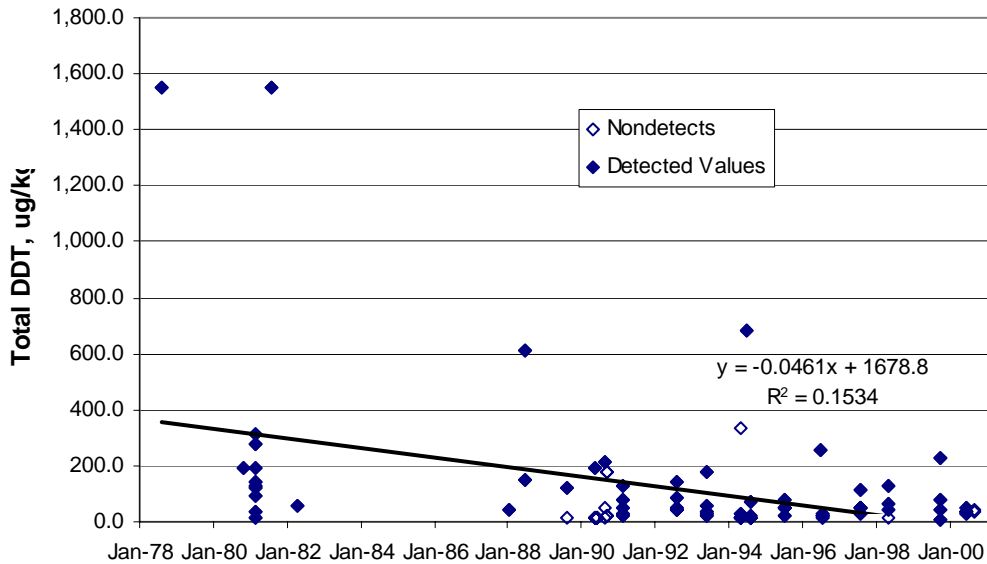
Sediments - Sampling in sediments began in Town Lake, where elevated levels (over EPA and TNRCC criteria for impacted sediments) of OC pesticides have persisted since sampling began in the 1970's. These types of pesticides have deleterious effects at low levels and when they are detected are frequently above indicators such as the TNRCC Ecological Benchmarks for sediment (TNRCC, 2000). Table 1 displays a summary of data for some OC parameters, those for which the TNRCC has established benchmarks. Overall, the majority of OC pesticides were detected in less than half the samples. When sampling was extended to creeks and springs, it was found that pesticides were detected more frequently in urban areas. Detection limits vary greatly for these sediments, even above the highest detected values due to organic matrix interference or laboratory limitations. Also, the frequency data may not always reflect the degree or level to which these pesticides are present in the environment. For these reasons, detectable presence in any sample is cause for concern.

Town Lake itself is the only water body with sufficient data above detection limits to look at trends in these pesticides. A detailed analysis (City of Austin, 2001) shows that over time, some decrease in organochlorine pesticides is apparent, particularly for the primary pesticide within the DDT family (Figure 1). Less evidence of DDE degradation or depuration is apparent.

**Table 1. Organochlorine pesticides in sediments (ug/kg)**

Pesticide	Number of sediment samples	TNRCC Ecological Benchmarks (ppb)	Maximum detected value (ppb)	Median	Minimum	Percent of samples w/pesticide detected
Aldrin	335	2.0	82.0	< 5.78	0.00	6.6
Alpha-BHC	262	6.0	6.9	< 7.25	0.05	6.1
Beta-BHC	259	5.0	175.0	< 8.33	< 0.05	12.7
Gamma-BHC	367	0.94	17.7	< 5.30	< 0.04	7.4
Total Chlordane	184	4.5	1,000.0	< 62.9	1.66	32.6
Technical Chlordane	157		380.0	< 53.0	3.00	32.5
DDD	345	3.54	746.0	< 18.0	< 0.10	37.7
DDE	355	1.42	480.0	< 21.2	< 0.08	44.5
DDT	351	1.19	2,761.0	< 16.9	0.1	39.9
DDD DDT DDE (Total)	398	7.0	3,171.1	< 40.0	< 0.9	51.8
Dieldrin	338	2.85	135.0	< 6.85	< 0.04	29.6
Endrin	339	2.67	530.0	< 8.74	0.06	8.6
Heptachlor Epoxide	341	0.6	12.9	< 5.78	< 0.04	18.5
Mirex	98	7.0	2.3	< 0.11	< 0.01	13.3

**Figure 1. DDT in Town Lake**



The USGS also collected a sediment core in 1998 from the basin area of Town Lake, where scouring was least likely to occur. Approximately 1 meter of sediment deposited at the site was obtained with the core. Ages of sediment layers in the Town Lake core were assigned on the basis of the cesium-137 profile and core lithology (USGS, 1999). For the OC pesticides, the core showed similar data to that reflected in the grab samples from the lake evaluated over time. The core, however, also enabled a review of the history in the lake sediments prior to ongoing sampling. A large DDT peak in the early 1960's, for example, was compared to other urban lakes and reservoirs and was found to be about four times higher, corresponding to a major spill that occurred in the lake in 1961. Chlordane results showing an apparent increase since 1985 may need to be verified as this pattern is not similar to grab-sample results. A study of the fish in

Town Lake (Texas Department of Health, 1999) documented fish tissue levels low enough for removal of the fish consumption advisory. Additional information on fish tissue levels can be found in a City of Austin update report on Town Lake (City of Austin, 2001).

Supporting the lake findings, OC pesticides are still being observed above biological effects levels in the sediment of some urban and suburban creeks. Later sampling through both testing of sediments captured by Best Management Practices (BMPs), such as water quality ponds, and a study of suspended sediments in stormwater (Mahler and Metre, 2001) indicate that these pesticides are still present in surface soils and are still being transported through the creeks to Town Lake.

Water Sampling - Since these pesticides adsorb strongly to sediments, they are not seen as often in the water column. Also, the sampling program has evolved from examining receiving waters and springs, where few samples show detectable levels, to focus on direct runoff from storms. Runoff has been examined by standard storm sampling, new methods such as the LVSS study mentioned above, and data from semi-permeable membrane devices (SPMD) designed and deployed to simulate biological uptake. The presence of pesticides as determined in these studies also demonstrates that they are still being washed off, but in concentrations that are frequently below standard water detection levels. Recently collected groundwater data from wells using the lower NAWQA (National Water Quality Assessment Program) detection levels also demonstrate the occurrence of pesticides in local aquifers.

**Table 2. Organochlorine pesticides in water (ug/l)**

<b>Pesticide</b>	<b>No. of water samples</b>	<b>TNRCC Freshwater Acute/Chronic Criteria for Aquatic Life Protection</b>	<b>Maximum detected value</b>	<b>Median</b>	<b>Minimum</b>	<b>Percent of samples w/pesticides detected</b>
Aldrin	487	3.0 (acute)	0.0118	0.0	0.0	2.1
Alpha-BHC	131		0.0077	< 0.01	< 0.002	3.8
Beta-BHC	116		0.0632	< 0.02435	< 0.005	12.1
Gamma-BHC	517		0.070	0.0	0.0	7.2
Total Chlordane	115	2.4 / .004	0.808	< 0.081	< 0.01	8.7
Technical Chlordane	382		1.40	0.0	0.0	8.6
DDD	499		0.96	0.0	0.0	9.0
DDE	514		0.40	0.0	0.0	13.0
DDT	499	1.1 / .001	3.30	0.0	0.0	12.2
Sum of DDTs	514		4.07	0.0	0.0	16.9
Dieldrin	514	2.5 / .002	1.20	0.0	0.0	12.8
Endrin	499	0.18 / .002	0.04	0.0	0.0	1.0
Heptachlor Epoxide	498		0.24	0.0	0.0	6.0
Mirex	232	.001 (chronic)	0.01	0.0	0.0	0.4

Future Sampling - The plan for future sampling for organochlorine pesticides is to continue to monitor Town Lake sediments, and local creek sediments where problems are identified, to document that degradation and gradual decline of these pesticides in our environment continue to occur. The sediment sampling associated with the Environmental Integrity Index (EII, a program to characterize creeks on a 3-year cycle) will also continue to provide guidance if any unusually high levels, or any increases in these pesticides, are seen at the mouths of creeks in the Austin area. In addition, lower detection levels for the

COA and USGS groundwater program will document the background level in the aquifer and allow us to compare the current Austin problem level with that of other areas of the nation. Control of these pesticides may be needed in sensitive areas and may be accomplished with capture of further soil wash-off from urban areas and where these pesticides were heavily used. Most of the programs and retrofits incorporated by the City accomplish this goal by capturing sediments.

## ORGANOPHOSPHORUS PESTICIDES

Organophosphorus pesticides (OPs) have replaced organochlorines (OCs) as the most prevalent pesticides used. These chemicals have a lower persistence, and their use was not restricted until recently. Table 3 demonstrates that many of these pesticides are beginning to be seen in surface waters of the United States, however, many testing programs do not analyze for these constituents.

**Table 3. Organochlorine pesticides in surface water**

	National Use Rank*	Class	Percent National Sites with Detection in Surface Water*	Testing by COA?
Diazinon	1	Organophosphorus	18	Y
Propoxur	2	Other		N
Allethrin	3	Other		N
Chlorpyrifos	4	Organophosphorus	6	Y
Pyrethrin	5	Pyrethrins		SPMD only
Malathion	13	Organophosphorus	4	Y
Chlordane	35	Organochlorine	18	Y

\*from Estimated Use in Home and Garden, 1989-1990 (Larson et al., 1997)

Diazinon is discussed in detail as representative of this group. Because they are more soluble than OCs, organophosphates are not as frequently seen in sediments and have only been detected in BMP sediments in recent years; perhaps due primarily to older elevated detection limits. Therefore, pesticide sampling strategies, which reduced water sampling with the hope that accumulated pesticides in sediments would be more easily detected, failed to provide creek data. In fact, although the detected values were frequently near the detection limit, many of these pesticides have been seen in stormwater flow in both urban and nonurban creeks. In recent years, however, water sampling through the USGS program has not continued with OP pesticide analyses due to budget considerations.

### Sediments

Table 4 summarizes the OP pesticides found in sediment in BMPs, creeks, and lakes. The percent of detected values is much lower than that of the OC pesticides, as expected. In the 1990's, sediments collected in BMPs were tested and some OP pesticides were identified (including diazinon at one site above the Sediment Quality Advisory Level (SQAL)). In that same period, limited testing was done in creeks, with no OP pesticides found. In lake sediments, the maximum value for diazinon in the table (100 ug/kg; this value may be suspect since each detected value was the same) was reported at all sites in Town Lake as part of the National Urban Runoff program in 1981. Later testing in the lake (1990, 1994, and upstream only in 1998) has not again identified these compounds in the sediments.

**Table 4. Organophosphorus pesticides in sediments**

<b>Pesticide</b>	<b>No. of sediment samples</b>	<b>EPA SQAL (EPA, 1997)</b>	<b>Maximum detected value</b>	<b>Median</b>	<b>Minimum</b>	<b>Percent of samples w/pesticide detected</b>
Azinphos methyl (Guthion)	82		55.3	< 86.2	0.8	7.3
Chlorpyrifos (Dursban)	126		440.0	< 85.0	< 0.6	1.6
Coumaphos (Co-Ral)	39		0.8	< 274.0	0.4	5.1
Demeton-o	69		1.2	< 120.0	1.2	5.8
Diazinon	168	19	100.0	< 99.2	< 0.6	7.7
EPN (Santox)	41		813.4	< 66.0	13.3	9.8
Fensulfothion	45		33.6	< 104.0	0.4	17.8
Malathion	145	67	3.5	< 74.2	< 0.2	1.4
Merphos	41		111.0	< 264.0	15.9	9.8

Water Samples

Organophosphorus pesticides are also infrequently seen in water samples, although diazinon was seen in numerous Barton Springs and creek stormwater samples as analyzed by the USGS. A summary of the OP water data is seen in Table 5.

**Table 5. Organophosphorus pesticides in water (ug/kg)**

<b>Parameter</b>	<b>No. of water samples</b>	<b>TNRCC Freshwater Acute/Chronic Criteria for Aquatic Life Protection</b>	<b>Maximum detected value</b>	<b>Median</b>	<b>Minimum</b>	<b>Percent of samples w/pesticide detected</b>
Chlorpyrifos (Dursban)	113	.085 / .041	0.02	< 0.05	< 0.004	2.7
Diazinon	467		1.3	< 0.01	0	34.3
Methyl Parathion	460		0.04	0	0	1.1
Malathion	464	0.01 (chronic)	0.59	0	0	8.6
Parathion (Parathion Ethyl)	471	.065 / .031	0.01	0	0	0.4

The import of detected values for malathion was evaluated by comparing them to its TNRCC chronic criteria for aquatic life protection. A small percent of both earlier creek samples and more recent runoff collected had malathion levels exceeding the criteria.

The EPA has not suggested guidelines for diazinon, or for many other organophosphates, but levels in Shoal Creek stormflow or baseflow (recent and historic), and historic data for many nonurban creeks exceed the Great Lakes criteria of .08 ug/L.

Future Sampling

Based on the occurrence of these pesticides, the better detection levels available, and the establishment of more criteria (TNRCC screening criteria), increased monitoring in creeks and runoff and during stormflow may be needed to assess the potential impacts of these chemicals. Even in Town Lake a screening of post-storm flow water quality may be indicated to assess the current effects of OP pesticides.

The potential for these chemicals to be harmful to the environment is reflected in the fact that the EPA has restricted use of both Dursban (chlorpyrifos) and diazinon, concluding that they may be more harmful than previously thought.

## HERBICIDES

Much less data is available on the aquatic impacts and measurements of herbicides in the environment. This situation occurs despite data that demonstrate that the mass of herbicides deposited on the land surface now greatly exceeds that of insecticides. In addition, where testing data are available, the percent of sites with detections (Larson et al., 1997) generally exceeds those found for pesticides (Table 6). Detected herbicides include chlorinated herbicides and triazines, as shown in Tables 6 and 7. Testing for these compounds differed from year to year as it was primarily associated with special or limited testing programs.

### Sediment

All of the herbicides found in the sediments were chlorinated herbicides, which are less soluble, adsorb strongly to sediments, and are slow to degrade. Triazine data for sediments are limited to results from 1991 Town Lake sampling and several urban creek mouths; no triazines were detected at these sites. The detected values are primarily associated with sediments in a wet pond capturing runoff from a mixed-use 164-acre area (the Central Park Wet Pond). Several herbicides were identified in the pond sediment at more than several thousand ppb, MCPA and MCPP (with concentrations >100,000 ppb), 2,4-D, 2,4-DB and 2,4-DP. With the exception of MCPA and MCPP, these were also found at low levels in the influent. Herbicides have also been found in sediments captured in other Best Management Practices (BMPs, e.g. inlet filters, ponds, oil/sediment trap), but they were rarely detected in recent creek sediment sampling (from limited data). Some herbicides were detected in the sediments of Town Lake in the early 1980's, but additional testing in the 1990's detected none.

**Table 6. Herbicides in sediment (ug/l)**

<b>Pesticide</b>	<b>No. of sediment samples</b>	<b>Maximum detected value</b>	<b>Median</b>	<b>Minimum</b>	<b>Percent of samples w/herbicide detected</b>
MCPP	44	532,000	< 65,104	1,940	75.0
MCPA	43	240,000	< 14,900	17.2	74.4
2,4-DP	45	3,240	< 69.6	0.19	68.9
Dinoseb	38	1,670	< 168.5	< 3	60.5
2,4-DB	29	3,028	< 107	10.8	58.6
Dicamba	50	503	< 47.92	0.6	46.0
2,4-D	144	6,320	< 42	1.1	31.3
2,4,5,T	137	542	< 11	0.37	29.2
2_4_5-TP (Silvex)	110	76.3	< 10	< 0.6	27.3

### Water samples

Although some chlorinated herbicides were detected in the water, they were at much lower levels than seen in the sediments. Values of 2,4-D in the sediments captured by the wet pond ranged from 6 to 6,000 ppb, while concentrations in the water flowing in and out never exceeded 2 ppb. Triazines were found in water and levels in the water were similar to those seen for some of the chlorinated pesticides.

**Table 7. Herbicides in water (ug/l)**

Pesticide	Pesticide Type	No. of water samples	Maximum detected value	Median	Minimum	Percent of samples w/herbicide detected
2,4-D	Chlorinated Herbicide	407	1.98	< 0.01	0	31.7
Prometon	Triazine	200	8.4	< 0.1	0	29.5
2,4,5-T	Chlorinated Herbicide	405	0.48	0	0	20.2
Atrazine (Aatrex)	Triazine	202	0.798	< 0.1	0	17.8
Simazine	Triazine	200	1.5	< 0.1	0	7.5
Hexazinone (Velpar)	Triazine	18	0.2	< 0.2	<0.2	5.6
2_4-DB (Butoxon)	Chlorinated Herbicide	45	8.99	< 1	<0.1	4.4
Bromacil	Uracil	42	0.3	< 0.5	<0.05	2.4
2_4_5-TP (Silvex)	Chlorinated Herbicide	407	2.9	0	0	1.7

Chlorinated herbicides were detected in the 1980's after storms in Town Lake at low levels, and in creek stormflow by the USGS. Testing has not been ongoing for herbicides, but limited data in the 1990's from creek stormflow showed herbicides detected on one date only at two sites on Shoal and Barton Creeks. The effluent from the Central Park wet pond was tested; however, no herbicides were found. Sparse data from spring testing show no chlorinated herbicides.

Tests for triazines in groundwater were conducted for Barton Springs only from 1982 through 1993, with only one detected level found. Testing resumed in the year 2000, and triazines have been detected on each sampling date. In the creeks, sampling in the 1980's found the maximum levels of triazines (Table 7), and although recent testing is very scant, a few detects have been seen on Barton and Williamson Creeks.

Future Sampling – Currently the only planned sampling program for herbicides is a screening study for springs in the central Austin area using an immunoassay method. The high levels of these herbicides in sediment may be cause for concern, but there are no established sediment criteria for comparison purposes. Nevertheless, since these compounds are found at elevated levels, it offers an opportunity to examine the sources, relative values, and trends through testing of BMP sediments and downstream in associated creek beds. These types of analyses have not been possible with the other pesticides found close to detection levels. In addition, ambient toxicity testing may indicate the significance of the levels for Austin creek sediments. This special study would require additional or diverted funds for these costly tests.

## **SUMMARY**

Although the frequency of detecting pesticides is low, one type or another has been detected in most of the media in Austin water bodies. Organochlorine pesticides still pose a problem, but they have been banned and should decrease over time. Organophosphorus pesticides, although not expected to be found in sediments, have been found there, and at least some samples exceed EPA advisory levels. In addition, diazinon has been seen in stormwater and at Barton Springs. Herbicides are just beginning to be evaluated, but levels in sediments in the Central Park wet pond may warrant further investigation into their significance.

The analyses of pesticides in the Austin area need to be targeted, particularly with regard to the difference in the use (banned vs. current) and the characteristics of the pesticides and herbicides themselves. The

information garnered from pesticide analyses can provide direction for City efforts, particularly for source control. The Community Education program in the Environmental Resource Management (ERM) division has recently compiled extensive information on the relative toxicity of various pesticide products for the "Grow Green" program ([www.growgreen.com](http://www.growgreen.com)), and the information from this summary and further sampling can assist in focusing the efforts of that program and in identifying data needs.

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