

Identifying Sediment Contamination Sources in the Barton Creek Watershed of Austin, Texas

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ABSTRACT

Contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, herbicides, and heavy metals are hydrophobic, will adsorb onto sediments, and thus are often non-detectable in creek water chemistry analyses. However, these contaminants can be detected in creek sediment samples. Laboratory costs of sediment analyses can prohibit the number of samples that can be analyzed, thus limiting the ability to isolate contaminant sources. The City of Austin Watershed Protection and Development Review Department (WPDRD) used enzyme linked immunosorbent assays (ELISA) as a fast, cost-effective screening method to perform numerous analyses for polycyclic aromatic hydrocarbons (PAHs) in sediments. This method was used successfully in identifying several localized sources of sediment contamination on four creeks in the Austin area, including lower Barton Creek. The identified contamination in Barton Creek sediment had previously been attributed to unknown sources due to lack of spatial resolution when high laboratory costs limited sampling.

Using ELISA as a screening tool has increased WPDRD's ability to identify sources of pollutants and eliminated the need for costly laboratory analyses for screening. The ability to collect up to 21 samples, run the analyses, and obtain results quickly has decreased the cost and time needed to get these results. The PAH results have subsequently been verified using standard laboratory methods of sediment analysis that have also identified other pollutants such as heavy metals and pesticides at sites that are contaminated with PAHs. These sites are under consideration for remediation and construction of stormwater controls under other WPDRD programs.

INTRODUCTION

Sediments are an integral part of the benthic environment, providing feeding, habitat, and rearing areas for many aquatic organisms (1). Many non-point source pollution related contaminants are hydrophobic and will adsorb to the sediments, settle in the creek bed, and accumulate at elevated levels in the benthic environment. These contaminants may be found in only trace amounts in the water column, if at all. (1). Compounds can build up over time as a result of inputs from many non-point sources. Rivers and creeks with rapid velocities are able to flush themselves of contaminants if the source is not ongoing; however, lakes, reservoirs, and in-stream pools act as settling basins and provide longer residence times for the sediments in water bodies. The residence time of contaminants in the sediments depends on many biological, chemical, and physical factors, such as degree of binding to sediments and in situ degradation rates (2). Sediments serve as both a short-term sink and a long-term source for contaminants in the aquatic environment. They can release accumulated contaminants to the water column and biota

very slowly or very quickly due to natural or artificial disturbances (2). While release stimulated by bacterial decomposition and solubilization can be slow in undisturbed conditions, rapid release and relatively high concentrations in the water column have been correlated to localized organic matter decomposition concentrating low-flow conditions and stormwater flushes (1).

Sediment-sorbed contaminants have been associated with a wide range of impacts on the plants and animals that live within and upon bed sediments. Chronic and, in some cases, acute toxicities of sediment-sorbed contaminants to algae, invertebrates, fish, and other organisms have been measured in laboratory toxicity tests (7). Human health effects have also been associated with sediment-sorbed contaminants, prompting development of health-based water quality criteria. The most direct route to humans is often consumption of fish tissue that has had the time to bioaccumulate various organic contaminants or metals.

One group of sediment-sorbed organic contaminants frequently associated with non-point source pollution is the polycyclic aromatic hydrocarbons (PAHs). Fin rot, skin and neoplastic lesions, and liver tumors have been found in fish living above sediment contaminated with PAHs. PAHs in sediments have shown a dramatic increase in lakes with urban watersheds across the country. This increase can also be seen in Town Lake data collected during the past 20 years. PAHs occur naturally in crude oil and coal and are produced during organic chemical processing of these hydrocarbon sources. They can also be produced as a byproduct of the combustion of hydrocarbons. Major sources include industrial and power plant emissions, car and truck exhaust, tires, asphalt roads, and roofs (9). Many of the sites identified through PAH screening as heavily contaminated in this study appear to have crumbled asphalt particles in the sediment matrix.

The City of Austin's Watershed Protection and Development Review Department (WPDRD) used the results of ongoing citywide studies to select creeks in the Austin, Texas area with elevated levels of PAHs and other contaminants in sediments. WPDRD staff had collected sediment at the mouths of all creeks entering the Town Lake watershed, and four creeks of concern were selected from these results for further PAH screening and source location as part of a Clean Water Act Section 319 EPA grant (3). Initial sites were selected using visual observation, based on availability of sediment and locations of concern. The first sampling run attempted to get an overall representation of the entire creek mainstem from the mouth to the headwaters as well as to pinpoint sites suspected of contamination due to proximity to outfalls, development, or infrastructure. Creeks with development located close to the streambanks have obvious inputs such as intersecting drainage pipes and ditches that proved to be significant sources of contaminants. By sequentially sampling and screening potential sources around sites of contamination, a specific input was tentatively located. Finally, sediment was collected at the worst contaminated of the screened sites and submitted to a contract laboratory for analysis.

This PAH screening method was also added to the City of Austin National Pollutant Discharge Elimination System (NPDES) Municipal Separate Storm Sewer System (MS4) discharge permit through an Endangered Species Act Section 7 Consultation with the U.S. Fish and Wildlife Service. The screening was added as a Reasonable and Prudent Measure for lower Barton Creek (below Loop 360) in support of protections for the endangered Barton Springs salamander.

FIELD METHODOLOGY

For sediment screening, samples were collected from bed sediments in the creeks using a Teflon-coated scoop or disposable pre-sterilized plastic scoops. Several subsamples (minimum of three) were collected and composited in a glass bowl, pre-rinsed at each site with native water. The sediment was then transferred to new, sterilized whirlpaks or sterilized glass containers and placed on ice for transport to WPDRD's laboratory for extraction and screening analysis or transported to a contract laboratory for verification analysis. Samples at the WPDRD laboratory were then refrigerated (4° C) and extractions were performed as soon as possible, always within the ELISA manufacturer specified holding time of 14 days. Analyses were performed within 7 days of extractions. Sample handling and preservation for the contract laboratories complied with EPA methodologies.

LABORATORY METHODOLOGY

The methodology used for sediment screening was the enzyme linked immunosorbent assay (ELISA) procedure for organic constituents. All WPDRD staff performing immunoassay analyses were trained and certified by Ohmicron Environmental Diagnostics (currently Strategic Diagnostics, Inc., SDI). All immunoassays rely on antibody coupled magnetic particles as the critical analytical reagent (4). The sample extract is added, along with an enzyme conjugate, to a disposable test tube, followed by paramagnetic particles coated with PAH specific antibodies. Both the analyte PAH and the labeled PAH (enzyme conjugate) compete for the antibody binding sites on the paramagnetic particles. At the end of the incubation period, a magnetic field is applied to hold the paramagnetic particles (which contain the analyte PAH and labeled PAH bound to the antibodies in proportion to their original concentration) in the tube and allow the unbound reagents to be decanted. After decanting, the particles are washed in a washing solution. The presence of PAH is detected by adding an enzyme substrate specific to PAH. The enzyme labeled PAH conjugate bound to the PAH specific antibody catalyzes the conversion of the enzyme substrate mixture to a colored product. After an incubation period, the reaction is stopped and stabilized by the addition of acid. Because the labeled PAH (enzyme conjugate) is in competition with the analyte PAH (in the sample) for the antibody sites, the color development is inversely proportional to the concentration of PAHs in the sample (5).

Sample extractions were performed with the sediment extraction kit provided by SDI. This method employs pre-measured vials of 100% methanol. A 10-gram sample is placed in 20 milliliters of methanol and shaken vigorously for one (1) minute. The sample is then allowed to settle for one (1) or more minutes and the liquid is removed and filtered. Filtered extract is then diluted with the appropriate extract diluent (a buffered saline solution containing preservatives and stabilizers specific to and without detectable levels of analytes). Analyses were performed using ELISA kits for PAH, PCB, 2,4-D and Chlorpyrifos. Each immunoassay requires eight standards and one control, multiplication by the appropriate dilution factor and calculations for dry weights for comparison purposes. Due to limited quantities of analysis materials, there were times when further dilutions were not performed if a sample was over range for a particular dilution.

The Elisa method is appropriate for screening and is not an EPA-approved method for determining concentrations of specific organics. Therefore, when a site was determined through screening to have elevated levels of a contaminant, additional samples were collected and submitted for analysis to a contract laboratory. Contract laboratory analyses for PAHs were performed using EPA Method 8270.

DATA EVALUATION METHODOLOGY

Screening results for sediment were compared to biological effects levels in the National Status and Trends Program produced by the National Oceanic and Atmospheric Administration (NOAA) in 1990 (7). Chemical concentration criteria in the NOAA study are reported as effects range-low (ER-L), the lowest 10 percent where biological effects were observed, and effects range-median (ER-M), the median concentration of contaminants where biological effects were observed. Most of the sites identified from screening results and subsequently submitted to a laboratory had verified concentrations above the ER-M of 35,000 ppb. Initially, all sediments were screened using ELISA for PAH, PCB, 2,4-D (chlorinated herbicide) and Chlorpyrifos (an organophosphorus pesticide). The first sampling conducted in December of 1997 resulted in nondetects for PCBs, 2,4-D and Chlorpyrifos. The second screening date in January of 1998 resulted in two detected values for 2,4-D on East Bouldin Creek. However, when resampled and submitted to a contract laboratory and analyzed for chlorinated herbicides, both sample results for 2,4-D were nondetect. Subsequently, ELISA screening for 2,4-D, PCBs, and Chlorpyrifos was discontinued, and remaining screening studies focused on PAHs.

LOWER BARTON CREEK SEDIMENT RESULTS

Sampling in Barton Creek was the most intensive of the watersheds studied due to permit requirements. Site locations in lower Barton Creek are illustrated by site number in Figures 1 through 4.

Figure 1
Barton Creek Sediment Sampling Sites

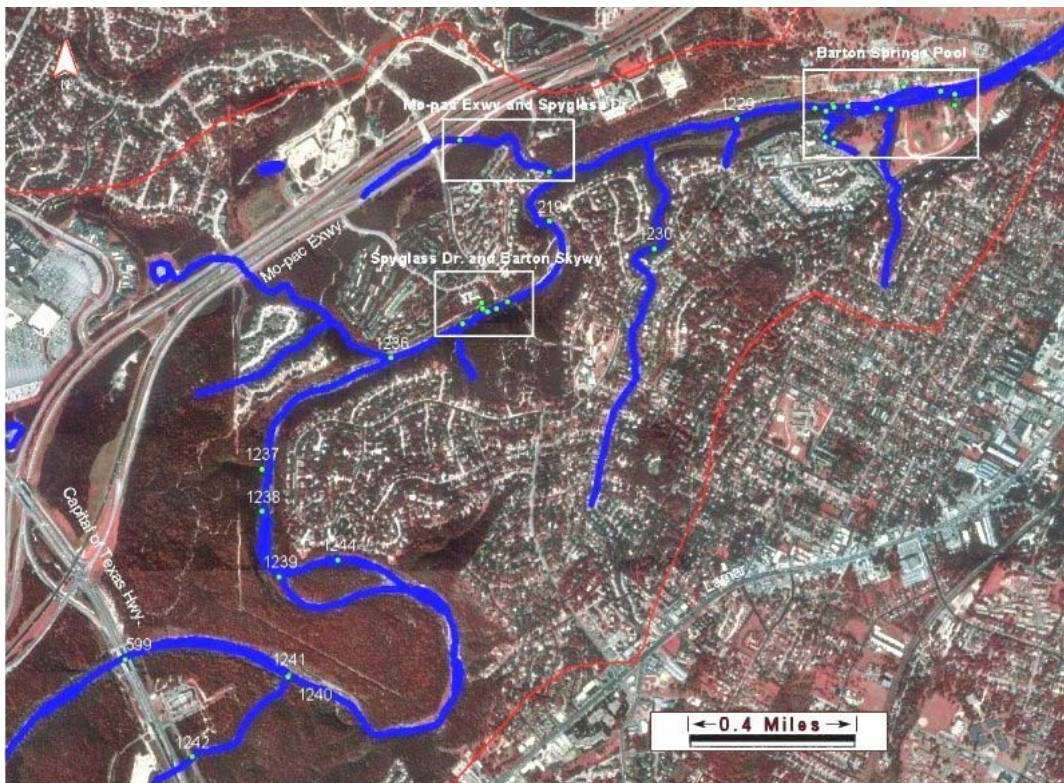


Figure 2
Sediment Sampling Sites Near Barton Springs Pool



Figure 3
Sediment Sampling Sites Near MoPac Expressway and Spyglass Drive



Figure 4
Sediment Sampling Sites Near Barton Skyway



Barton Creek shows consistently low levels of PAHs except in three main areas. These areas include two sites immediately upstream of Barton Springs Pool (sites #53 and #879), a site further upstream at Campbell's Hole (site #219), and near the Spyglass access to Barton Creek (site #1231) Table 1 shows all screening levels for Barton Creek downstream of Loop 360..

**Table 1
Ohmicron Screening Results**

Site Number	Site (listed upstream to downstream)	Number of sampling dates		Min	Max
	<i>Loop 360</i>				
599	Downstream of 360 Bridge	1			515
1241	Ups unknown trib.	1			1,146
1242	EG trib at Loop 360	1			2,287
1240	EG trib near Toys R Us	1			1,697
1244	Ups of Gus Fruh (BC)	1			539
1239	Bank sediments Gus Fruh Spring Trib	1			2,150
1238	Dry sample from ditch 3M from BC @ GF dam	1			39
	<i>Gus Fruh</i>				
1237	Drainage ditch dwnstrm GF (#5)	1			1,558
1236	BC @ Wet weather channel w/wood bridge	1			6,190
1235	3rd Site ups Spyglass @ Euro. Villas 40 M N. of 1.25 M sign	1			1,673
1234	2nd Site ups Spyglass @ 4" pipe	1		>	6,911
1280	Upstream of Spyglass at pipes	1			5,213
1233	Spring outfall ups Spyglass below trail sign	1			4,483
	<i>Spyglass Access</i>				
1231	BC at Spyglass access	1			15,873
219	Campbell's Hole	8		3,310	12,607
	<i>Campbell's Hole</i>				
1279	Grotto	2	>	6,489	> 6,498
1230	BC - trib @ Ridgeview	2		3,876	> 7,043
1229	Barton .25 ups Barton Springs	1			4,396
183	Upper Barton Springs	3		45	1,877
1228	BC at Apartments	2	>	5,322	> 641,708
1227	Zilker Park Parking Lot	2		4,243	12,264
879	Barton Creek Above Pool	9		2,914	57,894
	<i>Barton Springs Pool</i>				
1243	Trib Draining into BS Pool	1			1,273
1281	Sunken Garden Outfall	1			513
1390	Sunken Garden, 2nd Outfall	1			144
1360	Barton Creek dwnstream BSP at cement ramp	1			890

Sites Immediately Upstream of Barton Springs Pool

Screening samples were taken to focus on the source areas for high levels in Barton Creek immediately above and potentially contributing to Barton Springs Pool (sites #53 and #879). The nearest clean upstream sample 0.25 mile upstream of the pool (site #1229) was screened using ELISA, and extremely low PAH levels were determined. Therefore, potential sources downstream were investigated. Two adjacent subareas, which drain to the creek downstream of site #1229, above the impacted sites (#53 and #879), were identified as containing potential sources, including parking lots at Zilker Park on the north bank of the creek (site #1227) and apartment complexes on the south bank (sites #1228, #1266, and #1267). Sediments from these areas in smaller tributaries where they appear to drain to the creek were sampled and screened. The site draining Zilker Park parking lot showed elevated screening levels for PAHs, but levels were small compared to extremely high levels of PAH contamination in the small intermittent tributary draining from apartments on the opposite bank of the creek. A small watershed

containing a private apartment complex is the only identifiable source of elevated PAHs draining to this site. The site has been resampled several times, and laboratory analyses have been performed for PAHs, metals, and pesticides. Both mercury and organics levels well above the Texas Natural Resource Conservation Commission (TNRCC, now TCEQ) screening levels were found (10). PAH levels have been verified by contract laboratories as over 655,100 ppb total PAHs near the confluence of this tributary with Barton Creek. The drainage tributary source itself, immediately downslope from the apartment parking lot (site #1266), has confirmed levels of 2,287,148 ppb total PAHs. These sites have also shown detectable levels of chlorinated pesticides Beta BHC (91.2 ppb), Endrin (67.2 ppb), and Heptachlor (20.1 ppb). The upstream sample (site #1229) has also been analyzed at the laboratory to confirm that the source of contamination was not upstream from the site, and it was found to have lower levels of these constituents. The tributary draining the parking lots at Zilker Park (site #1227) has also been resampled and eliminated as a source of elevated contaminants due to consistently lower levels than in the mainstem of Barton Creek and the apartment tributary.

As the sediment of concern from the apartment tributary originates on private property, and no intervening storm sewers are located between the apartment site and the creek, WPDRD is investigating possible source controls and coordinating with the site landowner. These data have been submitted to TNRCC in order to identify concerns for state TMDL planning through the Clean Water Act 303(d) prioritization process (8). However, TNRCC requested additional confirmation through ambient sediment toxicity testing in addition to the sediment chemistry data before listing Barton Creek as a priority for TMDL development. Preliminary results from sediment toxicity testing using the amphipod *Hyallela azteca* indicate toxicity under UV light at several Barton Creek tributary sites at PAH levels of the same order of magnitude as those found in the sampling reported above. Planning for controls or remediation of sediments is under consideration by WPDRD and may include streambank excavation and stabilization of the apartment tributary as well as onsite remediation.

Campbell's Hole Sites

Subsequent sampling and analysis in Barton Creek between Barton Springs Pool and Loop 360 have also detected elevated levels of PAHs in the pool at Campbell's Hole (site #219). After priority identification with ELISA, the Campbell's Hole site was revisited and samples were submitted to a contract laboratory for verification. When samples from these sites were found to contain high levels of PAHs, they generally were accompanied by high levels of additional toxics such as heavy metals and/or pesticides.

Elevated levels of PAHs have also been detected in a mainstem Barton Creek site upstream of Campbell's Hole near the Spyglass access to the greenbelt (#1231). The dry tributary discharging to Barton Creek above site #1231 (at sites #1234 and #1280) drains a parking lot to a private apartment complex. Subsequent laboratory results have confirmed contamination at site #1234 with a total PAH value of 1,492,920 ppb. This parking lot may have been the source of sediment contamination at the Campbell's Hole site given that the next upstream site (#1236), contained significantly lower PAH screening levels (less than half the Campbell's Hole value).

MoPac Expressway and Spyglass Drive Sites

A tributary site downstream of Campbell's Hole was also identified as contributing elevated PAHs and pesticides (DDT and its congeners). This site (Waterfall Grotto, site #1279) drains road runoff from

MoPac, which was originally suspected of being a PAH source. However, from screening samples, contaminants appear to be entering the system downstream of MoPac and downstream of where the tributary crosses Spyglass Drive. The COA has no access to this area because it is private property; further investigations will be required to isolate sources of these contaminants. Most parameters are below detection limits when sampled upstream in the tributary close to MoPac drainage (site #1283). Therefore, it appears that highway runoff may not be the primary contributor to PAH levels in this tributary.

Follow-up Sampling and Analyses

Additional samples were collected during this period in areas upstream of Loop 360 for reference. Most of these samples contained screening levels of PAH that were comparably low. However, concentrations in samples taken in Barton Creek near Lost Creek Blvd. were higher than concentrations in samples taken from other Barton Creek sites upstream of Loop 360. These values were still comparable with lower levels found in other urban creeks. Additional investigations into the areas upstream of Lost Creek Blvd. have not been successful in identifying contaminant sources. Several laboratory analyses were performed on tributaries in and around the Short Spring Branch Tributary, indicating low levels of contaminants of concern. Additional sampling of these sites in the Lost Creek area may be warranted based on these initial results. Also, isolation of the source of the elevated values at the MoPac Expressway and Spyglass Drive tributary sites may require additional sampling if access to private property in this drainage area can be obtained.

CONCLUSIONS

Although the intermittent tributary sites discussed above do not interact with Barton Creek during periods of low rainfall and drought, levels of contaminants appear to drop in the mainstem creek during these conditions. However, these sites discharge into the creek during stormflow and may flow continually during wetter seasons. Therefore, they are of continuing concern in prioritizing control of non-point source pollution entering Barton Creek and Barton Springs Pool. During high flow and flooding conditions, these contaminants could enter Barton Springs Pool through overtopping of the upstream dam.

ELISA screening has been useful in helping the City of Austin's WPDRD to identify sources of contaminants into area creeks. This is a relatively inexpensive and rapid way to perform numerous sediment sample analyses, with a minimum of training. Laboratory costs of sediment analyses by EPA-approved methods can prohibit the number of samples that can be analyzed, limiting the ability to isolate sources. WPDRD has used ELISA as a fast, cost-effective screening method to perform numerous screening analyses for polycyclic aromatic hydrocarbons (PAHs) in sediments. Verification samples in almost all cases corroborated screening results on a relative, semi-quantitative basis. In most cases, the results acquired by ELISA are not exactly the same or even of the same order of magnitude as results given by other methods, although relative relationships between sites were consistent with laboratory results. This enabled WPDRD to accurately screen and select sites for further investigation at a relatively low cost.

Verification of the ELISA results by EPA methods has identified other pollutants such as heavy metals and pesticides at sites that are heavily contaminated with PAHs. These sites are under consideration for remediation and construction of stormwater controls under other WPDRD programs. Access and

infrastructure limitations make correction of sediment contamination difficult. Final disposition of identified sources has not been determined because of funding priorities of WPDRD; however, NPDES permitting requirement requires at least one retrofit structural Best Management Practice for water quality enhancement in the lower Barton Creek watershed as a Reasonable and Prudent Measure for the protection of the endangered Barton Springs salamander.

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