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Oak Grove Tire Shreds Project:
Tire Shreds below the Seasonal Groundwater Table
Years 2006-2008

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16. Abstract (Limit: 200 words)

The Minnesota Department of Transportation constructed a low traffic volume road section to determine the environmental fate and effects of chemicals from tire shred materials placed below the seasonal groundwater table. The road base was constructed during November of 2002 with over seven million pounds of tire shreds enclosed in geotextile fabric in the road base.

Surface and well water samples were analyzed for pH, temperature, dissolved oxygen, specific conductivity (SpCond), hardness, chemical oxygen demand (COD), total suspended solids (TSS), biochemical oxygen demand (BOD), aluminum, antimony, arsenic, barium, cadmium, total chromium, copper, iron, lead, manganese, nickel, selenium, zinc, mercury, gasoline range organics, diesel range organics, total polynuclear aromatic hydrocarbons (PAHs), and carcinogenic polynuclear aromatic hydrocarbons (c-PAHs) and eight tire specific semi-volatile organic chemicals. Selected parameter data are presented.

Elevated levels of barium, iron, and manganese were measured in all of the monitoring wells but not in the background well or surface water. The tire shreds contributed some PAHs to the surface water but in very low concentrations. Four tire material semi-volatile organics were detected in well water but not surface water samples.

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Years 2006-2008

Final Report

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The Oak Grove Tire Shreds project was funded by the Minnesota Local Road Research Board (LRRB), Minnesota Pollution Control Agency, and the Minnesota Department of Transportation, Office of Environmental Services. It is through their continued commitment to a safe and healthy transportation system that this project has occurred.

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EXECUTIVE SUMMARY

The Minnesota Department of Transportation in cooperation with Anoka County of Minnesota constructed a low traffic volume road segment to evaluate the road engineering aspects and monitor environmental fate, effects, and transport of chemicals from tire shred materials placed below the seasonal groundwater table. The road base was constructed during the fall of 2002. Funding for this project came from the Minnesota Local Road Research Board, the Minnesota Pollution Control Agency, and the Minnesota Department of Transportation. The project area was a tarred country road partially skirted by a ditch that provided surface water drainage from a grass sod farm. The original road base was low strength water laden soil. Over 7 million pounds of tire shreds enclosed in geotextile fabric replaced the endemic mucks in and below the road base. The road construction was completed with customary aggregate materials and asphalt wearing course over the tire shreds.

Due to various delays the groundwater monitoring wells were not installed until August 2004. The first well water and surface water samples were collected in January 2005. The sampling stations included one background well that served as the experimental control well. Five monitoring wells were installed within the tire shreds and were distributed along both sides of the road. The road side ditch paralleled the road on its northern side, then bisected the road through a concrete culvert, and continued south away from the road through the sod farm. Ditch surface water was sampled at the down stream end of the culvert and represented the combined water flow of the ditch and tire shreds well water. The confluence of the ditch water and the larger Rum River is located about five miles downstream.

The Oak Grove Tire Shreds Study has been a unique examination of tire material in road base compared to other field studies conducted in the United States. This provided an opportunity to evaluate the “real world” responses, both chemically and biologically, by the aquatic environment from this material. Furthermore, this study has reported the environmental performance of a large quantity of tire shreds below the groundwater table during the first five years of the road base life-cycle.

Since the beginning of this study, chemical oxygen demand, total suspended solids, specific conductance, barium, iron and manganese have increased in the well water from the road base. There also appeared to be ammonia and total organic carbon contributions from the tire shreds to the well water. Ammonia may be leaching at an undetermined rate from the tire shreds or could also be migrating from the sod farm adjacent to the study area. At present, a positive identification of the source of the ammonia in the well water is not apparent. The fairly consistent levels of ammonia measured in the well water samples suggest that the source is the tire shreds material. Additional study will be needed to confirm this.

The field measurements of well water have shown a slight pH depression during each year of the study in the wells on the east side of the study area. At least one other study reported a change in pH in well water taken from tire shreds. The pH depression in the Oak Grove study area does not appear to be dependent on the thickness of tire shreds or peat layers.

Specific conductance measurements of well water from all the wells have continued to increase during the study. Conductivities exceeding 1000 umhos/cm were measured in several of the wells. The increases in conductivity for some of the wells could be due to an increase in dissolved ionized chemicals, both inorganic (e.g. iron) and organic.

Polynuclear aromatic hydrocarbons were detected at low concentrations in wells in the thicker deposits of the study area. No carcinogenic PAHs were detected in well water samples. The PAHs detected in the first year samples may have been caused by the increase in ditch water elevation flooding shreds not previously covered in well water during the usual 10 inch ditch water level.

The well water in the tire shreds road base contained four of the eight tire related organic chemicals monitored. The organic chemicals detected in the well water samples were aniline, benzothiazole, 2-hydroxybenzothiazole and 4-acetylmorpholine. Well water concentrations of these compounds varied linearly with the thickness of submerged tire shreds in the road base. Aniline was detected in well water from the road base interior at concentrations exceeding the Minnesota Department of Health drinking water standard (10ug/L). Aniline, benzothiazole, 2-hydroxybenzothiazole and 4-acetylmorpholine were not detected in culvert or downstream water samples.

Ecotoxicity testing conducted in 2006 indicated that well water from the road base exhibited survival and reproductive toxicity to certain aquatic organisms. Testing conducted on the well water indicated that fathead minnows exhibited mortality responses to the leachate from tire shreds. Similarly, water fleas appeared to be particularly sensitive to tire material leachate as exhibited by the survival and reproduction toxicity. However, not all aquatic invertebrates appeared to be sensitive to the leachate as was seen with the survival of midges in the first ecotoxicity test.

When well water was treated for iron and ammonia reduction, reproductive toxicity responses remained for four of the six wells. This indicated that a stressor from the tires remained in the well water after iron and ammonia reductions. The responses may be due to aniline, however many other organic chemicals are present in tire material such as antioxidants, antiozonants, and flame retardants.

Partial survival toxicity was observed for water fleas with the culvert water. There was no survival or reproductive toxicity to Ceriodaphnia dubia with culvert water after iron and ammonia reduction.

None of the tire related organic chemicals were detected in water samples collected outside of the road base. Barium, iron, manganese and possibly zinc appear to be migrating from the road base but the extent of iron transport may be limited due to hydroxide precipitation. The elevated chemical concentrations, metals and organics, measured during this study appear to be mostly retained within the geotextile fabric wrapped tire shreds. The toxicity characteristics of tire material leachate in this study appear to be largely retained within the road base.

It is important to consider the uniqueness of this study as compared to other field studies. The mass of tire material placed in the road base was appropriate for the construction project but was far greater than most other field studies. Additionally, the use of a geotextile fabric wrap may be adding an element of restricted water flow through the road base. The restricted migration of chemicals by use of the fabric wrap could be a useful proactive act of anti-degradation of surface water quality when placing recycled material in wet environments.

1. INTRODUCTION

Tire shreds or chips have been produced from scrap tires and used in various ways in attempts to recycle the waste material into a beneficial resource. Waste tires have been used in the construction of freshwater and ocean deposited artificial reefs (Nelson et al. 1994, Hartwell et al. 1998). The use of tire material in other aquatic application has been more recently investigated and implemented. One application has been their use as lightweight fill material in road base construction. The use of tire shreds material for road base construction is allowed in Minnesota above the groundwater table through a Standing Beneficial Use Determination (SBUD) from the Minnesota Pollution Control Agency. More recently, investigations have looked at their use below the groundwater table as a buoyant light weight fill in wet road bases. In this application, leaching of chemicals into the surface water and groundwater is of concern.

There are several studies in the scientific literature where leachate from tire shreds material has been analyzed for inorganic chemicals. These include both laboratory scale studies and field studies. The evaluation of tire material leachate with respect to organic chemicals has been less frequently studied. There are only a few studies where organic chemicals were monitored in tire material leachate. Similarly, only a few studies have been conducted that report results of aquatic toxicity testing with tire shreds leachate.

The last two years of the Oak Grove Tire Shreds Study focused on monitoring tire material specific semi-volatile organic chemicals in the road base well water and adjacent surface water. Additionally, the well water and surface water were tested for toxicity to aquatic organisms.

Previous Studies

The following are some of the studies relevant to the second year of the Oak Grove study.

<u>The Effects of Scrap Automobile Tires in Water</u> (Kellough, 1991).
Leachate toxicity tests exhibited survival toxicity to rainbow trout but not Daphnia magna. One whole tire and one tire cut into pieces were leached in 400 liters of water. Tires leached for 30 days caused 100% mortality of rainbow trout within 24 hours. Chemical analyses of the treatment water for chlorinated hydrocarbons and polynuclear aromatic hydrocarbons revealed no chemicals present to cause this toxicity. Gas chromatography with mass selective detection showed the possible presence of chemical residues from the tire manufacturing process such as residual monomers, stabilizers and accelerators.

<u>Evaluation of the Potential Toxicity of Automobile Tires in the Aquatic Environment</u> (B.A.R. Environmental, 1992)
B.A.R. Environmental Inc. conducted tire leachate bioassay tests with rainbow trout, fathead minnows and Daphnia magna. Three sources of tires were used for the tests; breakwater tires that had been part of a floating tire breakwater for ten years, scrap tires used for 4 years on a single car and a new tire of similar size and dimension as the scrap tires. Only whole tires were used for creating leachate.

Fathead minnows and Daphnia magna exhibited no survival toxicity for all leachates from all tire types. The length of leaching time also did not affect the toxicity of the leachates.

Rainbow trout however exhibited mortality to all leachates from scrap and new tires. New tire LC50s were less than 20% strength solution while scrap tires were 2 to 4 times more toxic than new tire leachates. Scrap tire leachate retained its toxicity characteristic for 32 days while new tire leachate retained its toxicity for less than 16 days.

The Acute Lethality to Rainbow Trout of Water Contaminated by an Automobile Tire (Abernethy, 1994)

This study leached a single automobile tire with freshwater. The "tire water" exhibited 100% mortality within 48 hours to rainbow trout fry. Daphnia sp., Ceriodaphnia sp., and fathead minnows showed no lethal response to the tire water. Treatments of the tire water did not achieve toxicity reduction but activated carbon treatment removed all toxicity to rainbow trout. Chemical analysis of the leachate identified several organic compounds of which 4 were found in all tire water samples. These compounds were aniline, 4-(1-methyl-1-phenylethyl)-phenol, benzothiazole, and 4-(2-benzothiazolythio)-morpholine. Other compounds identified were various arylamines and alkylphenols. It was concluded that the toxicant was unknown but was expected to be relatively persistent, nonvolatile and water soluble.

Identification of Tire Leachate Toxicants and a Risk Assessment of Water Quality Effects Using Tire Reefs in Canals (Nelson et al., 1994)

The objective of this study was to estimate the water quality effects from tire material in limited volume freshwater environments for use as tire reefs. U.S. Bureau of Reclamation studies have reported the benefits of tire reefs for increasing the biodiversity of fishes and macro-invertebrates in freshwater canal fisheries. The presence of fishes and other aquatic organisms in tire reef areas support the assumption that tires are inert and non-toxic. Tire plugs were leached with Lake Mead, Nevada water for 31 days and 40 days. Additionally, one-half of a tire was leached with Lake Mead water for 30 days to determine the organic chemicals that would leach from an unshredded tire. This study concluded that the acute toxicity to Ceriodaphnia dubia was due to zinc leached from the tire plugs and that the pH of the Lake Mead water ($pH > 8.0$) increased the zinc toxicity for this species. The calculated LC50 was 1471 ug/L zinc for the 24-hour exposure of C. dubia.

The whole tire leach experiment revealed no detections of the organic compounds (< 1.0 ug/L) analyzed, however benzothiazole was detected at 1-2 mg/L concentrations. The analyte list included many industrial chemicals and pesticides. Several polynuclear aromatic hydrocarbons were included but not detected. Aniline which has been found in other studies was not detected.

The Aquatic Toxicity of Scrap Automobile Tires (Abernethy et al., 1996)

The objectives of this study were to "1) measure the rate and extent of chemical release from tires placed in flowing water, 2) compare the acute lethality of tires that had been previously submerged in an aquatic environment for various periods of time; and 3) characterize, identify and confirm the toxicant found in static tire water." The researchers concluded that a higher flow rate (at least 1.5 L/min. per 600 liter water volume) was non-lethal to trout for all tires tested. Also, leachate collected at the end of the submersion period was less toxic than at the beginning. A chemical fractionation was performed on the leachate which revealed a mixture of polar and non-polar organic compounds. This study reports a detailed list of organic chemical components of which some were identified with mass spectrometry. The report identifies aromatic amine compounds as possible principal toxicants. Aniline was found to be one of the more abundant aromatic amines in the tire crumb extract. The static tire water in this study was described as "pale green-yellow colour and has a fishy, ammonia-like odour". Total ammonia was analyzed in the treatment waters but was not detected.

Toxicity of Scrap Tire Leachates in Estuarine Salinities (Hartwell et al., 1998)
Hartwell et al. leached scrap tires in synthetic saltwater at three salinities; 5‰, 15‰ and 25‰. Sheepshead minnow and Daggerblade grass shrimp were exposed to 100% leachate solutions for 96 hours and exhibited decreasing toxicity with increasing salinity. Also, minnows were more sensitive than grass shrimp. Chemical analysis of the heavy metals did not indicate significant concentrations to cause the observed dose response. The identity of the toxic chemicals was not determined but it was concluded that the toxicity of the leachates would persist for several weeks.

Toxicity of Tire Debris Leachates (Gualtieri et al., 2005)
This study used tire particulates (10-80 um) created by rotating a new tire against a steel brush. Two procedures were followed to produce leachates from tire material. For the leachate used in the toxicity testing, the particulates were shaken in a glass bottle with water adjusted to pH of 3. These bottles were shaken for 24 hours. Toxicity testing was conducted with three species of which Daphnia magna was one. The researchers concluded that tire dust deposited on the road side may release inorganic and organic chemicals after interacting with rain and/or runoff water. Particular attention was paid to zinc concentrations in the leachate. The calculated LC50 for D. magna was 58.3% leachate strength after 24 hours and 53.5% strength after 48 hours.

Evaluating the Risk to Aquatic Ecosystems Posed by Leachate from Tire Shred Fill in Roads Using Toxicity Tests, Toxicity Identification Evaluations, and Groundwater Modeling (Sheehan et al., 2006)
This study examined tire leachate in well water from two sites. One site was constructed with tire shreds above the local groundwater table and the second with tire shreds placed at and below the groundwater table. The two sites were constructed in August 1993 and January 1994, respectively. Tire shreds at both sites were about 7.6 cm in size but the mass of the material used was not specified. Three monitoring wells were installed at the second site below the groundwater table. They were placed up gradient from the tire shreds, within the tire shreds, and down gradient.

Sheehan et al. report collecting leachate from tire material placed below the water table and tested for aquatic toxicity. Well water was sampled twice at the second site, about one year apart

(October 2000 and November 2001), after the tire shreds had been in place for 6-7 years. The same exposure experiments were conducted with both samples of well water. Leachate water was tested with two aquatic species, Ceriodaphnia dubia (water flea) and Pimephales promelas (fathead minnow). Water fleas were tested for survival and reproduction and the fathead minnows were tested for survival and growth. Chronic level exposures (6-8 days) were conducted at five different leachate strengths (6.25, 12.5, 25, 50, and 100%) to estimate a No Observed Effects Concentration (NOEC), Lowest Observed Effects Concentration (LOEC), lethal concentration for 50% of the test population (LC50), and the inhibition concentration for reproduction or growth for 25% of the test population (IC25).

Leachate water exposures resulted in 100% survival of fathead minnows from the 6 and 7 year well water samplings. The growth IC25 for minnows was calculated to be 77% and 91% leachate strength, respectively. The growth NOEC was 50% and 12.5%, respectively.

Ceriodaphnia dubia survival for the 6 year well water sample was 66% and 100% for the 7 year sample. Reproduction was reduced in both treatment well water samplings and the control well water (IC25 = 16% and 28% respectively). The reproductive NOEC was 12.5% and 25%, respectively.

A water fractionation, Toxicity Identification Evaluation (TIE), approach was also applied to the water samples to separate the toxic components into treated water fractions and then tested for toxicity. The well water treatments included centrifugation, C18 Solid Phase Extraction, ethylenediaminetetra-acetic acid, and sodium thiosulfate. None of the water treatments removed the toxicity characteristic completely from the well water.

Dissolved iron concentrations measured within the tire material were significantly greater than those measured at the control and down gradient wells. This study also reported a depressed well water pH and the formation of iron hydroxide precipitate.

The researchers concluded that no single TIE process removed all the observed toxicity from the up gradient well water samples. However, centrifugation and sodium thiosulfate removed essentially all survival reducing toxicity. EDTA removed most, but not all, of the effects on survival. As in the previous testing, reduced reproduction was again observed in all the TIE treatments. It was estimated that undiluted leachate from tire shreds below the water table was toxic to C. dubia, probably because of iron released from steel belts in the tires. The researchers stated that the observed toxicity was probably due to metals, particularly iron hydroxide precipitates. A NOEC of 12.5% was calculated for tire material leachate to be protective against effects to C. dubia.

<u>Acute toxicity of leachates of tire wear material to Daphnia magna-Variability and toxic components</u>. (A. Wik and G. Dave, 2006)
Tire particles were created from twenty-five tires of different manufactures and leached in water for 72 hours at 44°C. Through chemical Toxicity Identification Evaluation it was concluded that non-polar organic chemicals contributed to most of the observed toxicity. Ultraviolet (UV) activated toxicity was not significant for filtered leachate, however significant toxicity was

observed to D. magna with UV activated unfiltered leachate. The temperatures at which the filtered and unfiltered exposure solutions were created could account for the difference in UV activated responses.

Oak Grove Tire Shreds Study (First year results, 2005)
The Minnesota Department of Transportation constructed a low volume road test area to determine the environmental fate, effects, and transport of chemicals from tire shred materials placed below the seasonal groundwater table. The road base was constructed during the fall of 2002. Funding for the project came from the Minnesota Local Road Research Board, the Minnesota Pollution Control Agency, and the Minnesota Department of Transportation. The project area was a tarred country road partially skirted by a ditch that provided surface water drainage from a grass sod farm. The original road base was low strength water laden soil. Over seven million pounds of tire shreds enclosed in geotextile fabric replaced the endemic mucks in and below the new road base. The road construction was completed with customary materials and asphalt wearing course over the tire shreds.

The first year results of monitoring well water from the Oak Grove Tire Shreds Study indicated an increase in chemical oxygen demand (COD), specific conductance, total suspended solids, barium, iron, and manganese within the tire shreds road base. There was also a slight pH depression in three of the monitoring wells on the east end of the study area.

The groundwater in the study area is characterized as very hard according to the U.S. Geological Survey (http://water.usgs.gov/owq/Explanation.html). The carbonate dominated well water could very likely form metal carbonate precipitates thereby limiting the migration of heavy metals outside the study area. Additionally, the engineering design of the road base included wrapping the tire shreds in geotextile fabric that may also have been limiting the migration of dissolved metals out of the road base to surface water.

Tire Chemistry

A very informative discussion of tire ingredients is provided in the University of Maine publication "Water Quality Effects of Using Tire Chips below the Groundwater Table" (Downs et. al., 1996). Certain relevant information will be included here. The full document can be found at the Rubber Manufacturers Association website (https://www.rma.org/publications/scrap_tires/index.cfm?CategoryID=567).
Tires are made of several structural components that include the tread, innerliner, sidewall, carcass, and bead. They are constructed of both natural and synthetic rubbers, antioxidants, curatives, fillers (carbon black), fiberglass, and steel wire. Belts and bead wire are produced with steel that may contain carbon, manganese, silicon, phosphorus, sulfur, and trace amounts of copper, chromium, and nickel. Zinc, copper, and tin may be present as a coating on the steel wire. Mercury is not listed or discussed in the tire manufacturing section of the above named report by Downs et al., 1996.

The State of California Integrated Waste Management Board (CIWMB) published the "Effects of Waste Tires, Waste Tire Facilities, and Waste Tire Projects on the Environment" in 1996.

This report describes the manufacturing of tires and the chemical additives such as antioxidants, antiozonants, flame retardants, and fillers added to the tires for various reasons.

Many chemicals, excluding the reinforcing belts of nylon or steel, are used in the manufacturing process of truck and automobile tires. These chemicals include the polymer or rubber used in the body manufacture, carbon black, organic acids, wax, accelerators, bonding agents, aromatic oil, antioxidants, antiozonants, softeners, extenders, sulfur, organic solvents, and proprietary ingredients. Carbon black, used as the major pigment in tires, is the highest percent composition additive in tire rubber. The black color hides the staining and strengthens the tire against abrasion (CIWMB report, 1996). The exact identities of many of these chemicals are considered proprietary by the tire manufacturers.

Benzothiazole-based thiazole rubber chemicals have been widely used in the rubber manufacturing industry. Produced in the United States since the late 1920's, the acceptance of these chemicals in the manufacture of tires has been largely due to stability, functionality and low cost. Over 90% of the thiazole usage in tire sidewalls, tread, retread, carcass, belt skin, liner, bead filler/chafer and base tread has been as cure-rate accelerators. Typical ranges of application of these compounds as cure-rate accelerators for rubber is from 0.5 to 5 percent of the rubber (RAPA 2003).

Tire manufacturers use several kinds of benzothiazole-based derivatives with branched alkyl, cyclo-alkyl, cyclo-alkyl monothio, and morpholino type adducts as accelerators and vulcanizing agents (CIWMB report, 1996). Benzothiazole-based thiazoles are defined as possessing a benzene ring plus a thiazole ring with substitutions at the #2 position on the thiazole ring.

Oak Grove Study Physical Setting

The Minnesota Department of Transportation (MN/DOT) with the cooperation of the Anoka County Road Maintenance with funding contributions from the Minnesota Pollution Control Agency, and the Minnesota Local Road Research Board initiated a field study in the fall of 2002 to determine the groundwater and surface water impacts from using shredded tire material below the seasonal groundwater table. A detailed description of the study site and road base construction can be found in the first year report. Briefly, a suitable site was identified where road base soils were saturated by groundwater and also included a roadside surface water drainage ditch. Groundwater seeping to the ditch is hard water containing >150 mg/L hardness measured as calcium carbonate. The groundwater is characteristically alkaline with a pH > 7.0.

This site was at the intersection of Anoka County roads 221st Avenue NW and Drake Street NW. The study area would be the immediate eastward section of road from this intersection. The water flow in the roadside ditch was highly variable where water depth ranged from less than 6 inches, mid channel, during dry periods to over 30 inches depth in the five foot wide ditch during heavy precipitation events. The planned dimensions of the tire shred deposit were 1300 feet long by 22 feet wide. Tire shreds were placed at an average depth of 7 feet however the depth and thickness may have varied during installation as evidenced by the soil boring logs (Appendix A).

A total of 7.6 million pounds or about 12,735 cubic yards of steel and glass belted tire shreds were placed in the rural Anoka County road base. Shredded tire material was not washed or cleaned in any way prior to placement in the road base. After the endemic soils were removed, the shredded tires were placed within a layer of geotextile permeable fabric and finally enclosed in "burrito wrap" fashion to form the new road base. A geotextile wrap was used to keep the tire material from migrating into the soft undersoils. The resulting tire shreds road base would be subjected to fluctuating water levels due to precipitation, spring snow melting, and other localized events. It was expected that groundwater would flow into and through the tire shreds in the road base.

Within this report, "culvert water" will mean the surface water samples collected at the southern end of the concrete culvert that crosses 221st Avenue NW and lies below the surface of the asphalt pavement. This term was chosen to distinguish "culvert water" from other surface water samples that will be collected at other locations as the study progressed beyond the first year.

Similarly, the term "well water" in this report will signify the groundwater sampled from within the tire shreds at monitoring Wells 2, 3, 4, 5 and 6. The collection of a groundwater sample will always signify water collected from Well 1, the background well, and be stated as such.

The original work plan of this study included the sampling of tire shred material for direct analysis for metals and organic chemicals. This was not performed by the initially contracted company, therefore only general tire component information can be described. Since the shredded material was a mixture of glass and steel belted tires, a chemical characterization could have been quite variable since stockpiles of tires are non-homogeneous.

There were several assumptions made about the road material and the constructed road base in this project. It was assumed that groundwater flow within the tire shreds deposit was towards the drainage ditch culvert and that water sampled at the culvert represented the combined surface water and tire shreds groundwater exiting the study area. It was also assumed there could be localized places within the road base where water flow rate and direction would be different from the general surface water flow and direction and these localized spots could be near a monitoring well. The non-homogeneity of the shredded tires (i.e. glass belted versus steel belted tires) could create localized hot and cold spots with respect to certain water quality parameters.

It was expected that environmental influences from other factors not related to the tire shreds could also occur during the study to confound the interpretations of the data. Other factors that could confuse the monitoring data were runoff from the road surface to the ditch, current and historic leaking storage tanks of petroleum products, refuse burn sites, woodland and grassland burn sites, local use of pesticides and fertilizers on agricultural land, and abandoned or discarded machinery leaking fluids of various kinds.

Study Area Monitoring Wells

Monitoring wells were installed in the study area as described in the first year report. Field logs from monitoring Wells 2, 3, 4, 5, and 6 showed varying depths of peat at the deepest extent of the bore hole (Appendix A). Wells 2 and 5 field logs showed peat layers beginning at a depth of about 11 feet and extending to the bottom of the hole at 15 feet. The 10 foot well screens for these wells traversed through the tire shreds layer.

Borehole logs for Wells 3 and 4 showed peat beginning at about 8 feet and extending to 12 feet or greater. The 5 foot well screens for these two wells extended into the tire shreds layer but did not traverse the entire thickness of the layer. The tire shreds layer at these bore holes, according to the field logs, were notably thinner than Wells 2 and 5. Well 4 appeared to have more of the screen in the peat layer than the tire shreds layer.

The well screen for Well 6 also traversed a 2 foot thick layer of tire material but the field log did not indicate the presence of peat throughout the borehole. Similarly, the field log for Well 1 indicated an absence of peat throughout the borehole.

Monitoring Well 1 was located on the north shoulder of the west bound lane of 221st Avenue NW and was assumed to reside up-gradient from the study area. Bore hole logs showed that peat was not in the lower layers (below 7 feet) of Well 1 as was found in the other wells, but soils above 4 feet were similar in descriptive composition with the other wells. In this respect, Well 1 was not completely comparable in geologic stratigraphy with the other wells.

Field Measurement Data

Depth to Groundwater

The depth to groundwater was measured by tape measure and electronic sensor. Measurements were taken before and after sample collection. Field data are found in Appendix B.

Temperature, pH, Specific Conductance, and Dissolved Oxygen

Water temperature, pH, specific conductance and dissolved oxygen readings were taken with a Hydrolab DataSonde 4 Water Quality Multiprobe. Measurements were taken for each well and also the culvert water at the time of sample collection.

Water Sample Collection

Monitoring well samples were collected by drawing well water with an Accuwell PTP-100 Peristaltic pump using Teflon tubing for transfer lines. Recharge of the wells was immediate such that wells were not emptied between purgings. Culvert water samples were collected at the downstream end of the culvert on the south side of 221st Avenue and represented grab samples.

All water samples collected for general water chemistry were collected unfiltered in pre-cleaned polyethylene bottles of the appropriate size and kept on ice until delivered to the laboratory. General water chemistry samples were considered to represent whole water concentrations.

Metals water samples were collected by pumping well water through an in-line disposable filter cartridge of 0.45 um pore size. Samples were preserved with nitric acid. The metal water concentrations represent dissolved metal concentrations. Mercury samples were collected separately and were not filtered but collected as whole water and analyzed as such. Samples were kept on ice until delivered to the analytical laboratory.

Water samples for Polynuclear Aromatic Hydrocarbons (PAHs) were collected in 1 liter amber glass bottles and kept on ice until delivered to the laboratory. PAH samples were not filtered and represent whole water concentrations.

A Standard Operating Procedure for collecting groundwater samples from the Mn/DOT Environmental Modeling and Testing Unit is provided in Appendix C.

Quality Control/Quality Assurance

During each sampling event, quality control samples were collected that included one sample duplicate and one equipment blank. Equipment decontamination was performed before and between collecting samples at each well.

Field Blanks

Field blanks were collected by processing laboratory grade high purity water in the same manner as the well water. Field blank concentrations for the general water chemistry parameters are found in Appendix D. Most of the analyte concentrations were below the respective reporting limit. There were low level detections of iron and zinc; both below the reporting limits.

Field blanks for the PAH analyses were below detection for all the PAHs. Field blank concentrations for PAHs can be found in Appendix D.

Field Duplicate Samples

Duplicate analyses were acceptable in most cases. Duplicate sample results are found in Appendix D. Where less than reporting limit values were listed, the reporting limit was substituted to provide actual numbers to calculate a Relative Percent Difference (RPD). The RPD was calculated by dividing the difference between the duplicates by the mean of the duplicates.

Internal Laboratory Quality Control

The internal laboratory quality control for water chemistry and heavy metals analyses included method blanks, spikes, and duplicates. All analytical chemistry methods to generate data were established regulatory methods or accepted good laboratory practices performed by contracted laboratories. The results from these tests were retained by the respective laboratory and used in the internal tracking with quality control charts. Most analyses were conducted under in-control analytical conditions. Laboratory analyses would have stopped or data flagged if out-of-control conditions had been detected.

The internal laboratory quality control for organics analyses included laboratory control blanks, spikes, and duplicates. Laboratory Control Spikes (LCS) and Laboratory Control Spike Duplicates (LCSD) for PAH analyses were extracted along with the project samples. Recoveries from these samples can be found in Appendix D. All spike recoveries were within acceptable limits for the particular laboratory except where noted on the laboratory report. The majority of spike recoveries were within the general range of 50-150% recovery except in the case of the more polar compounds. None of the sample concentrations were recovery corrected but rather taken as listed on the laboratory report. Laboratory method detection limits (MDL) can be found in Appendix D for the appropriate parameter.

Analytical quality control for the tire related organic chemicals included laboratory control blanks, spikes, and duplicates. Laboratory Control Spikes (LCS) and Laboratory Control Spike Duplicates (LCSD) with a mixture of polar and non-polar compounds were used to estimate the recoveries of tire compounds. Also included were Matrix Spike (MS) and Matrix Spike Duplicate (MSD) samples where spiked well water was extracted along with the project samples. Recoveries for LCS, LCSD, MS and MSD analyses were within acceptable ranges for most compounds and can be found in Appendix D.

Surrogate compounds added to each of the well water and surface water samples provided individual sample recovery efficiencies. Recoveries of these surrogate compounds are also found in Appendix D and were within acceptable ranges for most compounds. Again, the more polar chemicals showed greater variability and lower recoveries than non-polar chemicals.

2. METHODS AND MATERIALS

Data Analysis

Test for Normality

Statistical analysis was performed as described in the first year report. As before, analysis was conducted on parameters where the minimum number of measured data points was three (i.e. n=3 or greater). Parameters where a value less than the reporting limit were given were included in the tests (i.e. values between the laboratory method detection limit and the laboratory reporting limit). No data substitutions were made for reported "less than" values. The Shapiro-Wilk Normality test was used for testing sample normality (more appropriately, an indicator of non-normality) with the Statistix 8.0 software produced by Analytical Software, Tallahassee, Florida.

This statistical test is most appropriate when the data number between 3 and 2000 (n=3 – 2000). The null hypothesis (Ho) for this test was: the parameter data were from a population approximating a normal distribution. The Shapiro-Wilk Normality Test produced a W statistic and p-value. Calculated W statistics greater than 0.80 and p-values greater than 0.10 (Statistix 8 User's Manual) resulted in accepting the assumption that the sample was from a normally distributed population. If either case proved false, the Ho was rejected. For all parameters where n=3 or greater, the acceptance or rejection of the Ho is listed in the table with the corresponding conclusion about normality.

Shapiro-Wilk Normality test results produced with Statistix 8.0 for all the wells and culvert are found in Appendix E.

Tests for Outliers

Outliers in a limited size data set can have a significant effect on the descriptive statistics and the t-test conclusion. Data testing with Grubbs outlier test (Appendix F) was conducted to identify outliers only. Values reported by the laboratory as "less than" were converted to one-half the "less than" value (US EPA, July 2000) and tested as such. These data conversions were used only for outlier tests; not for any other testing. Additionally, none of the outliers were removed from the data set.

Grubbs test was conducted by testing the high and low values of the data set in sequential order. One-tailed tests were performed separately on high and low values with $\alpha=0.05$ and the degrees of freedom (DF) equal to n-1. If the high or low value was found to be an outlier, the test was repeated with the remaining data and new DF. Data for temperature, dissolved oxygen, and specific conductivity were the only general chemistry parameters tested for outliers. None were identified.

Grubbs test for outliers was conducted on the tire related semi-volatile organics where measured concentrations were reported. No outliers were identified.

Data Analysis-Comparisons of Sample Means

The Satterthwaite's Two-Sample t-test (US EPA July 2000) with unequal variances was used to compare means of the parameters among the wells and culvert samples. It was assumed that the t-test was sufficiently robust to render a meaningful conclusion even with moderate departures from population normality (Zar, 1984). Where sample data were missing, no data substitutions were made.

The acceptance criteria for the t-test were the absolute value of the calculated t statistic with unequal variances should be less than the appropriate critical value from the t distribution with a 95% confidence interval (α=0.05) on a two-tailed test. Also, a p-value greater than 0.05 was required to increase confidence in the calculated test statistic. If either the t statistic or p-value comparison failed, Ho was rejected. In cases where the t statistic was very close to but less than the critical value and the p-value was very close to but greater than 0.05, the F Test was used to make a final decision about accepting or rejecting Ho. If the calculated F statistic was a strong indicator of equal variances, the Ho was accepted. If the F statistic did not add confidence to the indications of the t-test, Ho was rejected. The t-test and F test were the only parametric tests used for statistical significance. Non-parametric testing was not performed.

3. RESULTS

Depth to Well Water

As stated above, (see Materials and Methods), the depth to well water was measured at each well during each of the sampling events. In Table 1 below, the range of depth to well water distances was greatest for Wells 2, 4, and 5 over the 2006 sampling events.

Table 1: Mean depth to well water in 2006.

Well	Mean (ft.)	Std. Dev. (ft.)	Min. (ft.)	Max. (ft.)	Range (in.)
1	6.5	0.3	6.0	7.0	12
2	4.7	0.5	4.1	6.0	23
3	5.3	0.2	4.9	5.8	11
4	5.3	0.5	4.8	6.6	22
5	4.6	0.5	4.0	5.9	23
6	6.1	0.2	5.7	6.7	12

Ditch Water Height

Ditch water height hydrographs indicated that a sustained elevation of ditch water occurred on June 12, 2006 when the ditch water exceeded 20 inches of water height and continued until July 17, 2006. The water height then gradually declined until July 25th, 2006 when water height reached a more normal 10 inches. A second ditch water height increase occurred nine days before the September 26th sampling event but had returned to the typical 10 inch water height by the 26th.

Thickness of Tire Shreds in Water

The thickness of submerged tire shreds in well water was calculated with the following equation:

Tire shreds in water = Tire layer thickness – [(Depth to groundwater) – (Depth to tire layer)]

The estimate from this equation is only meaningful when the “depth to water” measurement is greater than the “depth to tire layer” measurement resulting in a non-negative “tire shreds in water” value. The tire layer thickness and depth to tires measurements were taken from the well bore hole logs at the time of well installation (Appendix A). Mean thickness of tire shreds in well water during 2006 can be found below in Table 2 and Appendix G. It was assumed that the top of the well head, from which the depth to well water was measured, would remain at the same elevation throughout the study period. Each well in Table 2 is designated as an “east side” or “west side” well to show which side of the culvert the well is located. As can be seen, Wells 2 and 5 have the thickest layer of tires in water according to the well drilling logs, followed by Wells 3 and 4. Well 6 had less than one-half foot of tire material in the bore hole.

Table 2: Mean thickness of tire shreds in well water for 2006.

Well	Mean depth to water (Feet)	Depth to tires (Feet)	Tire Shreds Layer Thickness (Feet)	Mean Thickness of Tires in Water (Feet)
1 (west side)	6.5	0	0	0
2 (west side)	4.7	4.5	7.0	6.8
3 (east side)	5.3	4.0	3.0	1.7
4 (east side)	5.3	4.0	3.5	2.2
5 (west side)	4.6	4.0	6.5	5.9
6 (east side)	6.1	4.0	2.5	0.4

Table 3 lists the length of well screen in tire material and length of screen in peat. The table shows that Wells 4 and 5 are more similar when only the peat layer is considered. Like wise, Wells 2 and 3 are more similar with comparable peat layer thickness. None of the length of well screen in peat (Wells 2-5) were drastically different as compared to the differences in tire shreds thickness.

Table 3: Length of screen in tire shreds and in peat.

Well	Length of screen in tire shreds (Feet)	Length of screen in peat (feet)
1 (west side)	0	0
2 (west side)	7	1.1
3 (east side)	2.5	2.0
4 (east side)	1	3.5
5 (west side)	6	3.5
6 (east side)	2.5	0

General Water Chemistry

General water chemistry parameters, in addition to the field chemistry measurements, were measured in the September 2006 samples in support of the bioassay testing described later. Total suspended solids, chemical oxygen demand, alkalinity, ammonia, and total organic carbon were measured in the culvert water and well water samples. These data can be found in Appendix H. As stated above, these data are from unfiltered water samples and represent whole water concentrations.

The 2006 water chemistry data indicated a trend with specific conductance. Wells 3 and 4 conductivity readings exceeded 1000 umhos/cm and were the highest readings of the year. Wells 2 and 5 values exceeded 1000 umhos/cm but were consistently lower than Wells 3 and 4. Well 6 water conductivity also exceeded 1000 umhos/cm but was well below this reading during the November sampling. The water level at Well 6 during this sampling was below the tire shreds material. None of the 2.5 feet thickness (Appendix G) of tire material was submerged at this time which may account for the reduced conductivity during the November sampling.

The 2006 sample results for pH indicated a difference between wells on the east side of the culvert bisecting the study area (First Year Report, March 2007) and wells on the west side. Comparisons using the Two Sample t-Test showed similarities in pH between wells 2 and 5 on the east side and Wells 3, 4, and 6 on the west side. Results of the t-Test can be found in Appendix I. Generally, the wells on the east side of the culvert exhibited a pH less than 7.0 while the wells on the west side exhibited a pH greater than 7.0.

Elevated levels of total ammonia were discovered in well water from the study area in preparation for ecotoxicity testing as reported by LSRI (Appendix K) during September 2006. Surface water samples contained less than 1 mg/L ammonia. Measured concentrations were quite consistent between Wells 2-5. Significantly less ammonia was measured at Well 6 while Well 1 was similar to surface water concentrations. Ammonia correlated with tire material in well water only moderately strong (r^2=0.78).

Linear Correlation Analysis

Linear correlation coefficients were calculated for the general chemistry parameter concentrations at the monitoring wells during the September 2006 samples and the calculated thickness of tire shreds in well water for the respective wells at that time. The correlation coefficients can be found in Table 4 below. The strongest correlations were found between chemical oxygen demand/tires in water and total organic carbon/tires in water. Specific conductance and tires in water showed a weak correlation.

Table 4: Correlation coefficients with general chemistry parameter concentrations and thickness of tires in well water in September 2006.

Parameter/Submerged Tires	Correlation Coefficient (r^2)
COD/Tires in water	0.97
TSS/Tires in water	-0.35
Alkalinity/Tires in water	-0.55
Ammonia-N/Tires in water	0.78
TOC/Tires in water	0.98
pH/Tires in water	0.39
Specific Conductance/Tires in water	0.05

Metals

Well water and culvert water samples were analyzed for barium, copper, iron, manganese, antimony and zinc during 2006. The concentrations of the heavy metals were determined from filtered water representing dissolved metal concentrations. Antimony and copper were not detected in these samples. Elevated levels of barium, iron, manganese and possibly zinc were measured in wells 2-6. Well 1 barium concentration in September 2006 was the highest measured for that well during the present study (1,100 ug/L).

Linear Correlation Analysis
Similar to the general water chemistry correlations, correlation coefficients were calculated (Table 5) between the four metals analyzed in the September samples and thickness of submerged tire shreds. No strong correlations were found ($r^2 > 0.90$), positive or negative, between the metal well water concentrations and thickness of tires in water.

Table 5: Correlation coefficients with metals and thickness of tires in well water in September 2006.

Parameter/Submerged Tires	Correlation Coefficient (r^2)
Barium/Tires in water	0.33
Iron/Tires in water	-0.46
Manganese/Tires in water	-0.54
Zinc/Tires in water	-0.16

Although the correlation coefficients for iron, manganese and zinc were weak, these were negative correlations indicating the thickness of tire shreds was inversely related to the concentrations of these metals in well water.

Organic Chemicals

Eight semi-volatile organic chemicals were analyzed in well water samples that were reported in the literature as detected in tire material field studies elsewhere. There were 5 sampling events in 2006 with all eight compounds analyzed in well water samples. Surface water and well water samples were unfiltered and represent whole water concentrations.

Aniline
Aniline concentrations ranged from below reporting limit (<10 ug/L) to 380 ug/L between all the monitoring wells throughout the 2006 sampling period. In general, aniline concentrations were fairly constant within each of the wells (Appendix J) during this period. Aniline was not detected in any of the Well 1 or culvert water samples collected during 2006.

Well 6 revealed the lowest concentrations of aniline with only two sample concentrations (14 ug/L) above the detection limit (MDL=10 ug/L). Wells 3 and 4 provided concentrations typically less than 100 ug/L with one measurement of 110 ug/L in Well 4 during June. Wells 2 and 5 revealed the highest concentrations of aniline with values ranging from 120-380 ug/L.

Benzothiazole
Benzothiazole was detected in all monitoring wells except Well 1, the background well. It was not detected in any of the culvert water samples. Benzothiazole concentrations ranged from 1.0-45 ug/L among all of the wells. Wells 2 and 5 water concentrations were, as with other parameters, the highest levels detected. Wells 3 and 4 samples were mid range with Well 6 showing the lowest concentrations and occasional non-detects.

2--Hydroxybenzothiazole

2-Hydroxybenzothiazole was detected in all 2006 well water samples from Wells 2-6. It was the most frequently detected compound and was measured in the highest concentrations (110-1500 ug/L) in the 2006 samples. The plots of the water concentrations with sampling station and thickness of tire shreds with sampling station are similar. The highest concentrations of 2-hydroxybenzothiazole were measured in Wells 2 and 5 indicating the greater thickness of tire shreds at these two wells. This compound was not detected in any of the Well 1 or culvert water samples.

4-Acetylmorpholine

4-Acetylmorpholine was measured in all of the well water samples collected from Wells 2-5 during 2006. It was also detected in Well 6 in two of the five samples collected during this period. Concentrations ranged from 3.2-24 ug/L in Wells 2-5. 4-Acetyl-morpholine was not detected in any of the culvert or Well 1 water samples.

Linear Correlation Analysis

Correlation coefficients were calculated for average organic chemical concentrations in well water with average thickness of submerged tire shreds using all five sampling events during 2006. These correlation coefficients can be found below in Table 6 and show a strong relationship between well water concentrations and thickness of tires in water for all the detected chemicals.

Table 6: Correlation coefficients with tire organic chemicals and thickness of tires in well water in September 2006.

Parameter/Submerged Tires	Correlation Coefficient (r^2)
Aniline/Tires in water	0.96
Benzothiazole/Tires in water	0.92
Hydroxybenzothiazole/Tires in water	0.92
Acetylmorpholine/Tires in water	0.96

Other tire related organic chemicals that were analyzed in well water and surface water but not detected (MDL 10 ug/L) were benzoic acid, 9(H)-carbazole, 4(1-Methyl-1-phenylethyl)phenol, and 4(2-Benzothiazolythio)-morpholine.

Polynuclear Aromatic Hydrocarbons (PAHs)

Well water samples were collected for PAH analysis during the September 26, 2006 sampling event only. Low levels of PAHs were detected in Wells 2, 3, 4, and 5. Total PAH concentrations for these samples were all less than 1.0 ug/L (ppb). No PAHs were detected in Wells 1, 6, culvert water, north ditch water or south ditch water. The highest PAH concentrations were measured in Wells 2 and 5 with Well 5 approaching 1.0 ug/L. Linear correlation analysis between total PAH concentrations and the thickness of tire material in well water provided a correlation coefficient of 0.90 suggesting that the total PAH concentrations increased with increasing tire material thickness in water.

Carcinogenic PAHs (c-PAHs)

No carcinogenic PAHs were detected in the September and November 2006 well or surface water samples.

4. DISCUSSION

General Water Chemistry

Measurements of general water chemistry in 2005 indicated a similarity between the wells in tire shreds on the east side of the culvert (Wells 3, 4 and 6) while the wells in tire shreds on the west side of the culvert were more similar in magnitude. Additionally, Well 1 and culvert water samples were similar between each other. These trends continued during the 2006 sampling period.

Specific Conductance

Specific conductance readings for culvert water samples were similar to the 2005 measurements. Conductivity in the culvert water averaged 408 umhos/cm in 2005 and was similar to Well 1 at 543 umhos/cm. Well water from the treatment wells was elevated with Wells 3 and 4 showing the highest conductivity approaching 1000 umhos/cm. The treatment well average conductivity ranged from 620 umhos/cm to 847 umhos/cm. However, conductivity measurements for all the wells in 2006 were higher than in 2005. Well 1 conductivity averaged 543 umhos/cm in 2005 but averaged 877 umhos/cm in 2006. Wells 3 and 4 were also highest in conductivity for 2006 and averaged 1024 and 1080 umhos/cm, respectively.

Satterthwaite's t-Test comparisons of the average specific conductance within all the wells and culvert water showed that Well 2 and culvert water were similar between years 2005 and 2006. All other wells were dissimilar but increasing in conductivity from the first year to the second year within the same well. During 2006, conductivity was measured over 1000 umhos/cm at least once in all of the wells during the year. In 2005, none of the wells exceeded 1000 umhos/cm during the sampling period.

Ammonia

The presence of ammonia in well water at elevated concentrations suggests the absence of nitrifying bacteria or the inhibition of nitrification. Any discussion about ammonia hereafter should be viewed as total ammonia unless stated otherwise.

During the sampling events of 2006 the well water dissolved oxygen was usually below 3 mg/L. Downing et al. (1964) report 0.3 – 1.0 mg/L dissolved oxygen is required for nitrification to proceed. The growth rate of nitrifying bacteria becomes independent of dissolved oxygen above 1.0 mg/L. Downing and Scragg (1958) report 0.2 mg/L dissolved oxygen was required in activated sludge for 50% ammonia nitrification to occur and that 0.5 mg/L DO resulted in complete nitrification.

Downing et al. (1964) found that nitrification reactions ceased completely below 0.2 mg/L and that a minimum range of 0.3-1.0 mg/L dissolved oxygen was required. Others (Bragstad & Bradney, 1937) have reported that 0.5 mg/L was the limiting DO below which nitrification ceased.

Schoberl P. and H. Engel (1964) found that the growth rate of Nitrosomonas was independent of the DO concentration above 1.0 mg/L and that the Nitrobacter growth rate was independent of dissolved oxygen levels above 2.0 mg/L.

Stenstrom and Poduska (1980) report that Nitrosomonas and Nitrobacter are sensitive to low DO. They found a reduced growth rate for Nitrosomonas below 2 mg/L and Nitrobacter below 4 mg/L. Also, nitrification stopped below 0.3 mg/L. The most reliable range estimated of DO for nitrification to occur is 0.5 – 2.0 mg/L.

Given the levels of ammonia present in the well water, it is likely that the actual dissolved oxygen concentrations are lower than those measured with the field equipment available. Very low levels of dissolved oxygen are difficult to measure accurately and require special instrumentation to accomplish. It is also apparent that the well water samples were absorbing oxygen from the atmosphere once sampled as evidenced by the iron hydroxide precipitates forming upon standing (First year report, March 2007). A much lower dissolved oxygen level in the well water could be the primary inhibitor of nitrifying bacteria growth in the road base. If low dissolved oxygen is the limiting factor inhibiting the microbial nitrification of ammonia in the tire shreds water to nitrite and subsequently to nitrate, the actual dissolved oxygen in well water should be lower than 3 mg/L.

Factors other than dissolved oxygen levels could also contribute to the inhibition of nitrifying bacteria growth such as dissolved organic carbon, dissolved copper, dissolved iron, temperature and pH as discussed by Painter (1970) and Starry et al. (2005). Downing et al. (1964) report that the optimum temperature for microbial growth is about 30°C to 35°C. The temperatures reported at the time of well water sampling never reached 20°C in wells 2-5 in 2006.

Well water hydrogen ion concentration may also have been a limiting factor in microbial population growth. Hofman and Lees (1952) found the optimum pH range for Nitrosomonas was pH 8-9. Meyerhof (1917) found the optimum pH range for Nitrobacter was pH 8.3-9.3. The pH range of well water for wells 2-5 in 2006 was consistently below these two ranges (<7.2 S.U.).

The elevated ammonia concentrations in the well water suggest that nitrifying bacteria were not present or were inhibited by insufficient dissolved oxygen or multiple factors.

Anaerobic Biodegradation

Aniline and Benzothiazole

Anaerobic biodegradation of aniline could contribute to the ammonia levels but to a minor degree. The aniline concentrations measured in the well water (100-300 ppb) are not sufficient to account for all of the ammonia (10,000-12,000 ppb). The aniline would probably be present in the well water at much lower concentrations if dissolved oxygen were above 2 mg/L.

Metals/Elements

Barium and iron concentrations during September 2006 were generally greater than the average concentrations during the 2005 season. Similarly, the manganese concentrations in 2006 were greater for Wells 1 and 6 but variable for the remaining wells. Zinc concentrations were highly variable with Well 3 showing the highest concentration. As stated in the Results section, no strong correlations were found between the metal concentrations and thickness of tire material in well water. Unlike the tire material organic chemicals, the tire shreds are not the sole source and may not be the major source of certain metals in the well water at this site.

Tire Organic Chemicals

Although the number of tire related organic chemicals monitored were few, all chemicals had been reported as detected in at least one previous study by other researchers. The eight organic chemicals chosen vary widely in water solubility and vapor pressure.

Biodegradation Model: Linear and Non-linear Model (EPIWIN Suite version 3.20)
The linear and non-linear biodegradation model is described in Howard et. al (1987 and 1992). Briefly, 186 chemicals were evaluated as chemicals that biodegrade quickly and 109 chemicals were evaluated as chemicals likely to not biodegrade quickly. Chemical structure “fragment probability values” were derived and applied within the model to predict potential for biodegradation. A detailed discussion can be found in the EPIWIN User Guide for BIOWIN Model.

Biodegradation: Ultimate and Primary Biodegradation Model
The rate of primary and ultimate biodegradation of chemicals predicted by the EPIWIN model is based on a survey of 200 chemicals evaluated by 17 biodegradation experts. Chemical fragment coefficients were formulated for primary and ultimate biodegradation.
Linear and non-linear regression model predictions are better than 76% correct depending on the model and the rate (fast vs. not fast) of expected biodegradation.

Biodegradation: Linear and Non-Linear MITI Biodegradation Model
The MITI Model was developed in Japan using 884 chemicals in the Ministry of International Trade and Industry (MITI) test. The chemicals consisted of 385 considered to be “readily biodegradable” and 499 considered to be “not readily biodegradable”.

Linear and non-linear model predictions are better than 78% correct depending on the model and the rate (readily vs. not readily) of expected biodegradation.

Aniline
Aromatic amine-type chemicals are some of the more common antioxidants used in tire manufacture and are used in large quantities (CIWMB report 1996). Many antioxidants and antiozonants are substituted aniline derivatives. Two of the common starting chemicals in antioxidants and antiozonants are diphenylamine and p-phenylenediamine.

Aniline is the chemical of greatest interest of the tire specific chemicals monitored because it is classified as a B2 probable human carcinogen (US EPA IRIS, http://www.epa.gov/iris/subst/0350.htm). The Minnesota Health Risk Limit (HRL) for aniline is 10 ug/L for cancer and 20 ug/L for non-cancer. Wells 2, 3, 4, and 5 showed aniline concentrations exceeding both cancer and non-cancer HRLs. The highest concentrations were found in Wells 2 and 5 where the thickest layer of tire shreds was expected from the bore hole logs. Aniline well water concentrations were below the cancer HRL at the section of road base (Well 6) where less than 0.5 foot of material in well water was expected.

Aniline has been used as a benchmark chemical in the Biochemical Oxygen Demand test conducted by federal, state and private laboratories for Clean Water Act and NPDES permits. The test is routinely used for characterizing wastewater for biodegradable material content but more frequently uses glucose-glutamic acid substrate. The testing laboratory, in many cases, uses seed from wastewater treatment plants that have been acclimated for biodegradation of xenobiotics. Chemical acclimated seed does not require an adaptation period and will readily biodegrade aniline (Lyons et al., 1984). Aquifer bacteria that have not been acclimated with xenobiotic chemicals may require an adaptation period with the new carbon source depending on the compounds in question. The study described by Aelion et al., (1987) used pristine aquifer microflora on aquifer solids to measure mineralization of several compounds. Aniline mineralization was greater (>15%) at the lower concentration (13 ng/g) than the higher concentration (224 ng/g) after 100 days. Their conclusions included that aquifer microbes are capable of biodegrading some xenobiotic compounds and without an adaptation period in some cases. This adaptation period appeared to be compound specific and may be dependant on specific field conditions.

The pathways of aniline aerobic biodegradation in surface waters were described by Lyons et al. (1984). Pond water fortified with aniline exhibited a steady decline in water concentration over 7 days resulting in slightly less than half elimination of the original concentration. Lyons et al. (1984) concluded that the principal pathway of aniline elimination from pond water was by dioxygenase attack resulting in catechol after oxidative deamination. The catechol ring structure is opened and further oxidized to complete mineralization to carbon dioxide and water. Lyons et al. (1984)concluded that given the heterotrophic bacteria in sewage sludge is different than the bacteria community in pond water the elimination of aniline in pond water would have much lower activity than sewage sludge. It is important to note that the species of bacteria that oxidize ammonia in nitrification are not the same species of bacteria associated with the aerobic biodegradation of organic compounds such as aniline.

The strong correlations between chemical oxygen demand, total organic carbon, and the tire related semi-volatile organics (Tables 3 and 5) suggest the tire shreds are a major source of that parameter or the sole source of that parameter in the study area. If the width of the tire shreds road base is assumed to be uniform throughout the length of that section of road, the thickness of tires submerged in well water can be viewed as the only variable for estimating the relationship between mass of tire material and well water chemical concentrations. Linear regression analysis of well water concentrations of tire chemicals with thickness of submerged tire material was used to estimate a thickness of submerged tire material that would produce aniline well water concentrations that would not exceed the Minnesota HRL of 10 ug/L. When using the mean well water concentrations for aniline in September 2006 and the mean thickness of submerged tire shreds, the estimated thickness of submerged tire material was 0.8 foot or 10 inches.

It is expected that volatilization and biodegradation would be significant routes of elimination from surface water if aniline migrates from the study area. Aniline is not expected to bioaccumulate in aquatic biota.

The National Library of Medicine database lists the organic carbon partition coefficient (Koc) for aniline as 43.8-497.7 in tested European soils. This range of values indicates a low to moderate potential for aniline binding to soils. Migration of aniline through soils is therefore expected to have moderate to high potential. The slight decrease in pH measured at wells 3, 4 and 6 on the east side of the culvert would result in an increase in binding potential to organic carbon and particulates near those wells. At wells where peat is in direct contact with the tire shreds water there could be an increased potential for binding to the peat.

The Henry's Law constant predicted by EPI Suite was 2.02E-06 atm-m3/mole (2.02E-3 L-atm/mole) indicating that aniline dissolved in surface water would likely volatilize, in the unionized form, to the atmosphere. Volatilization of aniline would therefore be an important elimination process from surface water.

Aniline was not detected in any surface water samples or samples from Well 1. This chemical appears to be retained within the road base.

Benzothiazole

Benzothiazole is not used in its pure form in the manufacture of tires. Rather, as discussed earlier, derivatives of this parent compound are used as accelerators and vulcanizing agents.

The Benzothiazole-based thiazoles Category Justification and Testing Rationale written by the Rubber and Plastics Additives Panel states that benzothiazole-based thiazoles (i.e. substituted mercaptobenzothiazoles) produced acute toxicities to fish, aquatic invertebrates and algae ranging from highly toxic to practically non-toxic (RAPA 2001).

The moderate water solubility and organic carbon partition coefficient (Koc = 295) indicate that benzothiazole will be moderately mobile in soil but may partition to particulates and sediments in surface water. It is expected to have low potential to bioaccumulate in aquatic organisms.

Aerobic biodegradation has been shown to occur rapidly in activated sewage sludge but at high concentrations may be toxic to microbes. An EPIWIN estimated half-life for benzothiazole in surface water is 114-832 days.

Although sewage sludge experiments show a potential for biodegradation, surface waters do not have the microbe population size and diversity or have not been acclimated for xenobiotic degradation. If biodegradation in surface waters occurs the initial lag time and half-life for ultimate biodegradation would be longer than with activated sewage sludge.

Benzothiazole was not detected in the culvert, north ditch or south ditch surface water samples and therefore appears to be largely retained within the tire shreds road base. Only low levels of the chemical were detected in wells 2-6 (< 50 ug/L) and was not detected in Well 1.

Considerably less information is available in government databases about the remaining tire related organic chemicals; 2-hydroxybenzothiazole and 4-acetylmorpholine.

2-Hydroxybenzothiazole
A lack of background information on 2-hydroxybenzothiazole makes an estimate of the environmental pathway of this chemical difficult. The presence of benzothiazoles is mostly restricted to aquatic environments (De Wever et al. 2001) and originate from products of the rubber industry. Its presence in well water samples is most likely from the leaching of tire material.

EPIWIN predicts a log Kow of 2.4, vapor pressure of 0.000142 mm Hg, and water solubility of 620 mg/L. BIOWIN predicts fast biodegradation by the Linear Model. Primary biodegradation is expected in days-weeks and ultimate biodegradation in weeks. MITI Linear and Non-linear models predicted no biodegradation.

The low vapor pressure and moderate water solubility suggest that 2-hydroxy-benzothiazole will not volatilize from surface water to the atmosphere but remain in the dissolved phase. The log Kow indicates that the chemical may adsorb to suspended particulates or to sediments in surface water. It is expected to have moderate potential to migrate in soils to groundwater.

2-Hydroxybenzothiazole was detected in all monitoring wells except for Wells 1 and 6. Measured concentrations were the highest of all the tire organic chemicals monitored. This chemical was not detected in the surface water or Well 1 water samples and appears to be retained within the road base.

4-Acetylmorpholine
As stated above, there are accelerators and vulcanizing agents with morpholino adduct structures that react in various ways and may produce substituted morpholine compounds during tire manufacture. A lack of experimental information about 4-acetylmorpholine makes discussion about its environmental formation pathways (e.g. hydrolysis, photolysis, etc.) and leaching potential difficult.

EPIWIN predicts a log Kow of -0.87, vapor pressure of 0.134 mm Hg, and water solubility of 51%. No toxicity data were available from the EPA ECOTOX database. It is predicted by EPIWIN to be essentially non-toxic to aquatic organisms. BIOWIN predicts fast biodegradation by all models. Primary biodegradation is expected in days and ultimate biodegradation in weeks. MITI linear and non-linear models both predict fast biodegradation for this compound.

4-Acetylmorpholine was the most water soluble tire related organic chemical monitored in well water. As such, it is expected to migrate in soils to groundwater. None of the culvert or down stream samples contained levels of 4-acetylmorpholine at or above the 10 ug/L method detection limit.

4-Acetylmorpholine was detected in Wells 2-5 in all sampling events in 2006. It was also detected in Well 6 in the June and November. However, it was not detected in Well 1 or surface water samples. This chemical appears to be retained within the road base.

Sample Extraction for Tire Organic Chemical Analysis
Because the water solubilities of the chosen tire organic chemicals vary over a wide range (Table 7), analytical method extraction efficiencies should also vary widely between the compounds. The more water soluble compounds are less likely to partition to the organic solvent used to extract water samples for analysis. Although surrogate compound extraction efficiencies were within acceptable limits for most compounds, the actual well water concentrations of the more water soluble (more polar) compounds may be greater. As evidenced by the lower extraction efficiencies of polar surrogate compounds, the polar compounds are more difficult to analyze with this method. Other analytical methods may be necessary to confirm actual well water concentrations of the more polar tire material compounds.

Table 7: Chemical properties of tire related organic chemicals
(Italics = EPIWIN database or predicted).

Chemical	Molecular Wt (gm/mole)	Specific Gravity (gm/ml)	Water Solubility (mg/L)	Vapor Pressure (mm Hg)	Log Kow
Aniline *	93.13	1.0217	33,800	0.490a	0.90
Benzothiazole *	135.18	1.2460	*1684*	0.014b	*2.17*
2-Hydroxybenzothiazole *	151.18	1.45c	*619.7*	*0.000142*	*2.44*
4-Acetylmorpholine *	129.16	1.09c	*514,000*	*0.134*	*-0.872*
Benzoic Acid	122.12	1.2659	*2493*	*0.0007*	*1.87*
9H-Carbazole	167.21	1.16	*3.3*	*0.00000075*	*3.23*
4-(1-Methyl-1-phenylethyl) phenol	212.29	1.06c	*36*	*0.0000168*	*4.22*
4(2-Benzothiazolylthio)-1-morpholine	253.36	1.35c	*5606*	*0.00000105*	*1.89*

* = Compound detected in well water.

a) Aniline Log Kow from CRC 1999-2000, 80th Edition, p. 16-43.
b) TOXNET National Library of Medicine database.
c) SPARC: SPARC On-Line Calculator. http://sparc.chem.uga.edu/sparc/

Aniline water solubility from CRC 1999-2000, 80th Edition, p 8-96.
Aniline vapor pressure from Daubert,T.E. and R.P. Danner; Data Compilation of Pure Compounds; Design Institute for Physical Property Data, American Institute of Chemical Engineers, 345 East 47th Street, New York, NY., Vol.1; 1985.

Tire Organic Chemical Ecotoxicity
Limited toxicity data were available from the US EPA ECOTOX database (below) for the organic chemicals of interest. Only data for benzothiazole and aniline were found.

Benzothiazole is moderately toxic to the fathead minnow and was the only exposure test found. Aniline can be considered to be very toxic to water fleas and moderately toxic to fathead minnow, bluegill and rainbow trout. Green algae and scud are resistant to aniline. These data indicate that organic chemicals leaching from tire material can have a wide range of effects on aquatic organisms.

US EPA ECOTOX Data

Aniline (Benzeneamine) CAS# 62-53-3

Scientific name	End Point	Duration	Concentration
Chlorella vulgaris	LC50	12-13 Days	>183.9 mg/L
Green algae			
Daphnia magna	LC50	48 Hrs.	0.080 mg/L
Water flea			
Gammarus pulex	LC50	48 Hrs.	112 mg/L
Scud			
Micropterus salmoides	LC50	6.5 Days	10.5 mg/L
Fathead minnow			
Lepomis macrochirus	LC50	96 Hrs.	49 mg/L
Bluegill			
Oncorhynchus mykiss	LC50	96 Hrs.	20 mg/L
Rainbow trout			

LC50 = Chemical concentration at which the test population exhibits 50% mortality.

Benzothiazole CAS# 95-16-9

Scientific name	End Point	Duration	Concentration
Pimephales promelas	LC50	96 Hrs.	69.7 mg/L
Fathead minnow			

LC50 = Chemical concentration at which the test population exhibits 50% mortality.

Bioassay Testing

February 2006

Water samples from the six monitoring wells and culvert water were collected in early February 2006 for the purpose of conducting toxicity testing with three trophic levels of aquatic organisms. The Lake Superior Research Institute (LSRI), University of Wisconsin-Superior, Superior, WI conducted the tests (TenEyck and Markee, April 2006). The report “Toxicity Evaluation of Water from Tire Shreds, In Oak Grove, Minnesota” can be found in Appendix K.

Briefly, tests were conducted with a larval fish Pimephales promelas (fathead minnow), insect larvae Chironomus dilutus (midge), and the cladoceran Ceriodaphnia dubia (water flea). The laboratory control water source was western Lake Superior; off shore from Superior, WI. All of the well water samples, except the background well, exhibited an orange colored precipitate that was assumed to be an iron compound. Several water quality parameters were measured before the toxicity tests were run. One of the parameters was ammonia. Elevated concentrations of ammonia were found in the water from Wells 2-6. The ammonia concentrations ranged from 1.7 mg/L-15.1 mg/L.

For each of the species tested, the background well water showed similar survival to the lab water survival. Also, the culvert water exhibited similar survival to the lab water survival for midges but lower survival for fathead minnows and water fleas. In all three species, Wells 2 and 5 showed the lowest survival. Well 6 water produced similar survival to culvert water with minnows and midges, however there was an observed reduction in water flea survival with culvert water.

Reproductive toxicity was also determined for water fleas. The reproduction in lab water and Well 1 were similar. Reproduction in culvert water was slightly reduced from lab water and Well 1. Reproduction for Wells 2-5 was zero and Well 6 was significantly reduced. Even though Well 6 showed a 100% survival for water fleas, reproductive success was greatly reduced.

The iron precipitate and/or ammonia concentrations in the well water samples could have been stressing the test organisms resulting in a significant acutely toxic effect. The LSRI report stated that while a partial minnow and water flea survival reduction was observed for Well 6 water, the ammonia concentration was similar to lab water. This may indicate the presence of low level chronic toxicity from another chemical or chemicals.

October 2006

A complimentary set of toxicity tests were conducted on well water and culvert water from the Oak Grove Tire Shreds study area in October 2006 (TenEyck and Markee, October 2006) and the LSRI report can be found in Appendix L. The strategy for this round of testing was to use the Toxicity Reduction Evaluation (TRE) approach to separate the chemicals causing the reduced survival and reproduction in fathead minnows (Pimephales promelas) and water fleas (Ceriodaphnia dubia) reported in the February 2006 tests. The proposed chemical fractionation strategy included aeration of the well water to form iron hydroxide precipitate with subsequent filtration to remove the iron complex particulates. A second subsequent treatment of the well water included filtering through a liquid chromatography column with zeolite to remove dissolved ammonia. It was assumed that the resulting well water after aeration and filtering through zeolite would retain the majority of tire material derived organic chemicals for toxicity testing. Since many of the organic compounds in the water were unknown, it was not possible to confirm this. Initial and daily ammonia and iron concentrations in exposure water can be found in the LSRI report.

The approach for reducing the iron in exposure water was effective. Iron removal by precipitation and filtration was 88% effective in all of the samples. As a result, the survival of Ceriodaphnia dubia was raised from 0% in the baseline sample to 90% in the filtered water.

Similarly, the approach for removing the ammonia in exposure water was also effective in reducing the total ammonia by as much as 81%. The total ammonia in water from Wells 2, 3, 4, 5, and 6 was reduced significantly by the zeolite treatment but was not removed to concentrations below detection. The unionized ammonia concentration, the toxic form of ammonia, was reduced to less than 2 mg/L in all zeolite treatments.

The seven day exposures of Pimephales promelus (fathead minnows) with three different exposure waters showed that Well 1 and culvert water were similar in survival results. In general, the well water from the tire shreds on the west side of the study area (Wells 2 and 5) exhibited lower survival in all water treatments than the well water from the east side of the study area (Wells 3, 4, and 6). Well 6 showed similar or slightly better survival than Wells 3 and 4 after 7 days exposure.

The results from the Ceriodaphnia dubia 7 day chronic exposure were generally similar to the fathead minnow exposures. Wells 2 and 5 on the west side of the study area were lower in survival than Wells 3, 4, and 6 on the east side. In contrast, Well 1 showed reduced survival (10% survival) after both water treatments. Well 2 and Well 1 were similar in this respect where survival in both treated waters were lower (0% and 10%, respectively) than the baseline survival (10% and 30%, respectively). For Well 3 the water treatment may have improved the survival and in Well 4 the treatment did improve the survival. Well 6 survival was similar to culvert water with survival greater or equal to 90% after iron and ammonia treatment.

Statistical Testing with Respect to Survival

Statistical analysis was performed to estimate the relationship of the survival data after each of the well water treatments with the well water concentrations of tire related semi-volatile chemicals. Generally, correlation coefficients greater than or equal to 0.80 ($r^2 \geq 0.80$) were found between the survival of fathead minnows and the semi-volatile chemicals in the well water at the time of the September 2006 sampling (Table 8).

Table 8: Correlation coefficients for well water concentrations with fathead minnow survival after ammonia and iron reduction September 2006.

Parameter/Survival	Correlation Coefficient (r^2)
Aniline/Fathead minnow	0.85
Benzothiazole/Fathead minnow	0.83
Hydroxybenzothiazole/Fathead minnow	0.80
Acetylmorpholine/Fathead minnow	0.86

Similarly, correlation coefficients were calculated for the strength of relationship between the survival of water fleas and semi-volatile compounds. Significantly weaker correlation coefficients were found with the water flea survival data. These data can be found below in Table 9.

Table 9: Correlation coefficients for well water concentrations with water flea survival after ammonia and iron reduction in September 2006.

Parameter/Survival	Correlation Coefficient (r^2)
Aniline/Water flea	0.63
Benzothiazole/Water flea	0.57
Hydroxybenzothiazole/Water flea	0.42
Acetylmorpholine/Water flea	0.59

It appears from this analysis that there is no strong relationship between the semi-volatile concentrations in the water that identify one or more of the compounds as affecting the survival of fathead minnows or water fleas.

Well Water Effects with Respect to Reproductive Success

All wells exhibited a reduction in water flea progeny but Wells 2-5 exhibited complete reproductive failure in the baseline and all treatment waters. The reduction of ammonia and iron did not improve the reproductive success of the water fleas.

Culvert water exhibited reproductive toxicity similar to Well 1. However, there was a decrease in progeny after Well 1 was treated for ammonia and iron. Conversely, the culvert water exhibited improved reproductive success after ammonia and iron reduction.

Well Water Effects with Respect to Submerged Tire Material Thickness

In an effort to estimate strength of the relationship between the survival of minnows and water fleas with the thickness of tire material in well water, correlation analysis was performed. As can be seen below, the baseline exposure in the minnows gave strong negative correlations ($r^2 \geq -0.78$) with submerged tire material thickness (Table 10) and iron and ammonia reduction treatments.

Table 10: Correlation coefficients for fathead minnow survival with thickness of tire material submerged in well water during September 2006.

Well Water/Submerged Tire Thickness	Correlation Coefficient (r^2)
Baseline/Fathead minnow	-0.93
Iron Reduction/Fathead minnow	-0.78
Iron & Ammonia Reduction/Fathead minnow	-0.90

Correlation coefficients for water flea survival (Table 11) were moderately strong ($r^2 \geq -0.60$) as inverse relationships. The negative relationship for minnows and water fleas indicates decreasing survival with increasing thickness of submerged tire material. The moderate strength of the relationship for water fleas suggests that there may be one or more factors influencing their survival in well water.

Table 11: Correlation coefficients submerged in well water during September 2006.for water flea survival with thickness of tire material.

Well Water/Submerged Tire Thickness	Correlation Coefficient (r^2)
Baseline/Water flea	-0.61
Iron Reduction/Water flea	-0.62
Iron & Ammonia Reduction/Water flea	-0.60

EPIWIN Predicted Ecotoxicity Data

Since the chemical makeup of a typical tire is a complex mixture of organic compounds, discussing the toxicity of the few chemicals analyzed in this study does not provide a robust evaluation. A more complete list of organic chemicals identified in tire leachate can be found elsewhere (Abernethy et al., 1996). However, EPIWIN data are provided below to demonstrate the wide range of dose-response concentrations predicted for tire organic chemicals. Most of the chemicals used in tire manufacturing have not been tested for dose-response to aquatic organisms.

Aniline CAS# 62-53-3

Scientific name	End Point	Duration	Concentration
Daphnid	LC50	48 Hr.	1 mg/L
Fish	LC50	14 Days	84 mg/L
Fish	LC50	96 Hr.	134 mg/L

Benzothiazole CAS# 95-16-9

Scientific name	End Point	Duration	Concentration
Green algae	EC50	96 Hrs.	47 mg/L
Daphnid	LC50	48 Hrs.	75 mg/L
Fish	LC50	96 Hrs.	69 mg/L

2-Hydrozybenzothiazole CAS# 934-34-9

Scientific name	End Point	Duration	Concentration
Green algae	EC50	96 Hrs.	47 mg/L
Daphnid	LC50	48 Hrs.	5.4 mg/L
Fish	LC50	96 Hrs.	31 mg/L

4-Acetylmorpholine CAS# 1696-20-4

Scientific name	End Point	Duration	Concentration
Green algae	EC50	96 Hrs.	22,237 mg/L
Daphnid	LC50	48 Hrs.	41,959 mg/L
Fish	LC50	96 Hrs.	47,745 mg/L

EPIWIN Predicted Biodegradation Rates

Biodegradation rates for four of the tire organic chemicals were predicted by the EPIWIN software. The predicted rates are given in general time frames and varied only slightly. For all compounds primary biodegradation was predicted to occur in days to weeks and ultimate biodegradation was predicted to occur in weeks. The Linear and MITI models gave similar results for three of the four compounds.

Aniline CAS# 62-53-3

Linear Model	Primary	Ultimate	MITI Linear
Fast	Days-Weeks	Weeks	Slow

Benzothiazole CAS# 95-16-9

Linear Model	Primary	Ultimate	MITI Linear
Fast	Days-Weeks	Weeks	Slow

2-Hydroxybenzothiazole CAS#934-34-9

Linear Model	Primary	Ultimate	MITI Linear
Fast	Days-Weeks	Weeks	Slow

4-Acetylmorpholine CAS# 1696-20-4

Linear Model	Primary	Ultimate	MITI Linear
Fast	Days	Weeks	Fast

From these model predictions one can see that primary biodegradation of these compounds (i.e. the parent compound is changed to a greater or lesser degree from the parent structure) was expected to occur rapidly. Ultimate biodegradation to carbon dioxide and water requires more time but was also predicted to be quite rapid. This information can be interpreted as meaning that these organic chemicals could cause toxic responses from certain aquatic species but the toxicity may diminish quickly because of the rapid biodegradation.

5. FULL STUDY RESULTS

The remainder of this report will summarize the data collected over the three and one-half year period the study was conducted. The use of tire shreds within groundwater at this location has presented a “real world” setting with which to study the changes in water chemistry. The data collected from this setting are now available for resource managers to compare bench scale studies with field studies to assess their accuracy.

Inorganic Parameters

Data plots over the entire study showed differing trends of certain parameters at all wells, upstream and downstream locations. The downstream measurements were represented by samples from the culvert and downstream sampling locations. These data plots can be found in Appendix M. Gaps in the curves are from periods when measurements were not collected.

Ammonia

Ammonia well water concentrations in wells 2-5 were consistently in the low parts per million range (6-12 mg/L) during the 2006, 2007, and 2008 sampling events. Correlation analysis indicated a strong relationship ($r^2 = 0.99$) between ammonia and thickness of tire material in water during April 2008. This indicated that the source of the ammonia in the road base could be the tire shreds. It is also possible that the peat deposits at each of these wells could be contributing to the ammonia levels in the tire shreds. However, the identification of the definite source(s) of the ammonia to the well water is beyond the scope of this study.

Chemical Oxygen Demand (COD)

Chemical oxygen demand is one parameter that shows a gap during 2005 and 2006. The general trend of the COD concentrations at the upstream and downstream locations indicate a COD range of 20-60 mg/L.

The plot of COD content in the study wells showed Wells 1 and 6 to be frequently below 100 mg/L. Well 1 is in undisturbed soils and Well 6 is at the east end of the constructed road base with a 2.5 foot tire shred layer present but no peat layer present. The COD content appears to be similar between paired Wells 2 and 5 and then again between Wells 3 and 4. It can be seen in Table 2 that Wells 2 and 5 were placed in the thickest layer of tire shreds in water (6.8 and 5.9 feet).

Wells 3 and 4 have a layer of tire shreds in water between 1.6 and 2.1 feet thick and show elevated COD content as compared to Wells 6 and 1. At both pairs of wells, the COD content of the well water appears to be decreasing over the three and a half year study period.

Total Organic Carbon (TOC)

Total organic carbon data were collected only during two periods of the study when natural TOC was expected to be at a maximum locally. The first period was initiated with the well water collection for the ecotoxicity testing in September of 2006 and continued into the spring 2007. The next period began November of 2007 and continued into June of 2008.

Surface water concentrations of TOC were generally between 5 and 15 mg/L. Upstream, culvert and downstream locations may show an increasing trend; however additional sampling will be necessary.

The well water TOC levels were similar for the paired wells; Wells 2 and 5 and Wells 3 and 4. These paired wells showed similar TOC levels with respect to the thickness of tire shreds in water rather than thickness of peat in the bore hole. It was expected that major contributions of TOC from peat to well water would have shown elevated levels in Wells 4 and 5. This was not seen in the graph.

Total Suspended Solids (TSS)

Total suspended solids concentrations in surface water were mostly consistent over the study period. Typically TSS concentrations were less than 30 mg/L in the upstream, culvert and downstream locations. Variations in these levels may have reflected local fluctuations in surface water height due to natural and human activities.

TSS levels in Well 1 in the study area over the study period were consistently less than 12 mg/L. The other wells in the road base appeared to be comparable with respect to their location on either side of the culvert. Wells 2 and 5 on the west side of the culvert were similar and consistently below 100 mg/L except for one sample at the beginning of the study. Wells 3 and 4 showed similar and higher levels on the east side of the culvert. Well 6 showed the highest TSS levels in the study area with several samples approximating or exceeding 100 mg/L. There does not appear to be a tire material dependence with respect to TSS, rather a distinction appears to exist between the east and west side of the study area.

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) concentrations measured in the first year of study (2005) indicated higher BOD content at Wells 2 and 5 compared to the other wells. Dissolved organic carbon may be a contributing factor in this measurement but may not be significant since the thicker peat layers were associated with Wells 4 and 5. Wells 2 and 5 were significantly higher in BOD even though Well 2 has the thinnest peat layer in the well screen. The BOD content appears to be associated with the thickness of the tire material and not the peat layer at the well screen.

Temperature (Celsius)

Temperature plots of the surface water during the study period show higher temperatures in the summer months and lower temperatures in the fall through spring as would be expected.

Similarly, well water temperatures were also elevated at these times but temperatures were not as high as the surface water. Surface water maximum temperature approached 25°C while well water maximum temperature was slightly less than 20°C. It is apparent that while well water was generally cooler in the summer months, increasing and decreasing well water temperatures reflected surface water temperatures fairly closely.

Dissolved Oxygen (DO)
Dissolved oxygen concentrations in the surface water of the study area fluctuated seasonally as would be expected. The lower DO levels were measured in the warmer summer months when primary production is highest but oxygen solubility in water is lowest in warm water. The opposite is seen with higher DO levels in the colder months when primary production is lower but oxygen has higher solubility in cold water.

The well water plot of dissolved oxygen shows great variability at the beginning of the study with less variability beginning in August of 2005 through November 2007. During this period the DO levels were fairly consistent; ranging between 1 and 3 mg/L.

Hydrogen Ion Concentration (pH)
The hydrogen ion concentration of well water and surface water will be discussed as synonymous with water pH. However, the water pH measurements were converted to hydrogen ion concentrations as mole/liter (water pH = - log $[H^+]$) of water for better graphic visualization. The pH of surface water at the upstream and downstream locations remained quite constant over the study period. The upstream and downstream plots appear quite similar with a moderate decline, below pH 7.0, in 2007. The plot of the culvert data also shows a modest decrease in pH over the study period, but not below pH 7.0.

The plots of pH in the well water for each of the wells show a gradual decline in pH over the study period. The two wells showing the greatest decline below pH 6.0 were Wells 4 and 5. Well 3 also showed a pH below 6.0 late in 2007. Nevertheless, the pH depression in wells east of the culvert was measured during each year. In fact, pH values were measured below 6.0 at Wells 3 and 4 during the November 2007 sampling.

Wells 2, 3, 4 and 5 each have a layer of peat at the bottom of the bore hole. The length of screen in the respective peat layer is greatest with Wells 4 and 5. The length of screen in peat for Wells 2 and 3 are fairly similar. The plots of pH for Wells 2 and 5 on the west side of the culvert are similar in apparent rate of decline. Also, the plot of Wells 3, 4 and 6 on the east side of the culvert are reasonably similar. It is interesting to note that the pH depression does not show a strong correlation with thickness of tire material submerged in well water during September 2006 and does not show a strong correlation with thickness of peat in the November 2007 sampling. It appears that the pH of the well water is not completely dependent on the thickness of tire shreds or peat layers.

Specific Conductance
The specific conductance of surface water at the upstream and downstream locations was typically between 400 and 450 umhos/cm and was quite consistent between the locations.

The plot of the conductivity in the well water shows all the wells to have a similar conductivity early in the study. The conductivity at all the wells tended to increase as the study progressed (Table 12). The most recent measurements showed all the wells had double the conductivity compared to the beginning of the study.

The comparison of the respective well plots (Appendix M) shows that Wells 3 and 4 at the beginning of the study were similar in conductivity with the other wells. However, beginning in mid 2005 these two wells begin to exceed the conductivity of the other wells. During the remainder of the study, Wells 3 and 4 appeared to exceed the conductivity in the other wells most of the time. Wells 1 and 6 also increased over the study period even though Well 1 is without a tire shreds layer. According to the graph, Wells 1 and 6 show the greatest variability. These two wells are at opposite ends of the study area.

Table 12: Range of specific conductances during the study period.

	Upstream	OG1	OG2	OG3	OG4	OG5	OG6	Downstream
2005	NA	440-620	490-690	590-930	570-980	470-690	490-890	380-430
2006	385-467	862-1022	687-1115	816-1397	849-1331	729-1116	443-1266	319-470
2007	420-440	530-1201	1119-1213	1102-1366	1300-1460	1110-1170	768-1329	432-455
2008	453	883	1344	1423	1699	1286	1508	456

Metals

During the first year of the study heavy metals were the main focus with several parameters analyzed in the well water samples. Most heavy metals were not detected or were detected at levels well below regulatory limits set for drinking water by the Minnesota Department of Health. The only metals that showed elevated concentrations or increasing concentration trends were barium, iron, manganese and possibly zinc. These elements were analyzed intermittently after the first year to show increasing or decreasing trends in well water. The estimated trends of individual metals are discussed below.

Barium

Upstream and downstream (and culvert) surface water concentrations of barium appear to be similar at ranges between 50-100 ug/L. If barium is migrating from the road base to the surface water the chemical addition appears to be at a slow rate.

Barium levels in the background well, Well 1, were slightly elevated with ranges between 50-150 ug/L. All other wells showed elevated concentrations usually exceeding 100 ug/L. Barium appears to have reached steady state in well water with relatively constant concentrations approximately 300 ug/L. There does not, at this time, appear to be a decreasing trend in barium levels in well water.

Well 6 with the least amount of tire shreds and no peat in the bore hole contained some of the highest levels of barium over the study. The barium concentrations in Well 6 well water may be linked with the immediately local geology.

Iron

Surface water concentrations of iron are somewhat location dependent. Upstream and downstream location samples appear to contain about 1000 ug/L iron or less. Culvert samples collected during the last half of the study period contained iron concentrations above 1000 ug/L. The loss of dissolved iron between the culvert and downstream locations could be due to the iron precipitating as iron carbonate or hydroxide after entering more oxygenated surface water.

Iron levels in Well 1 at the beginning of the study were similar to surface water concentrations but appear to be gradually increasing. All wells experienced increasing iron concentrations in their well water over the study. However, the order of increasing iron concentration appears to be in reverse order with thickness of tire shreds layer. Well 6 at the furthest eastward location with the least amount of tire shreds, no peat layer, and lowest pH produced well water with the highest iron concentrations. A westward progression revealed the iron content to decline with increasing thickness of tire material layer. All wells, however, showed an increasing trend in iron concentration over the study period. It is possible that the dissolved iron produced from the tire shreds is only a partial contribution to the total dissolved iron in the road base water. Iron does appear to be migrating from the road base but the extent of migration may be very limited.

Manganese

Upstream and downstream (and culvert) levels of manganese appear to be between 200-250 ug/L in the surface water. At each sampling location the manganese does not appear to be increasing or decreasing.

Manganese concentrations at Well 1 appeared to be holding steady at 250 ug/L which was similar to surface water concentrations. Occasional concentration fluctuations for manganese make for difficult interpretation of increasing or decreasing trends at this time. Although it does not appear that manganese is migrating very quickly from the road base, sufficient manganese is dissolving to create a steady concentration.

Zinc

Downstream and culvert levels of zinc are both in the low part per billion range (ug/L) and do not appear to be increasing. Zinc was not analyzed at the upstream location.

Zinc was consistently low at Well 1 and all other wells, however there were concentration fluctuations at Well 3. There does not appear to be an increasing or decreasing trend with zinc levels in the road base water.

Organic Parameters

Eight semi-volatile organic chemicals were analyzed in well and surface water samples. These eight chemicals were reported in the literature as detected in tire material field studies elsewhere. There were 5 sampling events in 2006, 3 sampling events in 2007, and 2 sampling events in 2008. All eight compounds were analyzed in well water samples in the 2006 and most of 2007. The three compounds consistently detected in the 2006 samples were continued during November of 2007 and 2008. None of the tire material organics were detected in Well 1, the background well, or surface water during the study.

Aniline

Aniline was first analyzed in well water samples in February 2006. Over the following two years, the well water concentrations have gradually decreased in the paired wells (Wells 2 and 5, Wells 3 and 4) on both east and west sides of the culvert. Aniline concentrations were found to correlate well with the thickness of submerged tire material. In pair-wise fashion, the well water concentrations have declined approaching the MDH HRL of 10ug/L. It is anticipated that given a few more years the well water levels of aniline will consistently not exceed the HRL. Seasonal temperature changes do not appear to be an influencing factor on chemical water concentrations. The source of aniline in well water appears to be the tire material in the road base.

Benzothiazole

Somewhat different than aniline, the well water levels of benzothiazole have declined in Well 2 and 5 but have remained approximately the same in Wells 3 and 4. Benzothiazole has mostly, steadily declined in Well 2 and 5 over the two years of sampling. Chemical levels in Wells 3 and 4 may also be declining but additional sampling would be necessary for better definition. There is no MDH HRL for benzothiazole at the present time. Seasonal temperature changes do not appear to have an affect on well water concentrations. The source of benzothiazole appears to be the tire material in the road base.

2-Hydroxybenzothiazole

Similar to aniline, the decreasing 2-hydroxybenzothiazole levels appear to be declining in a paired well pattern. Again, Wells 2 and 5 and Wells 3 and 4 appear to be declining in comparable patterns over the two year sampling period. Periods of increasing and decreasing chemical concentrations coincide with the seasonal well water temperature plot. This indicates that the well water concentrations are temperature dependent and may take several more seasons of sampling to determine if the water concentrations are declining. The source of the 2-hydroxybenzothiazole appears to be the tire material in the road base.

4-Acetylmorpholine

The well water concentrations for this chemical appear to be somewhat variable although may not be declining. This chemical is not of great concern given that 4-Acetylmorpholine is highly water soluble and expected to rapidly biodegrade. There does not appear to be seasonal temperature dependence for this chemical. The source of 4-actylmorpholine appears to be the tire material in the road base.

The microbial degradation of xenobiotics in laboratory studies are not completely comparable to microbial behavior in surface waters (Aelion et al., 1987). The physical, chemical and hydrogeologic variables in field studies are not easily integrated into predictive models with great accuracy. The predicted environmental behavior of chemicals discussed above should be viewed as indicators of tendency.

6. CONCLUSIONS

The Oak Grove Tire Shreds study has been a unique field study with the application of 7.6 million pounds of tire material as light weight fill in a road construction project. In this study, the tire material was deposited below the groundwater table and provided an opportunity to evaluate the "real world" responses, both chemically and biologically, to the aquatic environment.

Chemical Contributions from Tire Shreds to Surface Water

At present, the chemical concentrations that have increased in the culvert and downstream water since the beginning of the study are specific conductance, barium, iron, manganese, and possibly zinc and chemical oxygen demand. Ammonia was measured in surface water samples but the concentrations were typical ammonia levels. Aniline, benzothiazole, 2-hydroxybenzothiazole and 4-acetylmorpholine were not detected in the culvert and downstream water samples even though they were detected in well water samples.

Ecotoxicity testing of the culvert water showed a minnow and water flea survival comparable to laboratory control water after ammonia and iron reductions. Water flea reproductive success was also comparable to laboratory controls after reductions. There was partial survival toxicity for water fleas with the culvert water. There was no survival or reproductive toxicity to Ceriodaphnia dubia with culvert water after iron and ammonia reduction. The toxicity characteristics of tire material leachate in this study appear to be largely retained within the road base.

Chemical Contributions from Tire Shreds to Well Water

Since the beginning of the study, chemical oxygen demand, total suspended solids, specific conductance, barium, iron and manganese have increased in the well water from the road base. There also appear to be total organic carbon contributions from the tire shreds to the well water.

The field measurements of pH in well water have shown a slight pH depression during the first and second years of monitoring. At least one other study reported a change in pH in well water taken from tire shreds. It is the current tentative conclusion that the pH depression in the Oak Grove study is occurring because of the tire shreds. Additional monitoring will document the trend in pH.

Specific conductance measurements of well water from all the wells have continued to increase during the study. The increases in conductivity for some of the wells could be due to an increase in dissolved ionized chemicals both inorganic (e.g. iron) and organic. An explanation for the increase in specific conductance in Well 1 is not apparent. Local influences in the vicinity of the study area may be part of the explanation.

Polynuclear aromatic hydrocarbons were detected at low concentrations in wells in the larger deposits in the study area. No carcinogenic PAHs were detected in well water samples. The

PAHs detected in the first year samples may have been caused by the change in ditch water elevation flooding shreds not covered in well water during the usual 10 inch ditch water level.

The well water in the tire shreds road base contained four of the eight tire related organic chemicals monitored. The organic chemicals detected in the well water samples were aniline, benzothiazole, 2-hydroxybenzothiazole and 4-acetylmorpholine. Well water concentrations of these compounds varied linearly with the thickness of submerged tire shreds in the road base. Aniline was detected in well water from the road base interior at concentrations exceeding the MnHRL (10ug/L).

The ecotoxicity testing indicated that well water from the road base exhibited survival and reproductive toxicity to certain aquatic organisms. When well water was treated for iron and ammonia reduction, reproductive toxicity responses remained for four of the six wells. This indicated that a stressor from the tires remained in the well water after iron and ammonia reductions. The responses may be due to aniline, however many other organic chemicals are present in tire material.

From the data produced in this study, it is estimated that contributions of ammonia from the peat deposits to the well water in the road base is a minor contribution. The migration of ammonia through the geotextile fabric wrap into the road base is possible given the 0.6 mm slit width in the fabric. However, the migration of other chemicals detected in the well water to ditch water out of the road base would be equally likely. The fabric wrap appears to be restricting the migration of many of these chemicals to the adjacent ditch water. None of the tire related organic chemicals have been detected at the culvert or further downstream from the study area.

Conclusions about Well Water Effects with Respect to Earlier Field Studies

Previous studies with whole tire or tire chips have concluded that leachate concentrations were equal to or below state or federal drinking water standards. However, a few studies report that rainbow trout have shown dose-response sensitivities to tire material leachate.
Surface water quality criteria should be compared to leachate concentrations when estimating environmental effects.

The information from other studies discussed earlier in this reports and data collected in this study indicate that tire shreds will contribute metals and organic chemicals to road base water when placed below the groundwater table. Tire shred leachates have shown measured toxicity to freshwater Salmonids (rainbow trout, brook trout and brown trout) in other studies. Rainbow trout have been reported to be particularly sensitive to the leachate from tires. It is difficult to compare leachate concentrations from field or bench scale studies when smaller amounts of tire material have been used. Data from this study suggest that an increased mass of tire material in water results in increased concentrations of leached chemical. However, this may not hold true for all chemicals in the tire material.

A study conducted by Abernethy et al. (1994) reported aromatic amines as a possible toxicant for the rainbow trout but did not measure ammonia in the treatment waters. The field crew in this study also noted foaming of the sample water similar to the presence of a surfactant or fatty acid content. Abernethy et al. (1996) reported finding resin acids (long chain carboxylic acids) in the base extract of treatment water. The presence of aromatic or aliphatic resin acids could explain the foaming of the well water from Oak Grove since the total organic carbon was elevated in the well water.

Conclusions from the Oak Grove Tire Shreds Study

The differences in water chemistry described in the first year and this final report may be explained in part by the thickness of tire material in well water. The thicker tire material deposit is on the west side of the culvert while the thinner deposits are on the east side of the culvert. The strong correlations between the thickness of submerged deposits and COD, TOC, and organic chemical concentrations suggest the tire shreds to be the source of these chemicals.

The elevated chemical concentrations, metals and organics, measured during this study appear to be mostly retained within the geotextile fabric wrapped tire shreds road base. None of the tire related organic chemicals were detected in samples collected outside of the road base. Barium, iron, manganese and possibly zinc appear to be migrating from the road base but the extent of iron transport may be limited due to hydroxide precipitation.

Tire material will leach semi-volatile organic chemicals when placed below the groundwater table. The concentrations of aniline in groundwater in this study were dependant on the thickness of the tire layer in water in the road base. Other semi-volatile compounds will also leach into water but the fate of these chemicals will be dependant on the biodegradation potential of each compound.

The ecotoxicity testing conducted on the well water from the study site indicated that fathead minnows exhibited mortality responses to the leachate from tire shreds. Similarly, water fleas appeared to be particularly sensitive, exhibited by survival and reproduction toxicity, to tire material leachate. However, not all aquatic invertebrates appeared to be sensitive to the leachate as was seen with the survival of midges in the first ecotoxicity test.

Significant levels of ammonia were measured in samples of Oak Grove well water. Although the ammonia could be originating from the sod farm adjacent to the study area, the relatively consistent and elevated concentrations found in the well water samples compared to the surface water samples suggests the tire shreds material to be the source. From the data collected in this study, a positive identification of the source of ammonia in the well water can not be confirmed.

It is important to consider the uniqueness of this study as compared to other field studies. The mass of tire material placed in the road base was appropriate for the construction project but was far greater than most other field studies. Additionally, this study monitored the water quality in a submerged tire shreds deposit from the third year into the fifth year of the road base life-cycle. Most studies have only looked at the first 24 months or less.

The use of a geotextile fabric wrap may provide an element of restricted water flow through the road base. The restricted migration of chemicals by use of the fabric wrap could be a useful proactive act of anti-degradation of surface and groundwater quality when placing recycled material in wet environments.

7. ADDENDUM

Near the end of the study, the Minnesota Department of Health issued a letter informing the Oak Grove Tire Shreds Study about an analytical non-compliance with one of the contracted laboratories. This condition of non-compliance only existed for the Diesel Range Organics (DRO) analysis discussed in the first year report (March 2007). Since the DRO analysis in this study was of minimal importance, no attempts were made to correct the reported DRO concentrations. Similarly, the conclusions of the study would not be changed by the condition of non-compliance. The letter from the MDH can be found in Appendix O.

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APPENDIX A

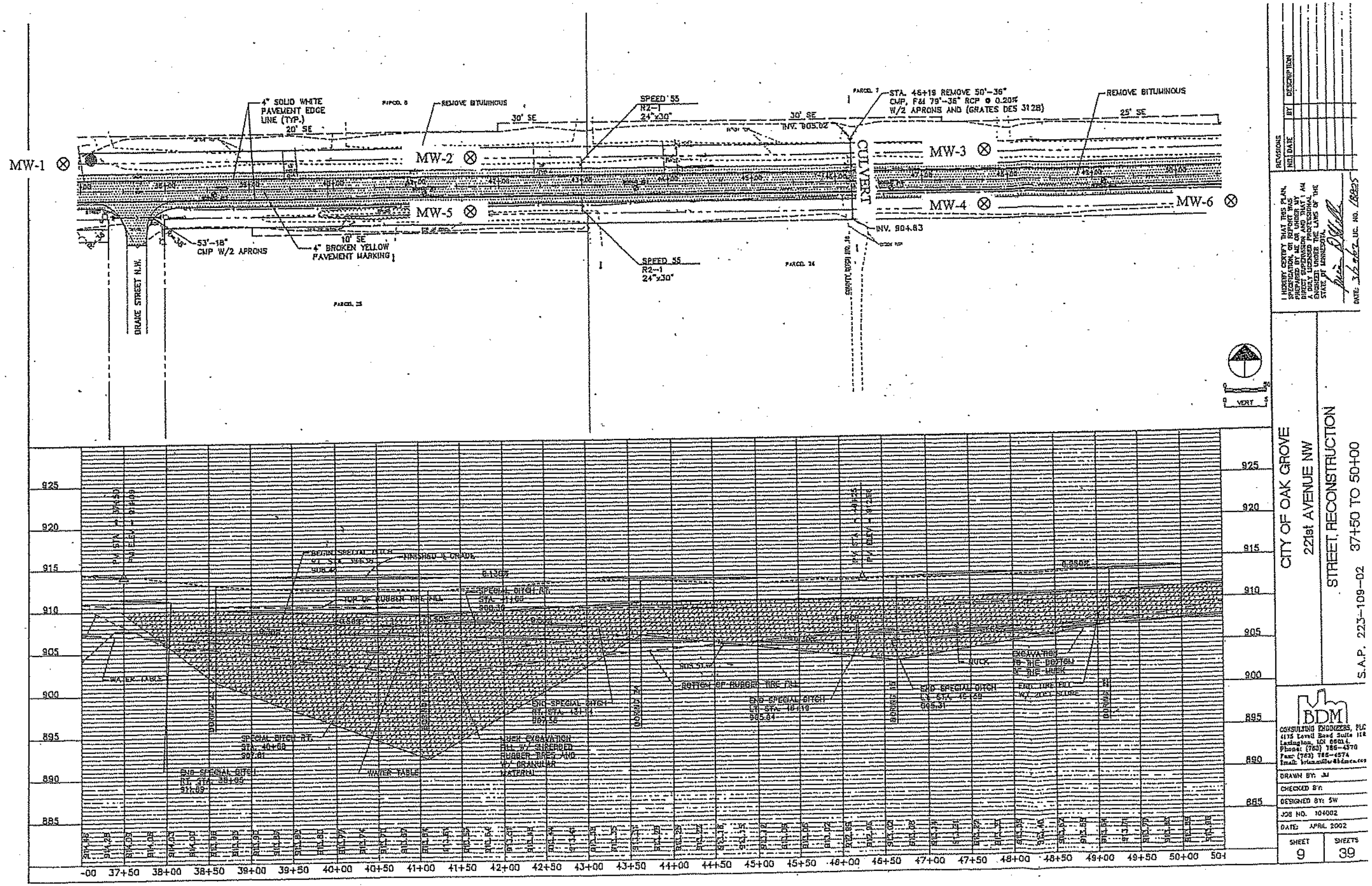
ROAD CONSTRUCTION DESIGN PLAN

AERIAL PHOTOGRAPH OF STUDY AREA

MAP OF STUDY AREA

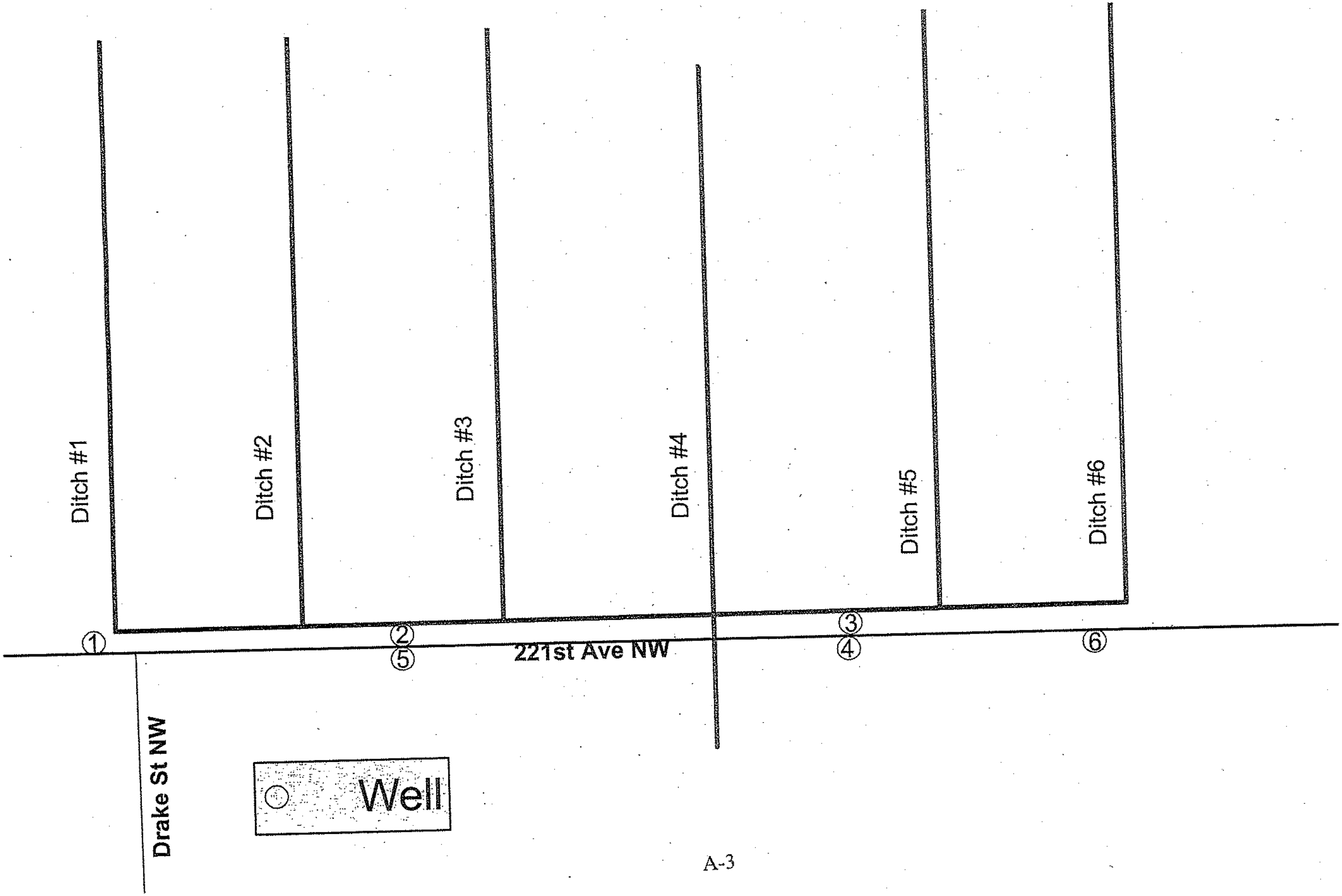
WELL INSTALLATION LOGS

ROAD CONSTRUCTION PHOTOGRAPHS


MW-1
MW-2
MW-3
MW-4
MW-5
MW-6
CULVERT
4" SOLID WHITE PAVEMENT EDGE LINE (TYP.)
REMOVE BITUMINOUS
20' SE
30' SE
25' SE
10' SE
SPEED 55
R2-1
24"x30"
STA. 46+19 REMOVE 50'-36" CMP, F&I 79'-36" RCP @ 0.20% W/2 APRONS AND (GRATES DES 3128)
INV. 905.02
INV. 904.83
53'-18" CMP W/2 APRONS
4" BROKEN YELLOW PAVEMENT MARKING
BRAKE STREET N.W.
BEGIN SPECIAL DITCH
FINISHED Ⓒ GRADE
TOP OF RUBBER TIRE FILL
BOTTOM OF RUBBER TIRE FILL
WATER TABLE
MUCK
MUCK EXCAVATION FILL W/ SHREDDED RUBBER TIRES AND W/ GRANULAR MATERIAL
EXCAVATION TO THE BOTTOM OF THE MUCK
END SPECIAL DITCH
SPECIAL DITCH RT.
925
920
915
910
905
900
895
890
885
37+50
38+00
38+50
39+00
39+50
40+00
40+50
41+00
41+50
42+00
42+50
43+00
43+50
44+00
44+50
45+00
45+50
46+00
46+50
47+00
47+50
48+00
48+50
49+00
49+50
50+00
CITY OF OAK GROVE
221st AVENUE NW
STREET RECONSTRUCTION
37+50 TO 50+00
S.A.P. 223-109-02
BDM
CONSULTING ENGINEERS, PLC
DRAWN BY: JM
CHECKED BY:
DESIGNED BY: SW
JOB NO. 104002
DATE: APRIL 2002
SHEET 9
SHEETS 39
REVISIONS
NO. DATE BY DESCRIPTION

A-1

FSA 2003 Aerial Photo


Ditch #1
Ditch #2
Ditch #3
Ditch #4
Ditch #5
Ditch #6
①
②
③
④
⑤
⑥
221st Ave NW
Drake St NW
Well

FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION
Mn/DOT – TIRE SITE
221ST STREET & DRAKE
OAK GROVE, MN

DRILLING METHOD: ROTOSONIC

SAMPLING METHOD: CONTINUOUS

BORING NO. MW-1

SHEET 1 OF 1

WATER LEVEL	8.0 ft	6.50	6.26	
TIME	11:00	15:20	16:00	
DATE	17 Aug	18 Aug	20 Aug	
CASING DEPTH	–	–	–	

DRILLING	
START	FINISH
TIME	TIME
10:00	13:00
DATE	DATE
17 Aug 04	

DATUM
ELEVATION
DRILL RIG
ANGLE
BEARING
SAMPLE HAMMER TORQUE FT.-LBS
SURFACE CONDITIONS OFF EDGE OF ROAD - ON 221ST STREET

DEPTH IN FEET (ELEVATION)	BLOWS/6 IN. ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0			Loose, moist, Dk Brown to Black SANDY GRAVEL (ROAD BASE- FILL)						
1	36" of 60" Recovery		m. Dense, moist, Lt. Brown M-C SAND, trace gravel & f. Sand (ROAD SUB BASE- FILL)						
2									No Odor or Visible Contamination 0 to 14 feet
3			m. Dense, Dry to Moist, Brown Very fine SAND, poorly graded (fill)						
4									
5	44" of 60" Recovery		m. Dense, moist, mottled Reddish brown and Brown Very fine SAND, poorly graded (Alluvium)						
6									
7									
8			m. Dense, wet, light gray and black, very fine to fine SAND (Alluvium)						
9									
10	20" of 48" Recovery								
11									grading to medium Sand, trace gravel with depth
12									
13									
14			Bottom of Boring @ 14 feet						
15									

DRILLING CONTR Boart Longyear

FS 25558

LOGGED BY T. Fyzek

DATE 17 Aug 04 CHK'D BY

Printed on recycled paper

FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION
Mn/DOT – TIRE SITE
221ST STREET & DRAKE
OAK GROVE, MN

DRILLING METHOD: ROTOSONIC

SAMPLING METHOD: CONTINUOUS

BORING NO. MW-2

SHEET 1 OF 1

WATER LEVEL	5.5 ft	4.75	4.51	
TIME	13:40	15:20	16:00	
DATE	17 Aug	19 Aug	20 Aug	
CASING DEPTH				

DRILLING	
START	FINISH
TIME 13:00	TIME 15:00
DATE 17 Aug 04	DATE

DATUM
ELEVATION
DRILL RIG
ANGLE
BEARING
SAMPLE HAMMER TORQUE FT.-LBS

SURFACE CONDITIONS OFF EDGE OF ROAD – ON 221ST STREET

DEPTH IN FEET (ELEVATION)	BLOWS/6 IN. ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0 1	12" of Core Recovery		Loose, Moist, Dk. Brown to Black, Sandy GRAVEL (Road Base - Fill)						
2 3			m. Dense, moist, Lt. Brown SAND, trace gravel & f. Sand (Road Subbase - Fill)						
3 4			m. Dense, moist, mottled Brown, v. fine SAND, Poorly Graded (Fill)						
5 6 7 8 9 10 11	8' of 10' Recovery		— MOIST, BLACK TIRES, SHREDDED IN CORE WITH 2" TO 6" SIZE PIECES w/. metal bands (fill)						water @ 5.5 feet while drilling No Visual degradation of tires
12 13 14 15			v. Soft to Soft, moist to wet, Dark Gray Silty organic PEAT with shells, seeds, insect parts, roots, etc. (PEAT)						no odor or visible contamination 0 to 15 feet

Bottom of Boring @ 15 feet

DRILLING CONTR. Boart Longyear

FS 25558

LOGGED BY T. Fryzek

DATE 17 Aug 04 CHK'D BY

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FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION	Mn/DOT – TIRE SITE 221ST STREET & DRAKE OAK GROVE, MN
DRILLING METHOD:	ROTOSONIC
SAMPLING METHOD:	CONTINUOUS
BORING NO.	MW-3
SHEET	1 OF 1
DATUM	
ELEVATION	
DRILL RIG	
ANGLE	
BEARING	
SAMPLE HAMMER TORQUE	FT.-LBS
SURFACE CONDITIONS	OFF EDGE OF ROAD – ON 221ST STREET

WATER LEVEL	5.0 ft	5.90	4.95	
TIME	17:00	15:20	16:00	
DATE	17 Aug	18 Aug	20 Aug	
CASING DEPTH				

DRILLING	START	FINISH
TIME	16:00	19:00
DATE	17 Aug 04	

DEPTH IN FEET (ELEVATION)	BLOWS/ 6 IN ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0	12" of 60" Rec.		Loose, moist, Dk Brown to Black, Sandy GRAVEL (Road Base – Fill)						
1			m. Dense, moist, Brown F to Coarse SAND, trace Gravel (fill)						
4			moist, Black TIRES, SHREDDED w/ metal bands (fill)						water @ 5 feet while drilling no visual degradation of tires
7	8' of 10' Rec.		V. Soft to Soft, wet, Gray to Dk. Gray, Clayey organic Silt with trace to some roots and organic matter (PEAT)						no odor or visible contamination 0 to 15 feet
14			Dense, wet, Lt. Gray, poorly graded Fine SAND (Alluvium)						
15			Bottom of Boring @ 15 feet						

DRILLING CONTR Boart Longyear

FS 25558

LOGGED BY T. Fryzek

DATE 17 Aug 04 CHK'D BY

Printed on recycled paper

FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION	Mn/DOT – TIRE SITE 221ST STREET & DRAKE OAK GROVE, MN
DRILLING METHOD:	ROTOSONIC
SAMPLING METHOD:	CONTINUOUS
BORING NO.	MW-4
SHEET	1 OF 1

WATER LEVEL	8.5 ft	5.50	5.0	
TIME	10:00	15:20	16:00	
DATE	18 Aug	18 Aug	20 Aug	
CASING DEPTH				

DRILLING	START	FINISH
TIME	9:00	11:00
DATE	18 Aug 04	

DATUM

ELEVATION

DRILL RIG

ANGLE

BEARING

SAMPLE HAMMER TORQUE FT.-LBS

SURFACE CONDITIONS OFF EDGE OF ROAD – ON 221ST STREET

DEPTH IN FEET (ELEVATION)	BLOWS/ 6 IN. ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0 1	12" of 60" Recov		Loose, moist, Dk Brown to Black, Sandy GRAVEL (Road Base - Fill)						
2 3 4			m. Dense, moist, Brown fine to Coarse SAND, trace Gravel (Fill)						
5 6 7	48" of 60" Recov		moist, BLACK TIRES, SHREDDED w/ metal Bands (Fill)						no visual degradation to tires
8 9 10 11	20" of 24" Rec.		V. Soft to Soft, wet, Dk Gray to Gray, organic SILT with roots, trace shells, small insect parts (PEAT)						water @ 8.5 ft while drilling Some light gray mottles @ 11.5 feet
12 13 14 15			Bottom of Boring @ 12 feet						No odor or Visible contamination 0 to 12 feet

DRILLING CONTR Bart Longyear

FS 25558

LOGGED BY T. Fryzek

DATE 10 Aug 04 CHK'D BY

Printed on recycled paper

FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION
Mn/DOT – TIRE SITE
221ST STREET & DRAKE
OAK GROVE, MN

DATUM
ELEVATION

DRILLING METHOD: ROTOSONIC

SAMPLING METHOD: CONTINUOUS

BORING NO. MW-5

SHEET 1 OF 1

WATER LEVEL	6.0	5.15	4.28	
TIME	12:00	15:20	16:00	
DATE	18 Aug	18 Aug	20 Aug	
CASING DEPTH				

DRILLING	
START	FINISH
TIME	TIME
11:00	13:00
DATE	DATE
18 Aug 04	

DRILL RIG
ANGLE
BEARING
SAMPLE HAMMER TORQUE FT.-LBS

SURFACE CONDITIONS OFF EDGE OF ROAD - ON 221ST STREET

DEPTH IN FEET (ELEVATION)	BLOWS/6 IN. ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0 1	22" of 60" Rec.		Loose, moist, Dk Brown, SANDY GRAVEL (Road-Base Fill)						
2 3 4			m. Dense; moist, Brown, fine to Coarse SAND, trace Gravel (fill)						
5 6 7 8 9 10	7' of 10' Rec		Moist, Black, TIRES, SHREDDED WITH metal bands (fill)						water @ 6.0 feet while drilling No visual degradation to tires
11 12 13 14 15			soft, moist to wet, Dark Gray Silty organic PEAT with shells, seeds, roots, etc (PEAT)						No odor or visible contamination 0 to 15 feet

Bottom of Boring @ 15 feet

DRILLING CONTR Boart Longyear

LOGGED BY T. Fenzel

DATE 16 Aug 04 CHK'D BY

Printed on recycled paper

FIELD LOG – SOIL BOREHOLE

SITE NAME AND LOCATION Mn/DOT – TIRE SITE 221ST STREET & DRAKE OAK GROVE, MN	DRILLING METHOD: ROTOSONIC SAMPLING METHOD: CONTINUOUS		BORING NO. MW-6 SHEET 1 OF 1
DATUM	ELEVATION		

WATER LEVEL	7 ft	4.8	5.85	
TIME	14:00	15:20	16:00	
DATE	18 Aug	19 Aug	20 Aug	
CASING DEPTH				

DRILLING	
START	FINISH
TIME 13:00	TIME 15:00
DATE 19 Aug 04	DATE

DRILL RIG

ANGLE BEARING

SAMPLE HAMMER TORQUE FT.-LBS

SURFACE CONDITIONS OFF EDGE OF ROAD – ON 221ST STREET

DEPTH IN FEET (ELEVATION)	BLOWS/6 IN ON SAMPLER (RECOVERY)	SOIL GRAPH	SAMPLE NUMBER AND DESCRIPTION OF MATERIAL	SAMPLER AND BIT	CASING TYPE	BLOWS/FOOT ON CASING	DEPTH IN FEET FROM	DEPTH IN FEET TO	DESCRIPTION OF OPERATION AND REMARKS
0–2	18" of 60" (recovery)		Loose, moist, Dk Brown Sandy GRAVEL (Road Base – FILL)						
2–4			m. Dense, moist, Brown fine to Coarse SAND (FILL)						
4–6.5			Moist, Black, TIRES, Shredded with metal Bands (FILL)						no visual degradation to tires water @ 7 feet while drilling
6.5–9	7½' out of 9' Rec		Dense, moist to wet, Lt Brown v. fine to fine SAND (Alluvium)						
9–14			Dense, wet, Lt. Gray fine to medium SAND (Alluvium)						no odor or visible contamination 0 to 14 feet
14–15			Bottom of Boring @ 14 feet						

DRILLING CONTR Boart Longyear

FS25558

LOGGED BY T. Fryzek

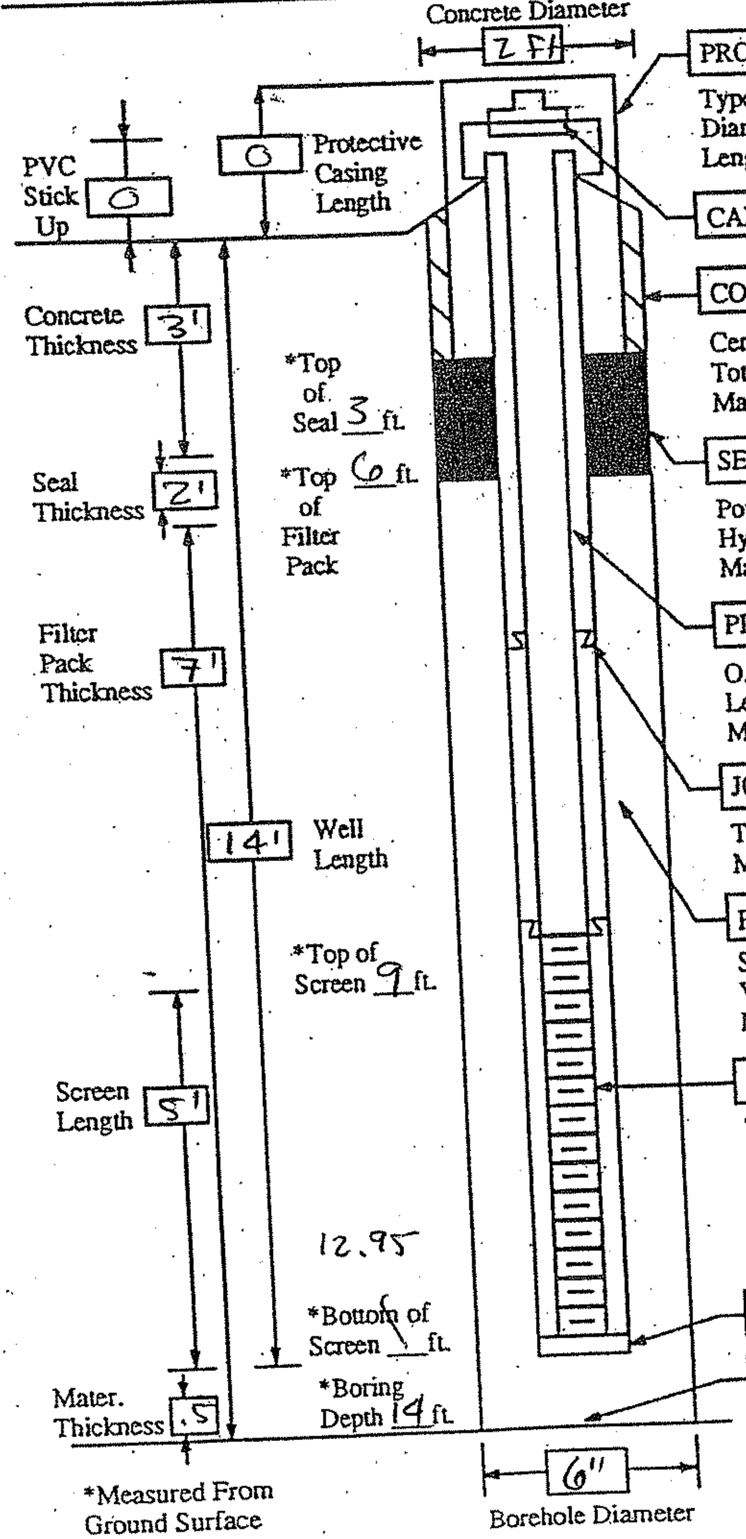
DATE 19 Aug 04 CHK'D BY

EARTH TECH
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: Mo/Dos-Tire Site Date: 17 Aug 04
Inspected By: I. Fryzck Project No. 78969 Well No. MW-1
Driller/Contractor Boart Longyear


Concrete Diameter 2 Ft
Protective Casing Length 0
PVC Stick Up 0
Concrete Thickness 3'
*Top of Seal 3 ft.
Seal Thickness 2'
*Top of Filter Pack 6 ft.
Filter Pack Thickness 7'
Well Length 14'
*Top of Screen 9 ft.
Screen Length 5'
12.95
*Bottom of Screen ___ ft.
Mater. Thickness .5
*Boring Depth 14 ft.
Borehole Diameter 6"

*Measured From Ground Surface

PROTECTIVE CASING
Type At Grade Vented Yes/[✓ No] Type
Diameter Locked YES
Length Key #

GUARD POSTS

CAP OR PLUG Vented Yes/[✓ No] Type EXPANSION

CONCRETE COLLAR
Cement ___ lbs.+Water ___ gal.
Total Quantity ___ gal.
Manufacturer

SEAL
Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated YES gal., Time
Manufacturer 3/8" Baroid Hole Plug

PIPE Type SS Schedule
O.D. 2' " I.D. 1.75 "
Length/Sec. No. of Sec.
Manufacturer

JOINTS Flush Threaded Yes/No YES
Teflon Taped Yes/No O-Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40
Source Red flint
Volume ___ gal.
Manufacturer Red flint

SCREEN
Type Schedule SS
Length/Sec. 5'0" No. of Sec. 1
O.D. 2" " I.D. 1.75"
Slot Size 0.10" No. Slots/ft.
Manufacturers Johnson

CAP OR PLUG Type manufactured bottom Length plug

MATERIAL

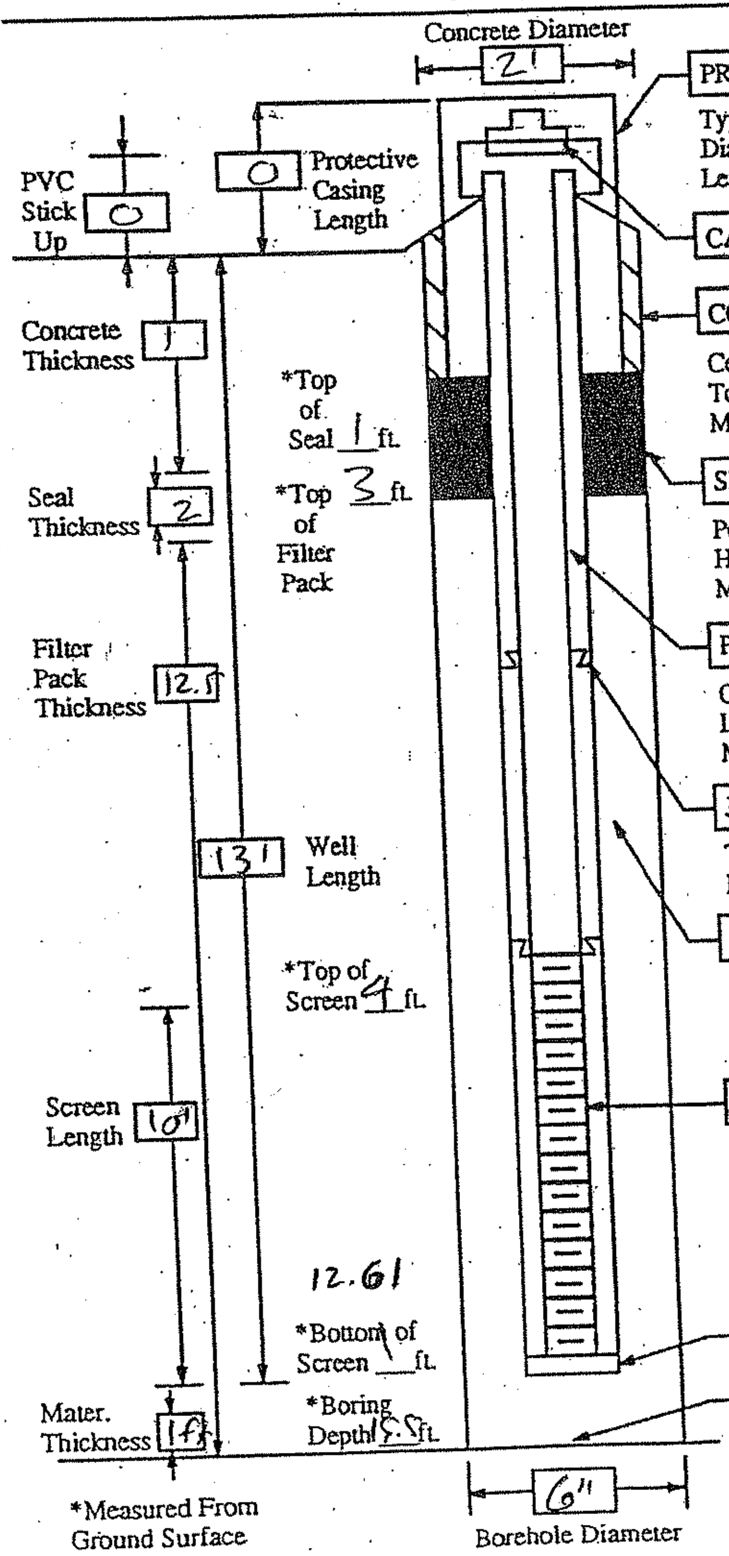
WATER SOURCE
Notes:

EARTH TECH
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: Mn/DOT - TIRE SITE Date: 17 Aug 04
Inspected By: T. Fryzek Project No. 78969 Well No. MW-2
Driller/Contractor Boart Longyear



Concrete Diameter 2'
PVC Stick Up 0
Protective Casing Length 0
Concrete Thickness 1
*Top of Seal 1 ft.
Seal Thickness 2
*Top of Filter Pack 3 ft.
Filter Pack Thickness 12.5
Well Length 13'
*Top of Screen 4 ft.
Screen Length 10'
12.61
*Bottom of Screen ___ ft.
*Boring Depth 15.5 ft.
Mater. Thickness 1ft
Borehole Diameter 6"
*Measured From Ground Surface

PROTECTIVE CASING **GUARD POSTS**
Type At Grade Vented Yes/[✓ No] Type
Diameter Locked Yes
Length Key #

CAP OR PLUG Vented Yes/[✓ No] Type EXPANSION

CONCRETE COLLAR
Cement ___ lbs.+Water ___ gal.
Total Quantity ___ gal.
Manufacturer

SEAL
Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated YES gal., Time
Manufacturer 3/8" Baroid Hole plug

PIPE Type SS Schedule
O.D. 2 " I.D. 1.75 "
Length/Sec. No. of Sec.
Manufacturer

JOINTS Flush Threaded Yes/No YES
Teflon Taped Yes/No O-Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40
Source Red flint
Volume ___ gal.
Manufacturer Red flint

SCREEN
Type Schedule SS
Length/Sec. 10' No. of Sec. 1
O.D. 2 " I.D. 1.75
Slot Size 0.10 No. Slots/ft.
Manufacturers Johnson
manufactured bottom plug

CAP OR PLUG Type Length

MATERIAL

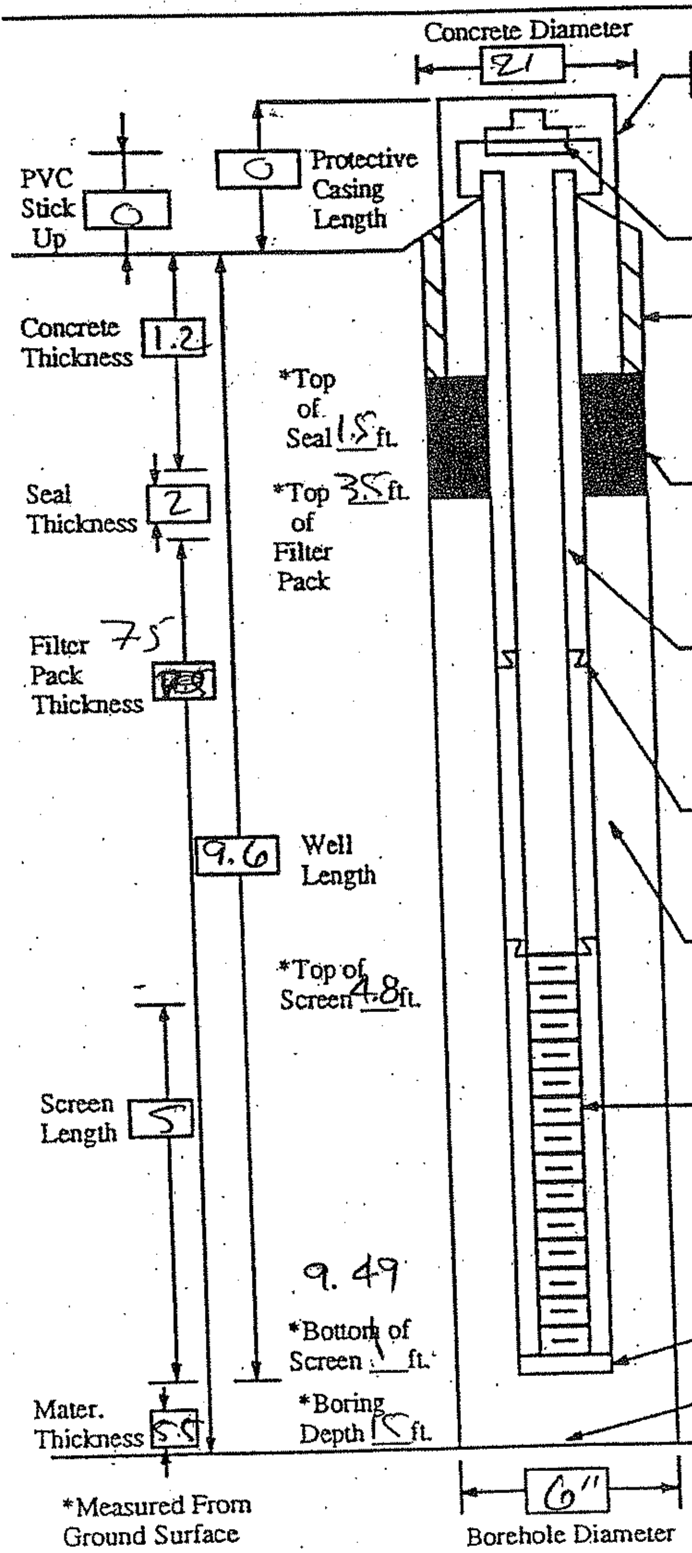
WATER SOURCE
Notes:

E A R T H T E C H
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: Mn/Dot - Tree Site Date: 17 Aug 04
Inspected By: T. Fryzek Project No. 78969 Well No. MW-3
Driller/Contractor Boart Longyear



Concrete Diameter 21

PVC Stick Up 0

Protective Casing Length 0

Concrete Thickness 1.2

*Top of Seal 1.5 ft.

Seal Thickness 2

*Top 3.5 ft. of Filter Pack

Filter Pack Thickness 75

Well Length 9.6

*Top of Screen 4.8 ft.

Screen Length 5

9.49

*Bottom of Screen 1 ft.

*Boring Depth 15 ft.

Mater. Thickness 5.5

*Measured From Ground Surface

Borehole Diameter 6"

PROTECTIVE CASING **GUARD POSTS**
Type At Grade Vented Yes/[✓ No] Type
Diameter Locked Yes
Length Key #

CAP OR PLUG Vented Yes/[✓ No] Type EXPANSION

CONCRETE COLLAR
Cement lbs.+Water gal.
Total Quantity gal.
Manufacturer

SEAL
Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated Yes gal., Time
Manufacturer 3/8" Baroid Hole Plug

PIPE Type SS Schedule
O.D. 2 " I.D. 1.75 "
Length/Sec. No. of Sec.
Manufacturer

JOINTS Flush Threaded [✓ Yes]/No
Teflon Taped Yes/No O–Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40
Source Red flint
Volume gal.
Manufacturer Red flint

SCREEN
Type SS Schedule SS
Length/Sec. 5' No. of Sec. 1
O.D. 2 " I.D. 1.75
Slot Size 0.10 No. Slots/ft.
Manufacturers Johnson
manufactured Bottom plug

CAP OR PLUG Type Length

MATERIAL gravel pack / sluff

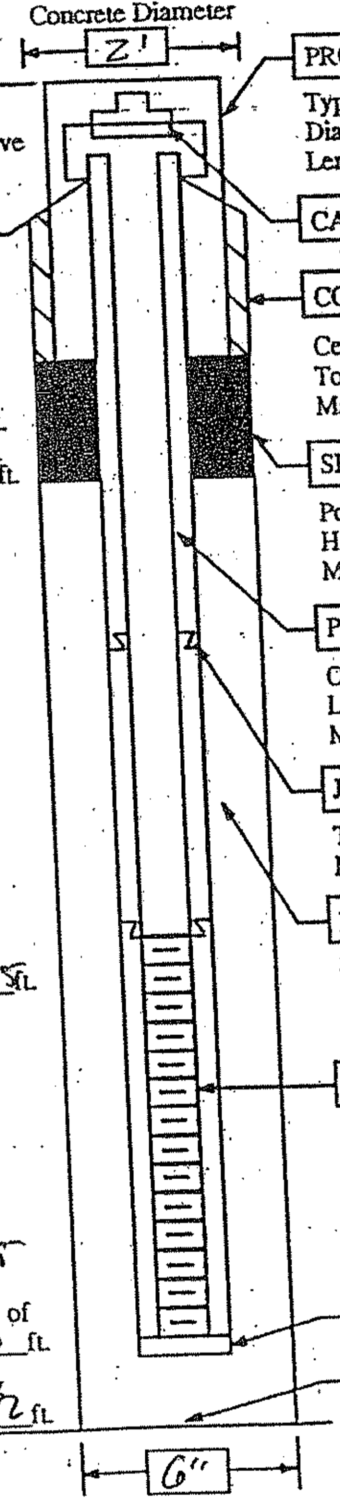
WATER SOURCE
Notes:

EARTH TECH
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: Mn/DOT - Tire Site
Date: 18 Aug 04
Inspected By: T. Fryzek
Project No. 78969
Well No. MW - 4
Driller/Contractor Boart Longyear



Concrete Diameter 2'

PVC Stick Up 0

Protective Casing Length 0

Concrete Thickness 2.5

*Top of Seal 2.5 ft.

Seal Thickness 2

*Top of Filter Pack 4.5 ft.

Filter Pack Thickness 7.5

Well Length 11.15

*Top of Screen 6.5 ft.

Screen Length 5

11.15

*Bottom of Screen 1 ft.

Mater. Thickness .5

*Boring Depth 12 ft.

Borehole Diameter 6"

*Measured From Ground Surface

PROTECTIVE CASING
Type At Grade
Vented Yes [✓ No]
Type
Diameter
Locked Yes
Length
Key #

GUARD POSTS

CAP OR PLUG Vented Yes [✓ No] Type EXPANSION

CONCRETE COLLAR
Cement lbs.+Water gal.
Total Quantity gal.
Manufacturer

SEAL
Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated YES gal., Time
Manufacturer 3/8" Baroid Hole Plug

PIPE Type SS Schedule
O.D. 2 " I.D. 1.75 "
Length/Sec. No. of Sec.
Manufacturer

JOINTS Flush Threaded [✓ Yes]/No
Teflon Taped Yes/No O-Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40
Source Red Flint
Volume gal.
Manufacturer Red Flint

SCREEN
Type SS
Schedule
Length/Sec. 5
No. of Sec. 1
O.D. 2 "
I.D. 1.75
Slot Size 0.100
No. Slots/ft.
Manufacturers Johnson
manufactured Bottom Pl

CAP OR PLUG Type Length

MATERIAL Filter Pack/Sluff

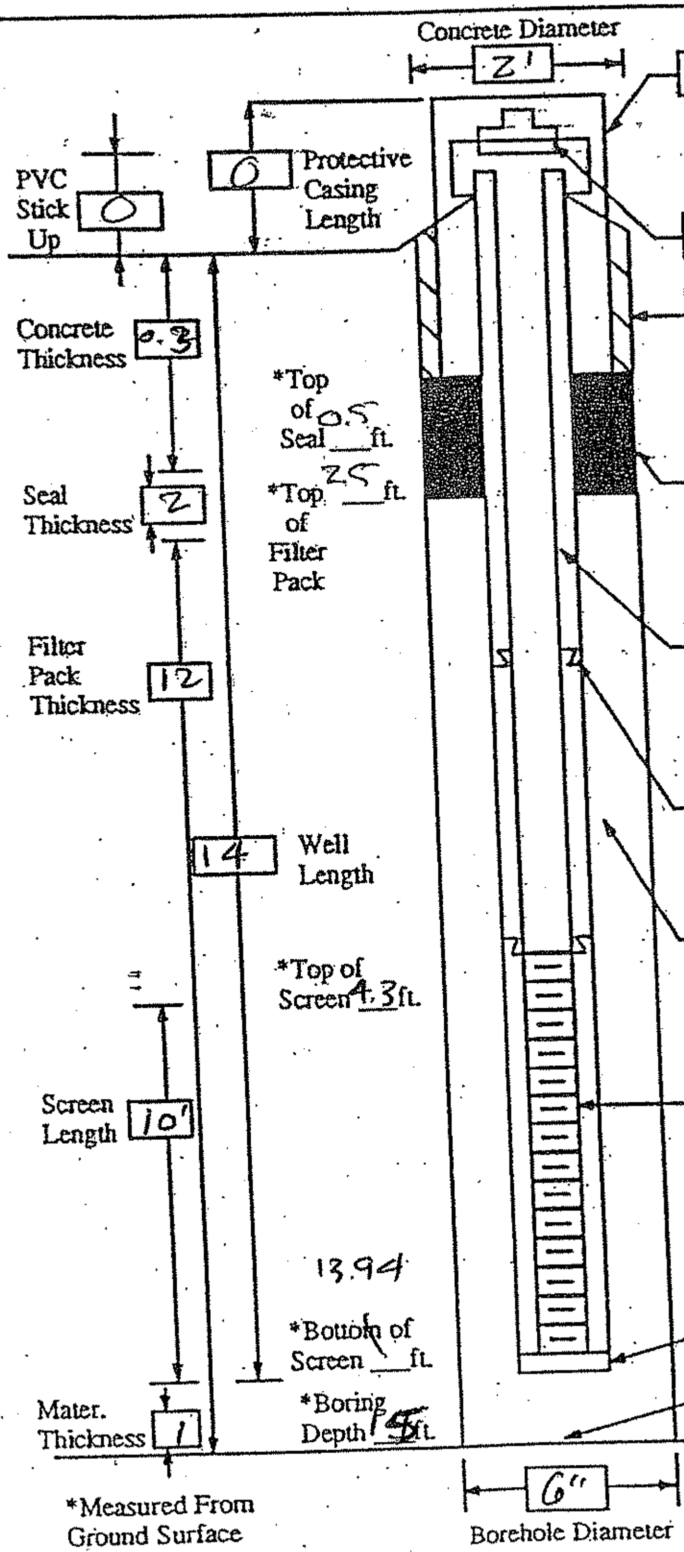
WATER SOURCE
Notes:

EARTH TECH
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: MnDOT - Tire Site
Date: 18 Aug 04
Inspected By: T. Fryzek
Project No. 78969
Well No. MW - 5
Driller/Contractor Boart Longyear



Concrete Diameter 2'
Protective Casing Length 0
PVC Stick Up 0
Concrete Thickness 0.3
*Top of Seal 0.5 ft.
Seal Thickness 2
*Top of Filter Pack 2.5 ft.
Filter Pack Thickness 12
Well Length 14
*Top of Screen 4.3 ft.
Screen Length 10'
13.94
*Bottom of Screen ___ ft.
*Boring Depth 15 ft.
Mater. Thickness 1
Borehole Diameter 6"

*Measured From Ground Surface

PROTECTIVE CASING
Type At Grade
Diameter
Length

GUARD POSTS
Vented Yes/[✓ No] Type
Locked YES
Key #

CAP OR PLUG Vented Yes/[✓ No] Type EXPANSION

CONCRETE COLLAR
Cement ___ lbs.+Water ___ gal.
Total Quantity ___ gal.
Manufacturer

SEAL
Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated YES gal., Time
Manufacturer 3/8" Baroid Hole Plug

PIPE Type SS Schedule
O.D. 2 " I.D. 1.75 "
Length/Sec. ___ No. of Sec.
Manufacturer

JOINTS Flush Threaded [✓ Yes]/No
Teflon Taped Yes/No O-Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40
Source Red Flint
Volume ___ gal.
Manufacturer Red Flint

SCREEN
Type SS Schedule
Length/Sec. 10 No. of Sec. 1
O.D. 2 " I.D. 1.75
Slot Size 0.100 No. Slots/ft.
Manufacturers Johnson
manufactured Bottom Plu

CAP OR PLUG Type ___ Length

MATERIAL filter Pack / Sluff

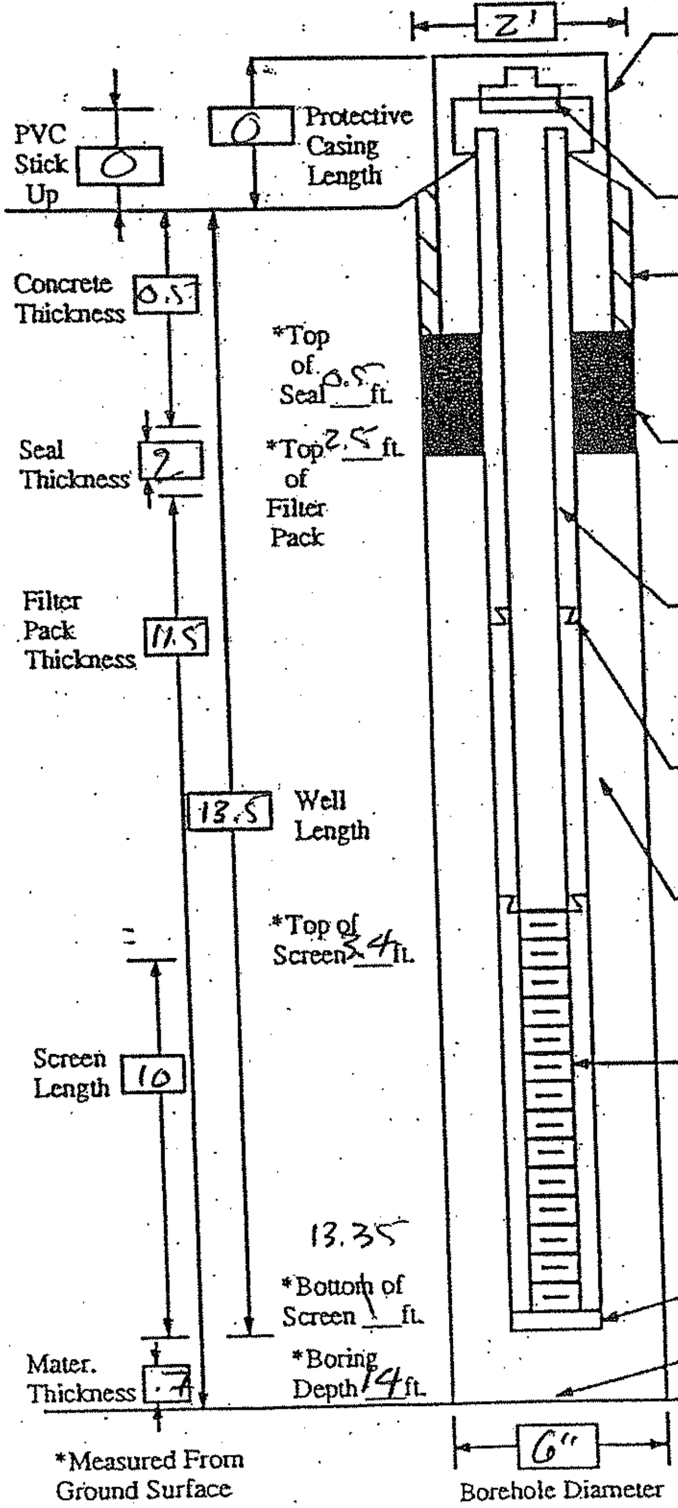
WATER SOURCE
Notes:

EARTH TECH
A tyco INTERNATIONAL LTD. COMPANY

Water Table Well Installation Diagram

Form 101

Site: MnDOT - Tire Site
Date: 18 Aug 04
Inspected By: T. Fryzek
Project No. 78969
Well No. MW - 6
Driller/Contractor Boart Longyear



*Measured From Ground Surface

PROTECTIVE CASING

Type At Grade Vented Yes/[✓ No] YES
Diameter Locked
Length Key #

GUARD POSTS

Type

CAP OR PLUG Vented Yes/[✓ No] Type EXPANSION

CONCRETE COLLAR

Cement ___ lbs.+Water ___ gal.
Total Quantity ___ gal.
Manufacturer

SEAL

Powder/[✓ Granular]/Pellets Quantity 5 gal.
Hydrated YES gal., Time
Manufacturer 3/8" Baroid Hole Plug

PIPE Type SS Schedule
O.D. 2 " I.D. 1.75 "
Length/Sec. No. of Sec.
Manufacturer

JOINTS Flush Threaded [✓ Yes]/No

Teflon Taped Yes/No O-Ring [✓ Yes]/No
Manufacturer Johnson

FILTER PACK Type(s) #40

Source Red Flint
Volume ___ gal.
Manufacturer Red Flint

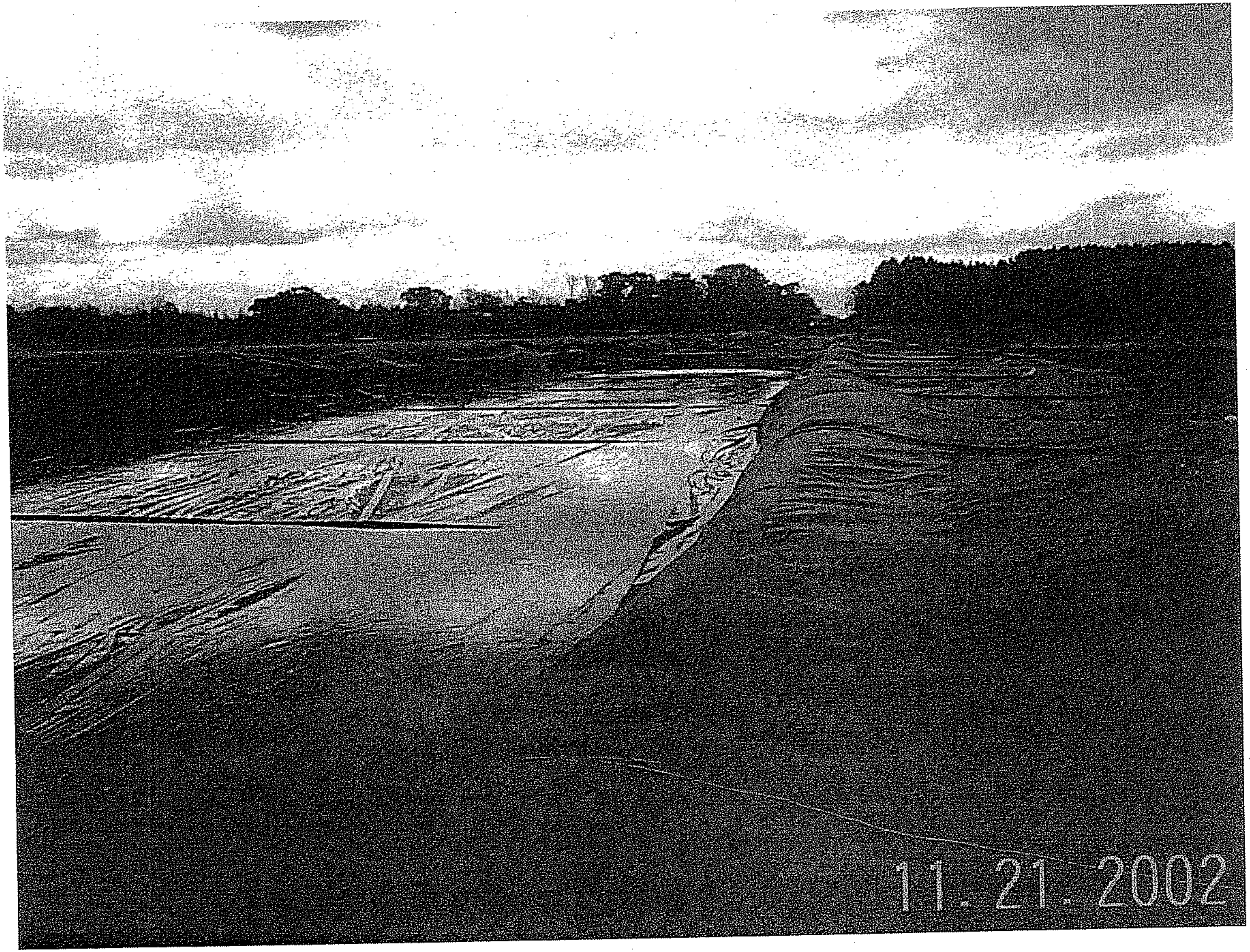
SCREEN

Type SS Schedule
Length/Sec. 10 No. of Sec. 1
O.D. 2 " I.D. 1.75
Slot Size 0.100 No. Slots/ft.
Manufacturers Johnson
manufactured Bottom Plug

CAP OR PLUG Type ___ Length

MATERIAL

WATER SOURCE
Notes: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11. 21. 2002


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APPENDIX B

FIELD DATA, 2006

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
2/6/2006					
Temperature	Celcius	0.3	0.9	0.5	0.7
Dissolved Oxygen	mg/L	9.7	12.3	13.6	11.7
pH	S.U.	6.6	7.2	6.9	7.0
Specific Conductance	uS/cm	406	414	445	424
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
2/13/2006								
Depth to groundwater	Feet	6.6	4.69	5.36	5.25	4.59	6.20	-
Temperature	Celcius	7.5	4.2	8.1	6.3	4.5	7.2	2.5
Dissolved Oxygen	mg/L	2.1	3.0	1.8	1.9	2.2	2.4	13.2
pH	S.U.	7.3	7.5	7.0	7.1	7.7	6.6	7.8
Specific Conductance	uS/cm	862	687	862	849	765	443	420
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
2/17/2006								
Depth to groundwater	Feet	6.65	5.95	5.45	6.55	5.87	6.25	-
Temperature	Celcius	6.8	3.7	5.6	4.7	2.8	6.9	-0.2
Dissolved Oxygen	mg/L	3.0	2.6	2.5	2.9	2.3	2.6	9.9
pH	S.U.	7.4	7.4	7.1	7.2	7.9	6.9	7.1
Specific Conductance	uS/cm	877	708	883	856	729	755	429
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
2/27/2006					
Depth to groundwater	Feet				
Temperature	Celcius	-	2.5	1.6	2.3
Dissolved Oxygen	mg/L	-	14.3	12.3	13.6
pH	S.U.	-	7.8	7.4	7.6
Specific Conductance	uS/cm	-	393	438	407
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
2/27/2006								
Depth to groundwater	Feet	6.68	4.84	5.51	5.41	4.74	6.30	-

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
3/15/2006					
Temperature	Celcius	0.6	3.3	2.5	2.6
Dissolved Oxygen	mg/L	9.3	11.4	12.5	10.2
pH	S.U.	7.2	7.4	7.8	7.3
Specific Conductance	uS/cm	368	399	456	402
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
3/15/2006								
Depth to groundwater	Feet	6.53	4.86	5.41	5.30	4.78	6.16	-

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
3/28/2006					
Temperature	Celcius	10.0	8.8	8.3	8.3
Dissolved Oxygen	mg/L	13.6	10.8	9.8	12.0
pH	S.U.	7.4	7.5	7.5	7.6
Specific Conductance	uS/cm	379	385	467	402
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
3/28/2006								
Depth to groundwater	Feet	6.42	4.81	5.32	5.22	4.72	6.15	-
Temperature	Celcius	7.0	4.6	7.1	6.7	4.4	8.2	8.3
Dissolved Oxygen	mg/L	2.7	6.3	2.3	3.0	1.9	2.2	12.0
pH	S.U.	7.4	7.6	6.8	7.0	7.8	6.8	7.6
Specific Conductance	uS/cm	864	742	816	1096	790	793	402
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
5/8/2006					
Temperature	Celcius	11.7	12.6	12.6	12.6
Dissolved Oxygen	mg/L	8.2	8.3	8.3	9.0
pH	S.U.	7.6	7.7	7.6	7.7
Specific Conductance	uS/cm	392	422	402	418
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
5/8/2006								
Depth to groundwater	Feet	6.11	4.12	4.89	4.78	4.03	5.72	-

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
6/5/2006					
Temperature	Celcius	23.32	21.6	23.8	21.6
Dissolved Oxygen	mg/L	11.4	9.6	13.4	10.3
pH	S.U.	7.57	7.9	8.2	8.0
Specific Conductance	uS/cm	462	408	441	319
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
6/5/2006								
Depth to groundwater	Feet	6.64	4.46	5.46	5.39	4.38	6.35	-

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
6/22/2006					
Temperature	Celcius	16.9	16.5	17.4	16.7
Dissolved Oxygen	mg/L	9.7	6.6	9.7	8.3
pH	S.U.	7.1	7.3	7.3	7.5
Specific Conductance	uS/cm	460	451	445	451
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
6/22/2006								
Depth to groundwater	Feet	6.60	4.53	5.56	5.47	4.45	6.35	-
Temperature	Celcius	12.4	12.3	15.3	12.6	12.1	12.1	-
Dissolved Oxygen	mg/L	1.7	1.6	1.6	1.7	1.5	1.6	-
pH	S.U.	7.2	7.2	6.5	6.8	7.2	6.2	-
Specific Conductance	uS/cm	921	1046	1397	1331	1093	1266	-
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
9/25/2006					
Temperature	Celcius	11.9	10.2	-	-
Dissolved Oxygen	mg/L	NA	7.3	-	-
pH	S.U.	7.4	7.3	-	-
Specific Conductance	uS/cm	448	418	-	-
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
9/25/2006								
Depth to groundwater	Feet	6.73	4.51	5.23	5.14	4.41	6.11	-
Temperature	Celcius	16.2	14.1	18.4	16.0	16.3	13.6	13.3
Dissolved Oxygen	mg/L	3.0	1.8	1.5	1.5	2.1	NA	NA
pH	S.U.	7.1	7.0	6.6	6.5	7.0	6.6	7.4
Specific Conductance	uS/cm	981	1115	1103	1180	1116	1010	446
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
9/26/2006					
Temperature	Celcius	-	15.5	-	15.5
Dissolved Oxygen	mg/L	-	6.3	-	5.5
pH	S.U.	-	7.3	-	7.5
Specific Conductance	uS/cm	-	436	-	436
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
9/26/2006								
Depth to groundwater	Feet	6.76	4.51	5.23	5.14	4.41	6.09	-
Temperature	Celcius	16.7	14.4	16.7	16.3	16.7	14.2	15.6
Dissolved Oxygen	mg/L	3.0	1.7	2.6	1.7	1.4	1.9	5.8
pH	S.U.	7.2	7.1	6.5	6.7	7.0	6.6	7.5
Specific Conductance	uS/cm	1007	1059	1165	1222	1097	1050	432
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
9/29/2006					
Temperature	Celcius	-	8.9	-	9.0
Dissolved Oxygen	mg/L	-	5.6	-	5.7
pH	S.U.	-	7.3	-	7.4
Specific Conductance	uS/cm	-	411	-	439
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
9/29/2006								
Depth to groundwater	Feet	6.82	4.51	5.28	5.19	4.42	6.14	-
Temperature	Celcius	15.7	13.5	17.6	15.2	15.5	13.2	9.0
Dissolved Oxygen	mg/L	2.5	2.0	2.4	1.5	1.4	1.8	5.8
pH	S.U.	7.1	7.0	6.5	6.6	7.0	6.5	7.4
Specific Conductance	uS/cm	927	1107	1173	1191	1090	1108	419
(1 uS/cm = 1 umhos/cm)								

Field Parameters 11/16/2006	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
Temperature	Celcius	-	3.3	-	5.0
Dissolved Oxygen	mg/L	-	10.1	-	9.1
pH	S.U.	-	7.2	-	7.5
Specific Conductance (1 uS/cm = 1 umhos/cm)	uS/cm	-	416	-	444

Field Parameters 11/16/2006	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
Depth to groundwater	Feet	6.99	4.80	5.75	5.63	4.72	6.65	-
Temperature	Celcius	12.4	10.5	14.0	11.9	10.8	11.6	4.5
Dissolved Oxygen	mg/L	2.6	2.2	1.9	2.4	2.2	2.5	7.3
pH	S.U.	7.1	6.8	6.5	6.6	6.8	6.5	7.5
Specific Conductance (1 uS/cm = 1 umhos/cm)	uS/cm	1022	1033	1113	1134	1066	815	417

APPENDIX C

SAMPLING PROTOCOL, GROUNDWATER MONITORING WELLS

TABLE OF CONTENTS

MINNESOTA DEPARTMENT OF TRANSPORTATION
SAMPLING PROTOCOL FOR GROUND WATER MONITORING WELLS

1.0 INTRODUCTION

This document defines procedures to be used for ground water quality measurements and for collecting and handling ground water samples obtained from monitoring wells at the Shredded Tire Roadway Study Site during the time period of 2004 to 2007. Deviations from these procedures may be required by unforeseen circumstances that develop during the program. Such deviations will be approved by the Principal Investigator or the field crew leader as described below. When approvals cannot be obtained in advance, deviations from the established procedures will be evaluated as soon as possible after sampling and the need for re-sampling will be evaluated. Deviations from the specified procedures will be clearly noted on the field sampling sheet used for the sampling of each well.

2.0 ADVANCE PREPARATION FOR SAMPLING

The order of sampling wells, laboratory arrangements, field measurement and sampling techniques, equipment selection and other quality assurance measures are based upon standards used throughout the industry, and were approved by the Principal Investigator.

2.1 Selection of Analytical Parameters

Analytical parameters were selected based on possible contamination released from vehicle tires.

2.2 Quality Assurance for Field Procedures

Particular care will be exercised to avoid the following common ways in which cross contamination or background contamination may compromise ground water samples:

- improper storage or transportation of equipment
- contaminating the equipment or sample bottles on site by setting them on or near potential contamination sources such as uncovered ground, a contaminated vehicle, or vehicle exhaust
- handling bottles or equipment with dirty hands or gloves
- inadequate cleaning of well purging or sampling devices

Special care will be exercised to prevent cross-contamination of sampling equipment, sampling bottles, or anything else that could potentially compromise the integrity of samples. Field methods quality assurance verification procedures are described below in Section 4.4, “Field Blanks and Duplicates”. Field personnel will work under the assumption that contamination exists in land surface soil and vegetation near sampling points, wash water, etc. Therefore, exposure to these media will be minimized by taking at least the following precautions:

- minimizing the amount of rinse water left on washed materials
- minimizing the time sampling containers are exposed to airborne dust or volatile contaminants in ambient air
- placing equipment on clean, ground-covering materials instead of on the land surface

Clean gloves made of appropriately inert material will be worn by the sampler. Gloves will be kept clean while handling sampling-related materials. New gloves will be used when soiled and between each sampling site.

2.3 Purging and Sampling Equipment

Well purging and sampling equipment includes the following:

- Accuwell PTP-100 Peristaltic pump
- pump discharge lines: new, decontaminated Teflon® tubing
- Forestry Suppliers Single Sample disposable Bailers, rope, VOC adaptor

2.4 Decontamination, Storage and Transport of Equipment

New pump tubing will be used the first time each well is sampled. Tubing will be dedicated to a single well for subsequent sampling events. Between sampling events, the tubing will be stored in a sealed, plastic bag. The bag will be labeled with the well name and stored in a secure, clean location. All sampling-related equipment including filtration devices, personal protection gear and materials coming into contact with actual sampling equipment or with sampling personnel will be decontaminated. Decontamination will be performed before, between and after working at each sampling point. All equipment will be handled in a manner that will minimize cross-contamination between wells and avoid introducing surface or ambient air contamination into a well. Equipment used during purging or sampling will be thoroughly cleaned prior to use in each individual well. After cleaning, the equipment will be visibly inspected to detect sticky residues or other substances that may survive normal cleaning. If inspection reveals that decontamination was insufficient, additional measures will be implemented as needed and documented, (i.e., additional cleaning, equipment replacement, etc.).

Before mobilizing for field work or performing any decontamination, a source of “control” water and organic-free reagent grade deionized water for decontamination will be selected and evaluated. The evaluation process will include sufficient laboratory analysis to assess the suitability of the proposed water. The proposed decontamination water will only be used for decontamination if analyses indicate it is appropriate for the complete set of project analytical parameters. Equipment that does not contact sample water or the inside of the well shall be rinsed with normal deionized water.

The internal surfaces of pumps and tubing that cannot be adequately cleaned by the above methods alone will also be cleaned by circulating decontamination fluids through them. Special care will be exercised to ensure that the “rinse” fluids will be circulated in sufficient quantities to completely flush out contaminants, detergents and desorbing agents.

When transporting or storing equipment after cleaning, the equipment will be protected in a manner that minimizes the potential for contamination. The tubing will be placed in a clean, plastic bag.

3.0 PRELIMINARY FIELD WORK

The following procedures will be implemented to ensure representativeness of samples collected by methods in Section 4, “Sample Collection”.

3.1 Field Inspections and Field Decisions

Before purging or sampling, all wells will be inspected to verify well depth and that the annular seal is intact at the surface. In addition, the condition of any relevant facts regarding the general physical condition of the well, the surrounding soil and vegetation or other objects in the immediate vicinity of the well will be inspected. Any unusual condition including the presence of wind-blown dust or odor in the ambient air will be recorded on the Field Sampling Sheet. If any condition that may interfere with obtaining representative analytical results is discovered, the condition will be rectified before proceeding with the sampling of the dissolved phase of well water.

3.2 Water-Level Measurements

A water level measurement will be taken immediately before purging at each well and will be taken immediately after sampling. These water levels will be entered on the Sampling Field Sheet.

Water level probes will be decontaminated by triple-rinsing with clean control water. The electric water-level sensor probe will be lowered down the well until the tone sounds indicating contact of the probe with the water surface.

The depth-to-water will be referenced to the measuring point at the top of the well casing.

3.3 Field Water Quality Measurements

Specific conductance, pH, temperature and dissolved oxygen will be measured in the field immediately before sample collection. Calibration information will be recorded on the Hydrolab Calibration Form and all measurements will be recorded on the Field Sampling Sheet.

General care, maintenance, calibration procedures, and operation of each measurement device will follow manufacturer's specifications as detailed in the instruction/owner's manual for each device.

Specific Conductance

Temperature

pH

Dissolved Oxygen

3.4 Well Purging and Stabilization

Only wells that were properly installed and developed at least two weeks in advance will be sampled. Before a well is sampled for the dissolved phase, it will be evacuated to ensure that samples contain fresh formation water. While the well is being purged, water quality parameters described above in Section 3.3, "Field Water-Quality Measurements", and the quantity of water evacuated will be recorded on the Field Sampling Sheet. Wells that do not have extremely slow recharge rates will be purged and sampled as described below. Purging will be conducted in a manner that, to the extent practical, removes all the "old" water in the well so it is replaced by fresh ground water from outside the well installation.

1. The well will be purged by withdrawing water from within two feet of the top of the water column.
2. Repeated vertical adjustment of the purging equipment intake may be necessary as the water level drops.
3. Sampling will immediately follow purging.
4. The same pump will be used for both purging and sampling at each individual well.

Samples for laboratory analysis will be collected only after a minimum of three water-column volumes have been purged. (Our general practice is to purge five water-column volumes.)

4.0 SAMPLE COLLECTION

This section describes procedures for setting the sampling pump and collecting ground water samples. Field data for these items will be recorded on the Field Sampling Sheet for each sampling point.

4.1 Pump Setting

The same pump will be used for sampling as was used for purging. Pumping will be continuous and sampling will immediately follow purging. If pumping is not continuous it will be noted on the Field Sampling Sheet. The sample collection pumping rate will be less than or equal to the purging rate. Any final rinse water remaining in any portion of the sampling pump or discharge lines will be completely purged with fresh well water before filling sampling containers. To insure this, at least two tubing-volumes will be purged from discharge lines before sample collection begins.

4.2 Sample Filtration

Sample filtration will be completed for dissolved metals and will be conducted as follows:

1. The filter holder and new filter will be thoroughly pre-rinsed with laboratory-controlled deionized or distilled water before use.
2. The new filters will be flushed with fresh sample water a minimum of two minutes before collecting samples.
3. The filter will be connected directly to the well sampling pump discharge line using positive pressure to force the sample through the filter.
4. From the filter, the flow will be routed directly into the sample collection container.
5. A 0.45 micron pore size filter will be used.
6. Agitation and aeration of the sample will be minimized.
7. Teflon® tubing will be used for the pump and filter discharge lines.

4.3 Filling Sample Containers

Individually prepared bottles will not be opened until they are to be filled with water samples. Special care will be taken to ensure that the procedures listed below are followed:

1. The area surrounding the wellhead will be kept as clean as practical to minimize the potential for contamination of samples.
2. Care will be exercised to minimize the potential for airborne contamination of sample water during collection. If vehicles or generators are left running during sample collection, containers will be filled upwind from engine exhaust sources. If conditions are dusty, an effort will be made to shield the sample collection area from windborne contamination.
3. A clean and dry sheet of relatively inert plastic shall be placed on the ground surface or a portable table shall be used at the site. If materials used in the sampling process must be put down, they will be placed on a clean portion of the plastic sheet or the table surface.
4. A clean pair of nitrile gloves will be worn at the onset of sampling activities at each new sampling point.
5. Sampling personnel will keep their hands as clean as practical and replace gloves if they become soiled while performing sampling activities.
6. Sampling personnel will not touch the inside of sampling containers, inside of bottle caps or rim of sample containers. If contact occurs, sample containers will be replaced.

Methods for filling sample containers for individual analyses are described below.

The sample water discharge point at the end of the tube will be held as close as possible to the sample container without allowing the sample tubing to contact the container. When necessary, sampling personnel will use their body to shield the sampling container from wind and airborne dust while filling. When strong winds, heavy rain, or dusty conditions are present, additional measures will be implemented to guard against background interference.

Volatile Organics

Forty ml (milliliter) purge and trap vials will be filled in a manner that minimizes turbulence, entrapment of air and overfilling. They will not be rinsed in the field but will be completely filled in a manner that leaves a positive meniscus at the top of the vial.

Hydrochloric acid prepared specifically for volatile organics analysis by the laboratory will be used to preserve samples. The acid will be added to vials at the laboratory in advance of sampling. Extra caution will be exercised to minimize overfilling.

4.4 Field Blanks and Duplicates

Sample blanks, will be collected to detect background or method contamination. Duplicate samples will be collected to evaluate variability in analytical methods. All QA/QC samples will be collected in the same type of container as the corresponding primary samples. The identity of the QA/QC samples will be recorded on the Field Sampling Sheet.

The collection schedule for QA/QC samples will be as follows:

1. One trip blank (composed of three replicate vials) for each cooler of VOC samples.
2. One field equipment blank for each sampling event.
3. One field ambient air blank for each sampling event.
4. Duplicates: all analytical parameters.

Field Blank Samples

Methods that will be used for preparing field blank samples are described below.

Trip blanks for VOCs will be filled and sealed by the primary volatile organics analytical laboratory with laboratory-controlled, HPLC-grade, organic-free water. The set of three pre-dilled 40 ml, purge and trap, blank sample vials will travel with the actual sample vials to and from the field in the cooler, to the well head, etc., so that the blanks are exposed to precisely the same conditions as the actual samples. The bottle blanks will not be opened until they are analyzed in the laboratory along with the actual VOC samples they have accompanied.

Field equipment/methods blanks will be collected in the field for all parameters, VOCs and non-volatile organics. Sample containers used for each blank will be the same as for the actual analysis of sample water for these parameter groups. All containers shall be pre-cleaned within the laboratory's QA/QC program in the same manner as primary sample bottles. The sample blank containers will be filled in the field. Laboratory-controlled, ultra pure, organic-free water will be used to fill all organic blank samples.

Field ambient air blanks will be filled in the field. VOC vials will be filled with laboratory-controlled, HPLC-grade, organic-free water. Trace metal containers will be filled with laboratory-prepared, triple distilled water. Containers will be opened and placed or held as closely as practical to the point (vertical positioning will be respected) at which actual sample containers are opened and filled. The sample blank containers will be filled with the ultra pure water by the same personnel and at approximately the same time as the primary (actual) samples are being collected. The sample blank water in each container will be exposed to the air on site for an amount of time equivalent to that for filling and closing a primary sample container.

Field duplicate samples One field duplicate sample set will be collected during each sampling event. Duplicate samples of actual ground water will be collected for each parameter following previously noted procedures. Sample blank water will be pumped through the sample tubing by the sampling pump and into the sample blank containers. Blanks for filtered samples will be collected by passing the blank sample water through the filtration device and the same type of filters used for collecting the primary samples.

5.0 DOCUMENTATION OF SAMPLING EVENT

This sampling protocol includes the use of Field Sampling Sheets and Chain of Custody forms; they are designed for documentation of field activities and collection of field data. They also provide a means to verify whether or not this protocol was followed during a number of key steps in the ground water sampling event.

5.1 Sample Identification

The COC (Chain of Custody) will be at least a two-part form. When samples are transferred to an analytical laboratory, the laboratory will receive only the laboratory part(s) of the form.

Each COC will contain a unique record number printed in the upper margin on the right side of the form. The container's row # appended to the record # on the form uniquely identifies each sample container (unique container ID #). In the case of a multi-container set, such as a set of three associated VOC vials - the set is uniquely identified.

Each sample container will be labeled with the following information using a waterproof marker on firmly affixed, water-resistant labels:

- unique container ID #
- sample collection date
- sample collection time
- initials of person collecting sample
- analyses required
- preservation method

5.2 Chain Of Custody

A COC record will be initiated in the field at the time of sampling; a copy will accompany each set of samples (cooler) shipped to any laboratory.

Each time responsibility for custody of the samples changes, the new and previous custodians will sign the record and denote the date and time. A copy of the signed record will be made by the receiving laboratory. The final signed COC will be submitted with analytical results in the Sampling and Analysis Report.

Chain of Custody Documentation

All signatures related to sample custody will be made in ink on the COC in a timely fashion. One or more signatures will be entered to identify the person or persons who are collecting the samples. Each time the custody of a sample or group of samples is transferred, a signature, date and time will be entered to document the transfer. The signatures, date and time will be entered at the time of transfer; the row # will be used to define which bottles were transferred. A sample will be considered to be in custody if it is in any one of the following states:

1. in actual physical possession
2. in view, after being in physical possession
3. in physical possession and locked up so that no one can tamper with it
4. in a secured area, restricted to authorized personnel

Pre-study briefings will be held to apprise participants of the objectives, sample locations, and COC procedures to be followed. After samples are collected under COC tracking, a de-briefing will be held in the field to verify the adherence to the COC procedures and to determine whether additional samples are required.

5.3 Field Conditions

Field conditions during the sampling event will be recorded on the Field Sampling Sheet. The Field Sampling Sheet will include a statement regarding the likelihood that any unusual field conditions had a significant impact on the integrity of results. Field conditions reported will include but not be limited to the following:

- air temperature
- wind speed and direction
- precipitation/moisture
- ambient odors
- airborne dust

6.0 SAMPLE PRESERVATION, HANDLING AND TRANSPORT

This section describes procedures that will be followed between the time samples are collected and the time they are either shipped or delivered to an analytical laboratory.

6.1 Sample Preservation

All samples will be thermally preserved in the field immediately after sample collection by placing the samples in an insulated coolers containing ice.

6.2 Sample Handling and Transport

All coolers shipped will be accompanied by a COC form. The samples will be kept at approximately 4 degrees Celsius during transport to laboratories. Before transporting samples, field personnel will perform the following tasks:

1. Verify that laboratory personnel understand and maintain COC and sample storage/preservation requirements.
2. Check labeling and documentation to ensure sample identity will be clear to laboratory personnel.
3. Hand deliver or ship samples in a manner that ensures samples will remain cool (about 4 degrees Celsius) until received by laboratory personnel.

References

Minnesota Pollution Control Agency. "MPCA Ground Water Sampling Guidance Document, Example Sampling Protocol". MPCA Water Quality Division. St. Paul, Minnesota. March, 1997.

Minnesota Department of Transportation. "Water Quality Procedures Manual". Minnesota Department of Transportation Water Quality Unit. St. Paul, Minnesota. April, 1990.

APPENDIX D

QUALITY ASSURANCE:
BLANKS, DUPLICATES, SPIKES, 2006

FIELD BLANKS

	Units	Field Blank 09/26/06	Field Blank 11/16/06	MDL	RL
Chemical Oxygen Demand (COD)	mg/L	<25	<25	4	20
Total Suspended Solids (TSS)	mg/L	<10	<10	2	20
Alkalinity	mg/L	<10			
Ammonia	mg/L	<10	<0.05		
Total Organic Carbon	mg/L	<15	<15		
DRO	ug/L	NA	NA	28	160
DRO with Silica Gel Clean Up	ug/L	NA	NA		
GRO	ug/L	NA	<30	17	85
Bromobenzene (GRO Surrogate)	%	NA	97.5		
Aluminum	ug/L			50	300
Antimony	ug/L	<250		0.4	2
Arsenic	ug/L			1	5
Barium	ug/L	<10	<10	2	10
Cadmium	ug/L			0.2	1
Chromium (total)	ug/L			4	20
Copper	ug/L	<50		10	50
Iron	ug/L	<50	10	10	50
Lead	ug/L			0.4	2
Manganese	ug/L	<25	<25	5	25
Nickel	ug/L			2	10
Selenium	ug/L			5	25
Zinc	ug/L	10	6	0.1	0.5

NA=Not analyzed.

Polynuclear Aromatic Hydrocarbons

	Units	Field Blank 09/26/06	Field Blank 11/16/06	MDL	RL
Acenaphthene	ug/L	ND	ND	0.010	0.050
Acenaphthylene	ug/L	ND	ND	0.010	0.050
Anthracene	ug/L	ND	ND	0.010	0.050
Benzo(a)anthracene	ug/L	ND	ND	0.010	0.050
Benzo(a)pyrene	ug/L	ND	ND	0.010	0.050
Benzo(e)pyrene	ug/L	ND	ND	0.010	0.050
Benzo(g,h,i)perylene	ug/L	ND	ND	0.010	0.050
Benzofluoranthenes (Total)	ug/L	ND	ND	0.03	0.15
Carbazole	ug/L	ND	ND	0.010	0.050
2-Chloronaphthalene	ug/L	ND	ND	0.010	0.050
Chrysene	ug/L	ND	ND	0.010	0.050
Dibenz(a,h)acridine	ug/L	ND	ND	0.010	0.050
Dibenz(a,h)anthracene	ug/L	ND	ND	0.010	0.050
Dibenz(a,j)acridine	ug/L	ND	ND	0.010	0.050
Dibenzo(a,e)pyrene	ug/L	ND	ND	0.010	0.050
Dibenzo(a,h)pyrene	ug/L	ND	ND	0.010	0.050
Dibenzo(a,I)pyrene	ug/L	ND	ND	0.010	0.050
Dibenzo(a,l)pyrene	ug/L	ND	ND	0.010	0.050
7H-Dibenzo(c,g)carbazole	ug/L	ND	ND	0.010	0.050
Dibenzofuran	ug/L	ND	ND	0.010	0.050
7,12-Dimethylbenz(a)anthracene	ug/L	ND	ND	0.010	0.050
1,6-Dinitropyrene	ug/L	ND	ND	0.24	1.2
1,8-Dinitropyrene	ug/L	ND	ND	0.20	1.2
Fluoranthene	ug/L	ND	ND	0.010	0.050
Fluorene	ug/L	ND	ND	0.010	0.050
Indeno(1,2,3-cd)pyrene	ug/L	ND	ND	0.010	0.050
3-Methylcholanthrene	ug/L	ND	ND	0.010	0.050
5-Methylchrysene	ug/L	ND	ND	0.010	0.050
1-Methylnaphthalene	ug/L	ND	ND	0.010	0.050
2-Methylnaphthalene	ug/L	ND	ND	0.010	0.050
Naphthalene	ug/L	ND	ND	0.010	0.050
5-Nitroacenaphthene	ug/L	ND	ND	0.010	0.050
6-Nitrochrysene	ug/L	ND	ND	0.010	0.050
2-Nitrofluorene	ug/L	ND	ND	0.010	0.050
1-Nitropyrene	ug/L	ND	ND	0.010	0.050
4-Nitropyrene	ug/L	ND	ND	0.010	0.050
Perylene	ug/L	ND	ND	0.010	0.050
Phenanthrene	ug/L	ND	ND	0.010	0.050
Pyrene	ug/L	ND	ND	0.010	0.050
Nitrobenzene-d5 (S)		71%	63%		
2-Fluorobiphenyl (S)		78%	73%		
Terphenyl-d14 (S)		92%	95%		

ND = Not detected.

TOTAL COMPDS. DETECTED		0	0		

DUPLICATE ANALYSES

PARAMETER	Units	Well 5 09/26/06	Well 5 Dup. 09/26/06	RPD	Culvert 11/16/06	Culvert Dup. 11/16/06	RPD
Chemical Oxygen Demand (COD)	mg/L	240	230	4%	20	240	169%
Total Suspended Solids (TSS)	mg/L	26	27	4%		13	100%
Alkalinity	mg/L	170	170	0%			
Ammonia-N	mg/L	10	10	0%	0.14	0.16	13%
Total Organic Carbon	mg/L	64	63	2%	5	73	174%
GRO	ug/L	82	NA		<30	<30	
Bromobenzene (GRO Surrogate)	%	98.6			97.6	100	
Aluminum	ug/L						
Antimony	ug/L	<250	<250				
Arsenic	ug/L						
Barium	ug/L	250	290	15%	62	60	3%
Cadmium	ug/L						
Chromium (total)	ug/L						
Copper	ug/L	<50	<50				
Iron	ug/L	14000	16000	13%	1100	1100	0%
Lead	ug/L						
Manganese	ug/L	150	160	6%	260	260	0%
Nickel	ug/L						
Selenium	ug/L						
Zinc	ug/L	20	20	0%	9	9	0%

DUPLICATES

Polynuclear Aromatic Hydrocarbons

	Units	Well 5 09/26/06	Well 5 Dup. 09/26/06	RPD	Culvert 11/16/2006	Dupl. 11/16/2006	RPD
Acenaphthene	ug/L	ND	ND		ND	ND	
Acenaphthylene	ug/L	ND	ND		ND	ND	
Anthracene	ug/L	ND	ND		ND	ND	
Benzo(a)anthracene	ug/L	ND	ND		ND	ND	
Benzo(a)pyrene	ug/L	ND	ND		ND	ND	
Benzo(e)pyrene	ug/L	ND	ND		ND	ND	
Benzo(g,h,i)perylene	ug/L	ND	ND		ND	ND	
Benzofluoranthenes (Total)	ug/L	ND	ND		ND	ND	
Carbazole	ug/L	ND	ND		ND	ND	
2-Chloronaphthalene	ug/L	ND	ND		ND	ND	
Chrysene	ug/L	ND	ND		ND	ND	
Dibenz(a,h)acridine	ug/L	ND	ND		ND	ND	
Dibenz(a,h)anthracene	ug/L	ND	ND		ND	ND	
Dibenz(a,j)acridine	ug/L	ND	ND		ND	ND	
Dibenzo(a,e)pyrene	ug/L	ND	ND		ND	ND	
Dibenzo(a,h)pyrene	ug/L	ND	ND		ND	ND	
Dibenzo(a,I)pyrene	ug/L	ND	ND		ND	ND	
Dibenzo(a,l)pyrene	ug/L	ND	ND		ND	ND	
7H-Dibenzo(c,g)carbazole	ug/L	ND	ND		ND	ND	
Dibenzofuran	ug/L	ND	ND		ND	ND	
7,12-Dimethylbenz(a)anthracene	ug/L	ND	ND		ND	ND	
1,6-Dinitropyrene	ug/L	ND	ND		ND	ND	
1,8-Dinitropyrene	ug/L	ND	ND		ND	ND	
Fluoranthene	ug/L	0.089	0.10	12%	ND	ND	
Fluorene	ug/L	ND	ND		ND	ND	
Indeno(1,2,3-cd)pyrene	ug/L	ND	ND		ND	ND	
3-Methylcholanthrene	ug/L	ND	ND		ND	ND	
5-Methylchrysene	ug/L	ND	ND		ND	ND	
1-Methylnaphthalene	ug/L	ND	ND		ND	ND	
2-Methylnaphthalene	ug/L	0.29	0.35	19%	ND	ND	
Naphthalene	ug/L	0.37	0.45	20%	0.042	0.045	7%
5-Nitroacenaphthene	ug/L	ND	ND		ND	ND	
6-Nitrochrysene	ug/L	ND	ND		ND	ND	
2-Nitrofluorene	ug/L	ND	ND		ND	ND	
1-Nitropyrene	ug/L	ND	ND		ND	ND	
4-Nitropyrene	ug/L	ND	ND		ND	ND	
Perylene	ug/L	ND	ND		ND	ND	
Phenanthrene	ug/L	0.13	0.14	7%	ND	ND	
Pyrene	ug/L	0.11	0.11	0%	ND	ND	
Nitrobenzene-d5 (S)		84%	85%	1%	60%	72%	18%
2-Fluorobiphenyl (S)		346%	93%	115%	67%	76%	13%
Terphenyl-d14 (S)		89%	92%	3%	81%	85%	5%

Tire Organic Chemicals

	Units	Well 5 09/26/06	Well 5 Dup. 09/26/06	RPD	Well 5 11/16/2006	Well 5 Dup. 11/16/2006	RPD
Aniline	ug/L	230	210	9%	190	290	42%
Benzoic Acid	ug/L	<10	<10		<11	<11	
Carbazole	ug/L	<10	<10		<11	<11	
2-Hydroxybenzothiozole (TIC)	ug/L	1300	1200	8%	1500	1500	0%
4(1-Methyl-1-phenylethyl)phenol (TIC)	ug/L	ND	ND		ND	ND	
4(2-Benzothiozolythio)-morpholine (TIC)	ug/L	ND	ND		ND	ND	
4-Acetylmorpholine (TIC)	ug/L	24	22	9%	20	18	11%
Benzothiozole (TIC)	ug/L	21	19	10%	17	22	26%

Polynuclear Aromatic Hydrocarbons

9/26/2006

PARAMETER

Surrogate Recoveries	OG 1 % Rec.	OG 2 % Rec.	OG 3 % Rec.	OG 4 % Rec.	OG 5 % Rec.	OG 6 % Rec.
Nitrobenzene-d5	68	87	83	85	84	74
2-Fluorobiphenyl	69	86	89	90	346*	76
Terphenyl-d14	91	64	84	89	89	80

	Culvert % Rec.	North Ditch % Rec.	South Ditch % Rec.	Field Dup. % Rec.	Field Blank % Rec.
Nitrobenzene-d5	73	78	83	85	71
2-Fluorobiphenyl	75	74	86	93	78
Terphenyl-d14	91	78	96	92	92

* = Outlier

9/26/2006

Laboratory Control Spikes

		LCS 11/16/06	LCSD 11/16/06	Mean	Std Dev
Acenaphthene	% Rec.	85	84	85	0.7
Acenaphthylene	% Rec.	103	105	104	1.4
Anthracene	% Rec.	100	103	102	2.1
Benzo(a)anthracene	% Rec.	104	108	106	2.8
Benzo(a)pyrene	% Rec.	99	102	101	2.1
Benzo(e)pyrene	% Rec.	99	103	101	2.8
Benzo(g,h,i)perylene	% Rec.	103	106	105	2.1
Benzofluoranthenes (Total)	% Rec.	99	101	100	1.4
Carbazole	% Rec.	101	103	102	1.4
2-Chloronaphthalene	% Rec.	77	75	76	1.4
Chrysene	% Rec.	123	126	125	2.1
Dibenz(a,h)acridine	% Rec.	103	106	105	2.1
Dibenz(a,h)anthracene	% Rec.	102	108	105	4.2
Dibenz(a,j)acridine	% Rec.	83	86	85	2.1
Dibenzo(a,e)pyrene	% Rec.	80	83	82	2.1
Dibenzo(a,h)pyrene	% Rec.	85	89	87	2.8
Dibenzo(a,I)pyrene	% Rec.	65	74	70	6.4
Dibenzo(a,l)pyrene	% Rec.	83	84	84	0.7
7H-Dibenzo(c,g)carbazole	% Rec.	100	103	102	2.1
Dibenzofuran	% Rec.	106	110	108	2.8
7,12-Dimethylbenz(a)anthracene	% Rec.	92	92	92	0.0
1,6-Dinitropyrene	% Rec.	0	0	0	0.0
1,8-Dinitropyrene	% Rec.	0	0	0	0.0
Fluoranthene	% Rec.	90	92	91	1.4
Fluorene	% Rec.	100	103	102	2.1
Indeno(1,2,3-cd)pyrene	% Rec.	85	81	83	2.8
3-Methylcholanthrene	% Rec.	99	99	99	0.0
5-Methylchrysene	% Rec.	102	104	103	1.4
1-Methylnaphthalene	% Rec.	80	78	79	1.4
2-Methylnaphthalene	% Rec.	79	76	78	2.1
Naphthalene	% Rec.	93	96	95	2.1
5-Nitroacenaphthene	% Rec.	95	100	98	3.5
6-Nitrochrysene	% Rec.	64	71	68	4.9
2-Nitrofluorene	% Rec.	93	97	95	2.8
1-Nitropyrene	% Rec.	60	64	62	2.8
4-Nitropyrene	% Rec.	76	80	78	2.8
Perylene	% Rec.	95	97	96	1.4
Phenanthrene	% Rec.	105	107	106	1.4
Pyrene	% Rec.	70	73	72	2.1

Tire Related SVOC

2/13/2006 NO DUPLICATE SAMPLE OR FIELD BLANK

PARAMETER

Surrogate Recoveries	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	73.6	74.3	84.1	77.7	80.4	84.9	81.5
2-Fluorobiphenyl	69.1	36.1	68.5	64.2	38.6	78.3	73.5
2-Fluorophenol	60.5	49.8	70.3	65.5	58.8	65.9	53.1
Nitrobenzene-d5	69.6	74.5	76.3	74.2	78.6	78.5	74.1
Phenol-d5	55.8	57.9	64.9	57.1	64.4	60.3	47.1
Terphenyl-d5	69.9	40.9	70.5	64.4	44.2	78.7	81.2

	Batch Blank	LCS	Matrix Spk	MSD
	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	81.1	77.3	78.8	76.6
2-Fluorobiphenyl	65.8	70.0	72.7	72.7
2-Fluorophenol	67.8	65.2	61.5	54.1
Nitrobenzene-d5	75.5	74.8	74.7	73.3
Phenol-d5	62.6	59.3	57.0	44.7
Terphenyl-d5	77.5	74.4	74.7	72.3
	71.7	70.2	69.9	65.6

2/13/2006

PARAMETER Laboratory Control Spikes	% Rec.
1,2,4-Trichlorobenzene	57.0
1,4-Dichlorobenzene	48.4
2,4-Dinitrotoluene	72.9
2-Chlorophenol	71.9
4-Chloro-3-methylphenol	76.9
4-Nitrophenol	78.9
Acenaphthene	71.6
N-Nitrosodi-n-propylamine	72.0
Pentachlorophenol	79.6
Phenol	62.9
Pyrene	76.5

2/13/2006

PARAMETER Matrix Spike	% Rec.	% Rec.
1,2,4-Trichlorobenzene	66.2	66.8
1,4-Dichlorobenzene	60.2	61.1
2,4-Dinitrotoluene	64.7	66.2
2-Chlorophenol	69.2	65.5
4-Chloro-3-methylphenol	61.2	60.3
4-Nitrophenol	74.5	81.0
Acenaphthene	72.6	72.2
N-Nitrosodi-n-propylamine	69.8	69.3
Pentachlorophenol	76.7	75.5
Phenol	57.4	49.4
Pyrene	57.2	55.9

3/28/2006

PARAMETER

Surrogate Recoveries	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Field Blank	Batch Blank
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	59.2	78.1	83.7	89.5	72.4	88.6	93.2	88.6	80.1
2-Fluorobiphenyl	79.0	62.0	77.1	82.5	68.3	79.3	94.0	79.3	83.6
2-Fluorophenol	52.3	56.3	63.7	72.5	61.9	71.6	81.1	71.6	72.2
Nitrobenzene-d5	78.9	79.0	77.5	82.0	74.8	78.7	95.0	78.7	82.7
Phenol-d5	53.3	60.6	57.1	68.8	64.8	68.0	75.1	68.0	68.9
Terphenyl-d5	90.2	77.8	83.1	91.7	74.2	92.0	107.0	92.0	101.0

6/22/2006

PARAMETER

Surrogate Recoveries	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	South Ditch	North Ditch	Batch Blank
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	84.4	90.9	100.0	88.5	78.8	83.7	73.0	75.7	94.5
2-Fluorobiphenyl	78.3	58.6	87.7	78.9	55.6	77.8	73.0	77.0	84.4
2-Fluorophenol	61.4	46.0	75.0	66.2	53.6	61.8	41.7	49.0	73.2
Nitrobenzene-d5	78.6	79.2	83.0	74.3	75.3	77.8	74.4	73.8	85.7
Phenol-d5	60.7	51.3	71.6	58.1	48.5	56.7	38.1	40.7	63.5
Terphenyl-d5	67.2	56.6	85.2	75.5	61.0	68.3	59.3	73.3	85.0

	LCS	Matrix Spk	Field Spike OG 3A	OG 5 Dup.	Field Blank	LCSDup
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	82.0	94.6	93.0	77.5	72.5	89.9
2-Fluorobiphenyl	78.8	83.0	77.3	51.8	72.4	79.8
2-Fluorophenol	65.7	70.6	68.7	37.4	54.4	74.3
Nitrobenzene-d5	80.0	86.0	72.7	70.6	73.3	81.5
Phenol-d5	58.7	61.4	63.2	38.3	58.7	65.7
Terphenyl-d5	78.5	90.9	78.3	61.1	79.1	82.9

6/22/2006

PARAMETER Laboratory Control Spikes	% Rec.	% Rec.
1,2,4-Trichlorobenzene	74.6	78.3
1,4-Dichlorobenzene	71.6	75.0
2,4-Dinitrotoluene	82.4	84.8
2-Chlorophenol	70.3	78.8
4-Chloro-3-methylphenol	73.9	82.4
4-Nitrophenol	63.1	74.6
Acenaphthene	77.6	80.6
N-Nitrosodi-n-propylamine	83.0	83.8
Pentachlorophenol	66.1	70.0
Phenol	59.2	69.0
Pyrene	85.9	89.3

6/22/2006

PARAMETER Matrix Spike	% Rec.
1,2,4-Trichlorobenzene	83.6
1,4-Dichlorobenzene	79.7
2,4-Dinitrotoluene	79.8
2-Chlorophenol	85.6
4-Chloro-3-methylphenol	89.5
4-Nitrophenol	78.5
Acenaphthene	82.0
N-Nitrosodi-n-propylamine	85.1
Pentachlorophenol	76.7
Phenol	61.8
Pyrene	70.0

9/26/2006

PARAMETER Surrogate Recoveries	OG 1 % Rec.	OG 2 % Rec.	OG 3 % Rec.	OG 4 % Rec.	OG 5 % Rec.	OG 6 % Rec.	Culvert % Rec.	North Ditch % Rec.	South Ditch % Rec.	Batch Blank % Rec.
2,4,6-Tribromophenol	87.5	85.4	98.0	78.3	82.6	89.6	88.1	87.5	86.4	92.2
2-Fluorobiphenyl	81.5	71.2	79.8	71.8	73.0	76.3	79.9	76.7	80.6	90.6
2-Fluorophenol	81.6	71.0	82.0	58.4	46.9	63.3	74.2	76.9	67.7	94.2
Nitrobenzene-d5	79.1	68.5	78.4	69.8	71.2	76.2	78.9	75.8	80.6	89.7
Phenol-d5	75.7	69.5	78.1	48.6	40.0	55.9	67.0	67.2	60.7	86.3
Terphenyl-d5	92.7	62.7	84.4	68.1	56.3	69.3	77.0	91.9	73.9	107.0

	LCS % Rec.	Matrix Spk % Rec.	Field Dup. % Rec.	OG 5 Dup. % Rec.	Field Blank % Rec.	MSDup % Rec.
2,4,6-Tribromophenol	87.4	89.7	67.7	67.7	83.7	92.8
2-Fluorobiphenyl	74.3	71.1	67.9	67.9	84.0	74.7
2-Fluorophenol	82.0	74.0	49.9	49.9	81.7	76.4
Nitrobenzene-d5	75.2	70.8	66.9	66.9	80.7	74.9
Phenol-d5	75.0	69.8	44.3	44.3	76.4	68.5
Terphenyl-d5	87.6	79.9	53.1	53.1	92.7	81.3

9/26/2006

PARAMETER Laboratory Control Spikes	% Rec.
1,2,4-Trichlorobenzene	76.0
1,4-Dichlorobenzene	72.1
2,4-Dinitrotoluene	76.4
2-Chlorophenol	78.8
4-Chloro-3-methylphenol	79.4
4-Nitrophenol	81.1
Acenaphthene	75.8
N-Nitrosodi-n-propylamine	78.5
Pentachlorophenol	66.2
Phenol	67.3
Pyrene	59.0

9/26/2006

PARAMETER		
Matrix Spike	% Rec.	% Rec.
1,2,4-Trichlorobenzene	72.4	77.0
1,4-Dichlorobenzene	67.5	72.2
2,4-Dinitrotoluene	70.3	72.3
2-Chlorophenol	73.7	75.1
4-Chloro-3-methylphenol	80.4	83.3
4-Nitrophenol	81.9	83.0
Acenaphthene	73.2	76.3
N-Nitrosodi-n-propylamine	74.4	77.0
Pentachlorophenol	71.1	69.3
Phenol	64.7	63.4
Pyrene	56.1	56.9

11/16/2006

PARAMETER								
Surrogate Recoveries	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Batch Blank
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	85.9	86.1	82.1	78.6	79.8	79.4	82.6	83.4
2-Fluorobiphenyl	79.2	62.8	77.5	77.1	63.9	68.6	75.9	79.7
2-Fluorophenol	73.5	73.6	62.4	61.8	65.3	64.9	61.7	72.8
Nitrobenzene-d5	77.6	77.7	78.4	75.5	72.2	70.2	79.8	78.2
Phenol-d5	70.9	71.6	64.6	44.8	62.1	61.8	58.1	67.6
Terphenyl-d5	80.9	52.3	80.7	77.9	59.7	77.9	90.2	90.2

	LCS	Matrix Spk	Field Dup.	Field Blank	MSDup
	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.
2,4,6-Tribromophenol	87.8	85.9	81.6	78.2	72.1
2-Fluorobiphenyl	80.3	79.8	55.6	79.7	67.8
2-Fluorophenol	73.2	76.8	55.2	74.5	59.8
Nitrobenzene-d5	78.8	79.0	72.5	81.3	66.6
Phenol-d5	66.1	72.7	57.7	71.8	56.9
Terphenyl-d5	90.2	84.4	61.1	91.5	70.1

11/16/2006

PARAMETER	
Laboratory Control Spikes	% Rec.
1,2,4-Trichlorobenzene	76.9
1,4-Dichlorobenzene	71.3
2,4-Dinitrotoluene	80.2
2-Chlorophenol	77.2
4-Chloro-3-methylphenol	82.5
4-Nitrophenol	80.6
Acenaphthene	79.8
N-Nitrosodi-n-propylamine	80.0
Pentachlorophenol	67.7
Phenol	65.6
Pyrene	70.8

11/16/2006

PARAMETER		
Matrix Spike	% Rec.	% Rec.
1,2,4-Trichlorobenzene	79.8	66.0
1,4-Dichlorobenzene	76.0	62.9
2,4-Dinitrotoluene	78.3	64.5
2-Chlorophenol	79.8	64.9
4-Chloro-3-methylphenol	80.6	66.3
4-Nitrophenol	81.3	63.5
Acenaphthene	80.6	67.9
N-Nitrosodi-n-propylamine	81.3	68.5
Pentachlorophenol	60.0	46.6
Phenol	72.0	56.5
Pyrene	68.9	59.6

APPENDIX E

SHAPIRO-WILK NORMALITY TEST: GENERAL WATER CHEMISTRY, METALS

Shapiro-Wilk Normality test results for tire organics in well water and culvert samples.
Ho: Data from a normal distribution. W>0.80, p>0.10

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Statistix 8.0
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Aniline

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Shapiro-Wilk Normality Test

Variable        N         W         P      Ho         Conclusion
CULVERT         5    0.5522    0.0001      Reject     Non-normal
OG1             5    0.6840    0.0065      Reject     Non-normal
OG2             5    0.6153    0.0010      Reject     Non-normal
OG3             5    0.8887    0.3507      Accept     Normal
OG4             5    0.9666    0.8531      Accept     Normal
OG5             5    0.8622    0.2363      Accept     Normal
OG6             5    0.7322    0.0202      Reject     Non-normal
```

Benzothiazole

```
Shapiro-Wilk Normality Test

Variable        N         W         P      Ho         Conclusion
CULVERT         5         M         M      Insufficient Data
OG1             5         M         M      Insufficient Data
OG2             5    0.9252    0.5640      Accept     Normal
OG3             5    0.9045    0.4351      Accept     Normal
OG4             5    0.9251    0.5636      Accept     Normal
OG5             5    0.9142    0.4931      Accept     Normal
OG6             5    0.7469    0.0278      Reject     Non-normal

A M is printed when the sample size is smaller than 3,
or when the values of a sample are all the same.
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Hydroxybenzothiazole

```
Shapiro-Wilk Normality Test

Variable        N         W         P      Ho         Conclusion
CULVERT         5         M         M      Insufficient Data
OG1             5         M         M      Insufficient Data
OG2             5    0.7750    0.0499      Reject     Non-normal
OG3             5    0.9379    0.6511      Accept     Normal
OG4             5    0.9001    0.4106      Accept     Normal
OG5             5    0.8422    0.1710      Accept     Normal
OG6             5    0.9524    0.7540      Accept     Normal

A M is printed when the sample size is smaller than 3,
or when the values of a sample are all the same.
```

Acetylmorpholine

```
Shapiro-Wilk Normality Test

Variable        N        W        P      Ho         Conclusion
CULVERT         5        M        M      Insufficient Data
OG1             5        M        M      Insufficient Data
OG2             5   0.8836   0.3260      Accept     Normal
OG3             5   0.9855   0.9616      Accept     Normal
OG4             5   0.9119   0.4791      Accept     Normal
OG5             5   0.9900   0.9796      Accept     Normal
OG6             5   0.7704   0.0455      Reject     Non-normal

A M is printed when the sample size is smaller than 3,
or when the values of a sample are all the same.
```

APPENDIX F

GRUBB’S OUTLIER TEST:

GENERAL WATER CHEMISTRY,

TIRE ORGANIC CHEMICALS

GRUBBS OUTLIER TEST
Ho: NO OUTLIERS VALUES SORTED

Temperature

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert
7.0	4.6	7.1	6.7	4.4	7.2	2.5
7.5	4.2	8.1	6.3	4.5	8.2	8.3
12.4	10.5	14.0	11.9	10.8	11.6	4.5
13.5	11.7	15.4	11.6	11.9	13.0	18.3
16.7	14.4	16.7	16.3	16.7	14.2	15.6

DF=4							DF=n-1			
11	9	12	11	10	11	10	MEAN			
4.1	4.5	4.4	4.1	5.2	3.0	6.9	STD DEVIATION			
1.279	1.186	1.006	1.382	1.344	1.110	0.836	G-Value	t(0.05,4)	2.776	UPPER SIDE
TEST										
ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				

11	9	12	11	10	11	10	MEAN			
4.1	4.5	4.4	4.1	5.2	3.0	6.9	STD DEVIATION			
1.071	0.991	1.180	0.933	0.999	1.207	1.066	G-Value	t(0.05,4)	2.776	LOWER SIDE
TEST										
ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				

Bold = One-half the reported less than value.

GRUBBS OUTLIER TEST
Ho: NO OUTLIERS VALUES SORTED

Dissolved Oxygen

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert				
1.4	1.1	1.9	1.7	1.4	1.8	5.8				
2.6	1.7	2.1	2.4	1.9	1.9	7.3				
2.7	2.2	2.3	2.9	2.0	2.2	12.0				
3.0	2.6	2.5	2.9	2.2	2.5	9.9				
3.0	6.3	2.6	3.0	2.3	2.6	5.8				
DF=4							DF=n-1			
3	3	2	3	2	2	8	MEAN			
0.7	2.0	0.3	0.6	0.3	0.4	2.7	STD DEVIATION			
0.752	1.720	1.174	0.804	0.918	1.095	0.875	G-Value	t(0.05,4)	2.776	UPPER SIDE
TEST										
ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				

DIVIDING BY ZERO

3	3	2	3	2	2	8	MEAN			
0.7	2.0	0.3	0.6	0.3	0.4	2.7	STD DEVIATION			
1.703	0.814	1.386	1.608	1.629	1.111	0.849	G-Value	t(0.05,4)	2.776	LOWER SIDE
TEST										
ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				

= One-half the reported less than value.

GRUBBS OUTLIER TEST
Ho: NO OUTLIERS

VALUES SORTED

Specific Conductivity

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert				
473	348	816	849	726	443	402				
862	687	862	1096	765	793	412				
864	742	1113	1097	790	815	417				
1007	1033	1165	1134	1066	1050	420				
1022	1059	1166	1222	1097	1072	432				
DF=4							DF=n-1			
846	774	1024	1080	889	835	417	MEAN			
222	291	171	139	178	254	11	STD DEVIATION			
0.796	0.981	0.826	1.026	1.172	0.934	1.401	G-Value	t(0.05,4)	2.776	UPPER SIDE
TEST ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				
846	774	1024	1080	889	835	417	MEAN			
225	213	160	143	32	209	8	STD DEVIATION			
1.655	1.996	1.304	1.614	5.047	1.876	1.912	G-Value	t(0.05,4)	2.776	LOWER SIDE
TEST ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED				

GRUBBS OUTLIER TEST

Ho: NO OUTLIERS VALUES SORTED

Aniline

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert
5	120	55	23	130	**5**	**4.6**
5	120	56	37	190	**5**	**5**
5	130	65	66	200	**6**	**5**
5.5	140	68	74	230	14	**5**
5.5	380	71	110	230	14	**5**

DF=4							DF=n-1			
5	178	63	62	196	9	5	MEAN			
0.274	113	7	34	41	5	0.179	STD DEVIATION			
1.095	1.784	1.115	1.414	0.830	1.091	0.447	G-Value	t(0.05,4)	2.776	UPPER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

5	178	63	62	196	9	5	MEAN			
0.274	113	7	34	41	5	0.179	STD DEVIATION			
0.730	0.512	1.115	1.149	1.610	0.798	1.789	G-Value	t(0.05,4)	2.776	LOWER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

Bold = One-half the reported less than value.

GRUBBS OUTLIER TEST
Ho: NO OUTLIERS VALUES SORTED

Benzothiazole

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert
0.25	31	7.2	7.6	33	1.0	**0.25**
0.25	32	2.9	12	25	8.1	**0.25**
0.25	30	4.2	3.9	22	1.5	**0.25**
0.25	45	12	6.9	21	2	**0.25**
0.25	17	5.1	4.9	18	**0.25**	**0.25**

DF=4							DF=n-1			
0	31	6	7	24	3	0	MEAN			
0	10	4	3	6	3	0	STD DEVIATION			
	1.411	0.331	0.688	1.014	0.735		G-Value	t(0.05,4)	2.776	UPPER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

0	31	6	7	24	3	0	MEAN			
0	10	4	3	6	3	0	STD DEVIATION			
	0.000	0.258	0.172	1.609	0.497		G-Value	t(0.05,4)	2.776	LOWER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

Bold = One-half the reported less than value.

GRUBBS OUTLIER TEST
Ho: NO OUTLIERS VALUES SORTED

2-Hydroxybenzothiazole

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert				
0.25	820	520	540	880	260	**0.25**				
0.25	870	470	640	780	200	**0.25**				
0.25	870	670	700	820	230	**0.25**				
0.25	1400	820	990	1300	140	**0.25**				
0.25	1500	750	950	1500	110	**0.25**				
DF=4							DF=n-1			
0	1092	646	764	1056	188	0	MEAN			
0.000	329	149	197	324	62	0	STD DEVIATION			
	1.239	0.699	0.944	1.371	1.254		G-Value	t(0.05,4)	2.776	UPPER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					
0	1092	646	764	1056	188	0	MEAN			
0	329	149	197	324	62	0	STD DEVIATION			
	0.826	0.847	1.137	0.543	1.157		G-Value	t(0.05,4)	2.776	LOWER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

Bold = One-half the reported less than value.

GRUBBS OUTLIER TEST

Ho: NO OUTLIERS VALUES SORTED

4-Acetylmorpholine

WELL 1	WELL 2	WELL 3	WELL 4	WELL 5	WELL 6	Culvert				
0.25	18	6.3	5.9	22	**0.25**	**0.25**				
0.25	20	11	17	17	**0.25**	**0.25**				
0.25	16	7.9	6.9	19	2.7	**0.25**				
0.25	24	13	11	24	**0.25**	**0.25**				
0.25	3.2	10	9.4	20	1.8	**0.25**				
DF=4							DF=n-1			
0	16	10	10	20	1	0	MEAN			
0	8	3	4	3	1	0	STD DEVIATION			
	1.658	0.137	0.146	0.148	0.657		G-Value	t(0.05,4)	2.776	UPPER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					
0	18	8	10	19	1	0	MEAN			
0	2	2	6	3	1	0	STD DEVIATION			
	0.000	0.879	0.657	1.060	0.577		G-Value	t(0.05,4)	2.776	LOWER SIDE TEST
	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED	ACCEPTED					

Bold = One-half the reported less than value.

APPENDIX G

ROAD BASE MONITORING WELLS:
THICKNESS OF SUBMERGED TIRES IN WELL WATER, 2006

Thickness of submerged tires in well water for each sampling event.

	WELLS	1	2	3	4	5	6
02/13/06	Tires in water (Feet)	0.0	6.8	1.6	2.3	5.9	0.3
02/17/06	Tires in water (Feet)	0.0	5.6	1.6	1.0	4.6	0.3
02/27/06	Tires in water (Feet)	0.0	6.7	1.5	2.1	5.8	0.2
03/15/06	Tires in water (Feet)	0.0	6.6	1.6	2.2	5.7	0.3
03/28/06	Tires in water (Feet)	0.0	6.7	1.7	2.3	5.8	0.4
05/08/06	Tires in water (Feet)	0.0	7.4	2.1	2.7	6.5	0.8
06/05/06	Tires in water (Feet)	0.0	7.0	1.5	2.1	6.1	0.2
06/22/06	Tires in water (Feet)	0.0	7.0	1.4	2.0	6.1	0.2
09/26/06	Tires in water (Feet)	0.0	7.0	1.8	2.4	6.1	0.4
09/29/06	Tires in water (Feet)	0.0	7.0	1.7	2.3	6.1	0.4
11/16/06	Tires in water (Feet)	0.0	6.7	1.3	1.9	5.8	-0.2*
	Mean	0.0	6.8	1.6	2.1	5.9	0.3
	Std. Dev.	0.0	0.5	0.2	0.4	0.5	0.2
	Min.	0.0	5.6	1.3	1.0	4.6	-0.2
	Max.	0.0	7.4	2.1	2.7	6.5	0.8

Tires in water = Tire Thickness – [(Mean depth to water) – Depth to tires)]

* Well water in November at Well #6 was below the bottom of the tire shreds.

APPENDIX H

SAMPLE DATA:

GENERAL WATER CHEMISTRY, METALS, POLYNUCLEAR AROMATIC HYDROCARBONS,

2006

Tire Shreds Project

General Chemistry	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Field Blank	Reporting Limit	MDL
9/26/2006													
COD	mg/L	40	7	250	120	120	240	78	35	33	<25	25	5
TSS	mg/L	140	3	24	72	54	26	84	7	24	<10	20	4
Alkalinity	mg/L	150	150	140	210	210	170	250	170	170	<10	10	2
Ammonia-N	mg/L	0.35	0.22	11	9.4	9.7	10	2.7	0.46	0.43	<0.05	0.05	0.01
Total Organic Carbon	mg/L	6	<15	62	33	34	64	16	7	6	<15	15	3
Gasoline Range Organics	ug/L	<85	<85	42	35	18	82	20	18	<85	<85	85	17
Metals													
Barium	ug/L	NA	140	290	330	320	250	250	70	NA	<10	10	2
Copper	ug/L	NA	<50	<50	<50	<50	<50	<50	<50	NA	<50	50	10
Iron	ug/L	NA	1100	14000	59000	41000	14000	97000	1300	NA	<50	50	10
Manganese	ug/L	NA	350	290	530	140	150	1100	330	NA	<25	25	5
Antimony	ug/L	NA	<250	<250	<250	<250	<250	<250	<250	NA	<250	250	50
Zinc	ug/L	NA	8	20	100	20	20	28	10	NA	<25	25	5

NA = Not analyzed.

Bold = One-half the reporting limit.

Metals concentrations are from filtered water.

Tire Shreds Project

General Chemistry	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Field Blank	Reporting Limit	MDL
11/16/2006													
COD	mg/L	26	6	250	120	120	240	46	20	37	<25	25	5
TSS	mg/L	11	NA	NA	NA	NA	NA	NA	NA	12	<10	20	4
Alkalinity	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	10	2
Ammonia-N	mg/L	0.14	NA	NA	NA	NA	NA	NA	0.14	0.15	<0.05	0.05	0.01
Total Organic Carbon	mg/L	5	<15	72	44	34	70	18	5	5	<15	15	3
Gasoline Range Organics	ug/L	<30	NA	NA	NA	NA	NA	NA	<30	NA	<30	85	17
Metals													
Barium	ug/L	NA	NA	NA	NA	NA	NA	NA	62	NA	<10	10	2
Copper	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	50	10
Iron	ug/L	NA	NA	NA	NA	NA	NA	NA	1100	NA	10	50	10
Manganese	ug/L	NA	NA	NA	NA	NA	NA	NA	260	NA	<25	25	5
Antimony	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	250	50
Zinc	ug/L	NA	NA	NA	NA	NA	NA	NA	9	NA	6	25	5

NA = Not analyzed.

Polynuclear Aromatic Hydrocarbons

									Up	Down	
9/26/2006		**Well 1**	**Well 2**	**Well 3**	**Well 4**	**Well 5**	**Well 6**	**Culvert**	**Stream**	**Stream**	
PARAMETER	**UNITS**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	**9/26/06**	MDL
Acenaphthene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Acenaphthylene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Anthracene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Benzo(a)anthracene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Benzo(a)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Benzo(e)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Benzo(g,h,i)perylene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Benzofluoranthenes (Total)	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.13
Carbazole	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
2-Chloronaphthalene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Chrysene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenz(a,h)acridine	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenz(a,h)anthracene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenz(a,j)acridine	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenzo(a,e)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenzo(a,h)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenzo(a,I)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenzo(a,l)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
7H-Dibenzo(c,g)carbazole	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Dibenzofuran	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
7,12-Dimethylbenz(a)anthracene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
1,6-Dinitropyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
1,8-Dinitropyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
Fluoranthene	ug/L	ND	0.065	ND	ND	0.089	ND	ND	ND	ND	0.045
Fluorene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Indeno(1,2,3-cd)pyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045

ND= Not detected

3-Methylcholanthrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
5-Methylchrysene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
1-Methylnaphthalene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
2-Methylnaphthalene	ug/L	ND	0.26	ND	ND	0.29	ND	ND	ND	ND	0.045
Naphthalene	ug/L	ND	0.29	ND	0.11	0.37	ND	ND	ND	ND	0.045
5-Nitroacenaphthene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
6-Nitrochrysene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
2-Nitrofluorene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
1-Nitropyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
4-Nitropyrene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Perylene	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.045
Phenanthrene	ug/L	ND	ND	ND	0.099	0.13	ND	ND	ND	ND	0.045
Pyrene	ug/L	ND	0.068	0.071	ND	0.11	ND	ND	ND	ND	0.045
Nitrobenzene-d5 (S)	50-150%	68%	87%	83%	85%	84%	74%	73%	78%	83%	
2-Fluorobiphenyl (S)	50-150%	69%	86%	89%	90%	346%	76%	75%	74%	86%	
Terphenyl-d14 (S)	50-150%	91%	64%	84%	89%	89%	80%	91%	78%	96%	
Carcinogenic PAHs (ug/L)		ND	ND	ND	ND	ND	ND	ND	ND	ND	
(BaP Equivalents Worksheet)											
TOTAL PAH		ND	0.683	0.071	0.209	0.989	ND	ND	ND	ND	
TOTAL COMPDS. DETECTED		0	4	1	2	5	0	0	0	0	

ND= Not detected

Ploynuclear Aromatic Hydrocarbons

11/16/2006

PARAMETER	UNITS	**Well 1**	**Well 2**	**Well 3**	**Well 4**	**Well 5**	**Well 6**	**Culvert**	**Up Stream**	**Down Stream**	MDL
								11/16/2006	11/16/2006		
Acenaphthene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Acenaphthylene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Anthracene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Benzo(a)anthracene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Benzo(a)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Benzo(e)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Benzo(g,h,i)perylene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Benzofluoranthenes (Total)	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.13
Carbazole	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
2-Chloronaphthalene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Chrysene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenz(a,h)acridine	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenz(a,h)anthracene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenz(a,j)acridine	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenzo(a,e)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenzo(a,h)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenzo(a,I)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenzo(a,l)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
7H-Dibenzo(c,g)carbazole	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Dibenzofuran	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
7,12-Dimethylbenz(a)anthracene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
1,6-Dinitropyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	1.1
1,8-Dinitropyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	1.1
Fluoranthene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Fluorene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Indeno(1,2,3-cd)pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045

ND= Not detected

3-Methylcholanthrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
5-Methylchrysene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
1-Methylnaphthalene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
2-Methylnaphthalene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Naphthalene	ug/L	NA	NA	NA	NA	NA	NA	0.042	ND	NA	0.045
5-Nitroacenaphthene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
6-Nitrochrysene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
2-Nitrofluorene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
1-Nitropyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
4-Nitropyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Perylene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Phenanthrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Pyrene	ug/L	NA	NA	NA	NA	NA	NA	ND	ND	NA	0.045
Nitrobenzene-d5 (S)	50-150%							60%	65%		
2-Fluorobiphenyl (S)	50-150%							67%	74%		
Terphenyl-d14 (S)	50-150%							81%	81%		
Carcinogenic PAHs (ug/L)								ND	ND		
(BaP Equivalents Worksheet)											
TOTAL PAH								0.042	ND		
TOTAL COMPDS. DETECTED								1	0		

ND= Not detected
NA= Not analyzed

APPENDIX I

TWO-SAMPLE T-TEST:

FIELD PARAMETERS, TIRE ORGANIC CHEMICALS

Two-Sample t-Test comparisons between general water chemistry concentrations of well and culvert water samples.
H_o: $u_1=u_n$

Parameter	**Wells 1 & 2**	**Wells 1 & 3**	**Wells 1 & 4**	**Wells 1 & 5**	**Wells 1 & 6**	**Well 1 & C**
Temperature	Accept	Accept	Accept	Accept	Accept	Accept
Dissolved Oxygen	Accept	Accept	Accept	Accept	Accept	Reject
Sp. Conductivity	Accept	Accept	Accept	Accept	Accept	Reject
pH	Accept	Reject	Reject	Accept	Reject	Accept
Parameter	**Wells 2 & 3**	**Wells 2 & 4**	**Wells 2 & 5**	**Wells 2 & 6**	**Well 2 & C**	**Wells 3 & 4**
Temperature	Accept	Accept	Accept	Accept	Accept	Accept
Dissolved Oxygen	Accept	Accept	Accept	Accept	Reject	Accept
Sp. Conductivity	Accept	Accept	Accept	Accept	Reject	Accept
pH	Reject	Reject	Accept	Reject	Accept	Accept
Parameter	**Wells 3 & 5**	**Wells 3 & 6**	**Well 3 & C**	**Wells 4 & 5**	**Wells 4 & 6**	**Well 4 & C**
Temperature	Accept	Accept	Accept	Accept	Accept	Accept
Dissolved Oxygen	Accept	Accept	Reject	Accept	Accept	Reject
Sp. Conductivity	Accept	Accept	Reject	Accept	Accept	Reject
pH	Reject	Accept	Reject	Reject	Accept	Reject
Parameter	**Wells 5 & 6**	**Well 5 & C**	**Well 6 & C**			
Temperature	Accept	Accept	Accept			
Dissolved Oxygen	Accept	Reject	Reject			
Sp. Conductivity	Accept	Reject	Reject			
pH	Reject	Accept	Reject			

Two-Sample t-Test comparisons between tire organic chemical concentrations of well and culvert water samples.
$H_o: u_1=u_n$

Parameter	**Wells 1&2**	**Wells 1&3**	**Wells 1&4**	**Wells 1&5**	**Wells 1&6**	**Well 1&C**
Aniline	Reject	Reject	Reject	Reject	Accept	Accept
Benzothiazole	Insufficient	Insufficient	Insufficient	Insufficient	Insufficient	Insufficient
Hydroxybenzothiazole	Insufficient	Reject	Reject	Reject	Insufficient	Insufficient
Acetylmorpholine	Insufficient	Reject	Reject	Insufficient	Reject	Insufficient
Parameter	**Wells 2&3**	**Wells 2&4**	**Wells 2&5**	**Wells 2&6**	**Well 2&C**	**Wells 3&4**
Aniline	**Reject**	Accept	Accept	Reject	Reject	Accept
Benzothiazole	Reject	Reject	Accept	Reject	Insufficient	Accept
Hydroxybenzothiazole	Reject	Accept	Accept	Reject	Insufficient	Accept
Acetylmorpholine	Accept	Accept	Accept	Reject	Reject	Accept
Parameter	**Wells 3&5**	**Wells 3&6**	**Well 3&C**	**Wells 4&5**	**Wells 4&6**	**Well 4&C**
Aniline	Reject	Reject	Reject	Reject	Reject	Reject
Benzothiazole	Reject	Accept	Reject	Reject	Accept	Reject
Hydroxybenzothiazole	Reject	Reject	Reject	Accept	Reject	Reject
Acetylmorpholine	Reject	Reject	Reject	Reject	Reject	Reject
Parameter	**Wells 5&6**	**Well 5&C**	**Well 6&C**			
Aniline	Reject	Reject	Accept			
Benzothiazole	Reject	Reject	Insufficient			
Hydroxybenzothiazole	Reject	Reject	Insufficient			
Acetylmorpholine	Reject	Insufficient	Insufficient			

APPENDIX J

SAMPLE DATA:

TIRE ORGANIC CHEMICALS, 2006

Tire specific semi-volatile organic chemicals.

	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	North Ditch	Field Blank	Reporting Limit	MDL
2/13/2006												
Aniline	ug/L	<10	140	65	74	200	14	<10	NA	NA	10	3.2
Benzothiazole	ug/L	<10	31	7.2	7.6	33	1.0	ND	NA	NA		
2-Hydroxybenzothiazole	ug/L	ND	820	520	540	880	260	ND	NA	NA		
4-Acetylmorpholine	ug/L	<10	18	6.3	5.9	22	<10	ND	NA	NA		
Benzoic Acid	ug/L	<10	<10	<10	<10	<10	<10	<10	NA	NA	10	2.8
Carbazole	ug/L	<10	<10	<10	<10	<10	<10	<10	NA	NA	10	1.2
4(1-Methyl-1-phenylethyl)phenol	ug/L	ND	ND	ND	ND	ND	ND	ND	NA	NA		
4(2-Benzothiazolythio)-morpholine	ug/L	ND	ND	ND	ND	ND	ND	ND	NA	NA		

	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	North Ditch	Field Blank	Reporting Limit	MDL
3/28/2006												
Aniline	ug/L	<10	120	68	66	130	<10	<10	<10	<10	10	3.2
Benzothiazole	ug/L	<10	32	2.9	12	25	8.1	ND	ND	ND		
2-Hydroxybenzothiazole	ug/L	<10	870	470	640	780	200	ND	ND	ND		
4-Acetylmorpholine	ug/L	<10	20	11	17	17	<10	ND	ND	ND		
Benzoic Acid	ug/L	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	2.8
Carbazole	ug/L	<10	<10	<10	<10	<10	<10	<10	<10	<10	10	1.2
4(1-Methyl-1-phenylethyl)phenol	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND		
4(2-Benzothiazolythio)-morpholine	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND		

NA = Not analyzed.
ND = Not detected.
NR* = Not reported. Chemical quantification relative to nearest internal standard

Tire specific semi-volatile organic chemicals.

	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	North Ditch	South Ditch	Field Blank	Reporting Limit	MDL
6/22/2006													
Aniline	ug/L	<10	130	71	110	230	14	NA	<10	<10	<10	10	3.2
Benzothiazole	ug/L	<10	30	4.2	3.9	22	1.5	NA	ND	ND	ND	NR*	NR*
2-Hydroxybenzothiazole	ug/L	<10	870	670	700	820	230	NA	ND	ND	ND	NR*	NR*
4-Acetylmorpholine	ug/L	<10	16	7.9	6.9	19	2.7	NA	ND	ND	ND	NR*	NR*
Benzoic Acid	ug/L	<10	<11	<11	<11	<10	<11	NA	<10	<10	<10	10	2.8
Carbazole	ug/L	<10	<11	<11	<11	<10	<11	NA	<10	<10	<10	10	1.2
4(1-Methyl-1-phenylethyl)phenol	ug/L	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	NR*	NR*
4(2-Benzothiazolythio)-morpholine	ug/L	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	NR*	NR*

	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	North Ditch	South Ditch	Field Blank	Reporting Limit	MDL
9/26/2006													
Aniline	ug/L	<10	380	55	37	230	<10	<10	<9.3	<10	<11	11	1.3
Benzothiazole	ug/L	<10	45	12	6.9	21	2	ND	ND	ND	ND	NR*	NR*
2-Hydroxybenzothiazole	ug/L	<10	1400	820	990	1300	140	ND	ND	ND	ND	NR*	NR*
4-Acetylmorpholine	ug/L	<10	24	13	11	24	<10	ND	ND	ND	ND	NR*	NR*
Benzoic Acid	ug/L	<11	<10	<10	<11	<10	<10	<10	<9.3	<10	<11	11	2.8
Carbazole	ug/L	<11	<10	<10	<11	<10	<10	<10	<9.3	<10	<11	11	0.4
4(1-Methyl-1-phenylethyl)phenol	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NR*	NR*
4(2-Benzothiazolythio)-morpholine	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NR*	NR*

NA = Not analyzed.
ND = Not detected.
NR* = Not reported. Chemical quantification relative to nearest internal standard

Tire specific semi-volatile organic chemicals.

	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	North Ditch	South Ditch	Field Blank	Reporting Limit	MDL
11/16/2006													
Aniline	ug/L	<10	120	56	23	190	<10	<9.3	NA	NA	<9.3	11	1.3
Benzothiazole	ug/L	<10	17	5.1	4.9	18	<10	ND	NA	NA	ND	NR*	NR*
2-Hydroxybenzothiazole	ug/L	<10	1500	750	950	1500	110	ND	NA	NA	ND	NR*	NR*
4-Acetylmorpholine	ug/L	<10	3.2	10	9.4	20	1.8	ND	NA	NA	ND	NR*	NR*
Benzoic Acid	ug/L	<11	<11	<11	<11	<13	<12	<9.3	NA	NA	<9.3	11	2.8
Carbazole	ug/L	<11	<11	<11	<11	<13	<12	<9.3	NA	NA	<9.3	11	0.4
4(1-Methyl-1-phenylethyl)phenol	ug/L	ND	ND	ND	ND	ND	ND	ND	NA	NA	ND	NR*	NR*
4(2-Benzothiazolythio)-morpholine	ug/L	ND	ND	ND	ND	ND	ND	ND	NA	NA	ND	NR*	NR*

NA = Not analyzed.
ND = Not detected.
NR* = Not reported. Chemical quantification relative to nearest internal standard.

APPENDIX K

LSRI REPORT, APRIL 2006

Toxicity Evaluation of Water From Tire Shreds, In Oak Grove, Minnesota.

By

Matthew TenEyck
and Tom Markee

Lake Superior Research Institute
University of Wisconsin-Superior
Superior, WI

Final Report

To

Minnesota Department of Transportation.
395 John Ireland Boulevard
St. Paul, Minnesota 55155-1899

(Robert Edstrom, Project Officer)

April 16, 2006

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INTRODUCTION

The Lake Superior Research Institute (LSRI), University of Wisconsin-Superior, Superior, WI. contracted with Minnesota Department of Transportation (MNDOT) to evaluate the toxicity of well water samples collected from Oak Grove, Minnesota. The study area maybe contaminated with water soaked in tire shreds. The study sites had been previously sampled for chemical analysis of water. Sampling sites, identified by MNDOT, served as either a reference (OG1) or contaminated (OGC, OG2-6) site. LSRI was contracted to perform water-only tests using the larval fish, fathead minnow, *Pimephales promelas*, the insect larvae *Chironomus dilutus*, and the cladoceran *Ceriodaphnia dubia*.

METHODS

Sample Collection and Preparation

Water samples were collected on 13th of February 2006 and then again on 17th of February 2006 by MNDOT staff. The water samples were transported to LSRI in coolers for immediate analysis and testing. Samples were received with minimal head-space and on ice. Prior to the collection of water samples, preliminary chemistry (temperature, dissolved oxygen, conductivity, and pH) field measurements were conducted by MNDOT staff at all sites. Upon receipt of the water samples at LSRI, water chemistry was measured again on stock solutions. Water characteristics were measured for temperature, dissolved oxygen, conductivity, pH, alkalinity, and hardness (Appendix Table 1). The dissolved oxygen at all of the sites was below the initial acceptable criterion (U.S. EPA, 1993) of 4.0 mg/L except for OGC. Ambient air was bubbled through both samples using glass pipettes at <100 bubbles per second for one half hour. This also allowed the samples to warm to a test temperature of 25.0 °C and increase the dissolved oxygen. After the aeration and warming of samples pH, ammonia, total alkalinity, total hardness, and conductivity were measured (Appendix Table 1).

Static-Renewal Water-Only Toxicity Tests

Static water only tests were performed with three freshwater organisms; the larval fish *Pimephales promelas*, the insect larvae *Chironomus dilutus*, and the cladoceran *Ceriodaphnia dubia*. The objectives of these tests were to determine if the contaminants in the water were harmful to these organisms. Survival was the endpoint for the fathead minnow and *C. dilutus* tests while survival and reproduction were the endpoints for the *C. dubia* test. The LSRI Standard Operating Procedures, "Conducting a 48-hour and 96-hour Renewal Test with Fathead Minnows (AT/4)," "Conducting Early-Life Stage Toxicity Tests with a Fathead Minnow *Pimephales promelas* (AT/1)," "Conducting Renewal Chronic Toxicity Tests with *Daphnia magna* (AT/3),"and "Conducting a 10-D Sediment Toxicity Test with *Chironomus dilutus* (AT/21) are based upon EPA methods (U.S. EPA, 2000) and adapted for use in this project. The midge *C. dilutus* has been used extensively in the short-term assessment of chemicals in sediments. Their response has been evaluated in interlaboratory studies and has been confirmed with natural benthic populations. Many investigators have used *C. dilutus* to evaluate the toxicity of freshwater sediments. This approach will be based on sediment exposure methodology using silica sand as a substrate with the over lying water as the source of toxicant. Briefly, the tests were initiated with juvenile life-stage organisms. *Pimephales promelas* were 7 days old, *C. dilutus* were 10 days old, and the *Ceriodpahnia dubia* were <24 hours-old. The tests were performed at nominal temperatures of 25.0 °C ± 1.0 °C and the test water was renewed daily(See Appendix Table 1).

The replicate beakers were fed equal volumes of food. *C. dubia* received 0.1 mL daily of a yeast, Cerophyll®, and trout chow mixture containing 1800 mg/L total suspended solids and 0.1 mL *Selenastrum* algae at 1.0* 10^8 cells/mL. *C. dilutus* was fed 1.0 mL daily of a 4.0 g/L Tetrafin® suspension. Fathead minnows were fed twice daily, six hours apart, 0.15 g (1000-1500 nauplii) of newly hatched (less than 24-h old) brine shrimp nauplii.

During the tests, measurements were taken for temperature and dissolved oxygen daily on the renewal solution. The pH was measured on days 1,3,5, and 7 in the renewal solution. Ammonia, alkalinity, hardness, and conductivity were measured on day 1 and 5 on the renewal water samples provided by MNDOT (Appendix Table 1).

Statistical Analysis

Analysis of variance (ANOVA) procedures were used to make comparisons between the control and treatment survival. SigmaStat® software procedures were used to perform all the statistical computations. If the data met assumptions of normality and homogeneity of variance, then parametric procedures were used. First, an ANOVA was performed followed by mean comparisons using Tukey's test. Non-normal data were transformed using the arc-sine square-root transformation (U.S. EPA, 1993) to meet the normality and homogeneity of variance requirements. If transformed data did not meet the normality and homogeneity of variance assumptions analysis on ranks was conducted. Mean percent survivals and mean reproduction were analyzed with a statistical significance level of α=0.05.

Quality Assurance/Quality Control (QA/QC)

Toxicity tests were initiated with healthy, vigorous animals. Reference toxicant tests were performed with test species prior to the start of the definitive test and data is available upon request. In the toxicity test, percent survival in the laboratory controls were compared to published test acceptability criteria (U.S. EPA, 1993) to determine overall performance of the animals and the test system. Test conditions were monitored daily for parameters that might affect the outcome of the test (i.e., temperature and dissolved oxygen). Daily and weekly calibration of test meters ensured optimal performance. Reference standards and duplicate samples were used in the analysis of ammonia, alkalinity, and hardness. Any deviations were discussed with the principal investigator and documented in the study notebook. The studies were conducted with a high degree of quality assurance/quality control criteria. The QC/QA documentation was noted on the raw data sheets and study notebooks.

RESULTS

Pimephales promelas 7-day Static-Renewal Water-Only Toxicity Test

Mean percent survival during the 7 days of exposure was high (90.0 percent) for animals exposed to the control and the reference water (Table 1). Animals exposed to all of the treatments had a mean survival range of 0-77.5 percent (Table 1). Treatments OG2, OG3, and OG5 had 0% survival by the second and third day. Survival was significantly ($p < 0.05$) reduced in treatments OG2-6 when compared to the lab water control (Table 1). Survival was significantly ($p < 0.05$) reduced in treatments OG2-5 when compared to OG1 reference site (Table 1). Raw data is presented in Appendix Table 2.

Chironomus dilutus 10-day Static-Renewal Water-Only Toxicity Test

Mean percent survival during the 10 days of exposure was high (97.5-100 percent) for animals exposed to the lab control and the reference water (Table 2). Treatments OG2 and OG5 had significantly ($p < 0.05$) reduced survival (62.5 and 52.5, respectively) when compared to the lab water control and reference site (Table 2). Raw data is presented in Appendix Table 3.

Ceriodaphnia dubia Survival and Reproduction Static-Renewal Water-Only Toxicity Test

Mean percent survival during the 8 days of exposure was high (100 and 90 percent) for animals exposed in the lab water control and the reference water (Table 3), respectively. Animals exposed to all of the treatments had a range of mean survivals from 0-100 percent (Table 3). Sites OG2 and OG5 had complete mortality (Table 3). Survival was significantly ($p < 0.05$) reduced in sites OG2-5 when compared to both the lab water control and the reference water site (Table 3). Reproduction was an average total of 18.3 ± 7.7 young in the lab control while the reference site OG1 had an average total of 15.5 ± 8.8 young (Table 3). Treatment sites OG2-5 had 0.0-20.0 percent survival also had no reproduction (Table 3). Site OG6 also had no reproduction but had 100% percent survival (Table 3). Raw data is presented in Appendix Table 4.

CONCLUSIONS

The Lake Superior Research Institute, University of Wisconsin-Superior, Superior, WI. contracted with Minnesota Department of Transportation to evaluate the toxicity of water collected from sites in Oak Grove, MN. The study sites were designated as a reference (Site OG1) or contaminated (OG2-OG6 and OGC) site. With the *Pimephales promelas* test species, survival was significantly reduced in the five below ground treatment wells. Ammonia values ranged from 1.7-15.1 ppm. While above ground OGC site experienced reduced survival the ammonia was 0.067 ppm. Ammonia could be a possible stressor adding to the toxicity of the fish. Conductivity was also high at sites OG1-OG6 when compared to the lab control.

The *Chironomus dilutus* test had significantly reduced survival at sites OG2 and OG5. It is not apparent what may be causing toxicity at these two sites. In comparison, to the fathead minnow test the midge larvae test in general is less sensitive than the fathead minnow test. It was noticed that in all of the treatment sites (OG2-6) and orange precipitate, believed to be iron, was present. As the water was aerated and warmed to the test temperature more and more precipitate was present. It was impossible to remove the precipitate from the silica sand substrate during the daily renewal. This may have contributed to some of the toxicity of the treatments.

A significant reduction in survival was observed in the *Ceriodaphnia dubia* test species at the sites OG2-5. Partial reductions in survival were observed at the OGC site. It was interesting to observe that at site OG6 reproduction was significantly reduced while 100% of the organisms were alive. This reduction in *C. dubia* reproduction and reduced survival in the fathead minnows may indicate that OG6 has some chronic toxicity present.

REFERENCES

U.S. EPA. 1993. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. EPA/600/4-90/027F. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. 20460.

U.S. EPA. 2000. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates. EPA/600/R-99/064. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. 20460.

Table 1. Average survival of *Pimephales promelas* exposed to water from Oak Grove, MN. Standard deviations are in ( ).

Treatment	Average percent survival
Lab Water	90.0 (1.2)
OG1	90.0 (1.4)
OG2	0.0[ab]
OG3	0.0[ab]
OG4	2.5 (0.5)[ab]
OG5	0.0[ab]
OG6	76.7 (0.6)[a]
OGC	77.5 (1.0)

[a] Survival significantly reduced relative to the lab water control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

[b] Survival significantly reduced relative to OG1control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

Table 2. Average survival of *Chironomus dilutus* exposed to water from Oak Grove, MN. Standard deviations are in ( ).

Treatment	Average percent survival
Lab Water	100 (0.0)
OG1	97.5 (0.5)
OG2	62.5 (1.0)[ab]
OG3	95.0 (1.3)
OG4	95.0 (1.9)
OG5	52.5 (1.0)[ab]
OG6	95.0 (1.0)
OGC	102.5 (0.5)

[a] Survival significantly reduced relative to the lab water control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

[b] Survival significantly reduced relative to OG1control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

Table 3. Average survival and reproduction of *Ceriodaphnia dubia* exposed to water from Oak Grove, MN. Standard deviations are in ( ).

Treatment	Average percent survival	Average number of young
Lab Water	100.0 (0.0)	18.3 (7.7)
OG1	90.0 (0.3)	15.5 (8.8)
OG2	0.0[ab]	0.0[ab]
OG3	20.0 (0.4)[ab]	0.0[ab]
OG4	10.0 (0.3)[ab]	0.0[ab]
OG5	0.0[ab]	0.0[ab]
OG6	100.0 (0.0)	1.5 (2.0)[ab]
OGC	70.0 (0.5)	10.2 (5.8)[ab]

[a] Survival or reproduction significantly reduced relative to the lab water control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

[b] Survival or reproduction significantly reduced relative to OG1control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

Appendix Table 1. Water Chemistry Measurements on Oak Grove, MN. Samples.

Temps (° C)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	24.6	24.0	24.2	24.0	24.2	24.0	24.1	24.0
2	23.0	22.5	23.4	23.0	24.1	24.2	24.3	24.1
3	23.4	23.4	25.1	24.3	24.8	26.8	24.8	23.5
4	26.8	27.2	27.3	27.2	27.8	27.9	26.7	26.8
5	23.7	24.4	24.7	24.5	24.7	24.8	24.6	24.5
6	25.4	22.5	22.5	23.0	23.1	24.8	23.0	23.1
7	23.6	23.8	26.0	24.8	26.6	25.4	25.4	28.0
8	27.1		27.4	28.1	28.4	28.1	28.0	28.5
Average	24.7	24.0	25.1	24.9	25.3	25.8	25.1	25.1
Min	23.0	22.5	22.5	23.0	23.1	24.0	23.0	23.1
Max	27.1	27.2	27.4	28.1	28.4	28.1	28.0	28.5

D.O. (mg/L)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	7.1	7.2	6.0	4.4	6.9	3.5	6.8	4.0
2	7.9	8.0	7.9	8.0	8.0	7.9	8.0	7.3
3	8.8	9.4	7.2	6.7	5.5	6.8	7.4	4.3
4	7.3	7.8	6.8	8.1	6.9	6.9	6.3	6.8
5	7.4	7.2	7.0	7.2	6.8	7.0	7.1	7.1
6	6.7	7.8	7.4	6.9	6.8	6.4	6.0	6.7
7	6.9	6.7	7.3	6.5	6.9	6.8	6.9	6.5
8	6.9		7.1	6.7	6.7	6.6	6.7	6.5
Average	7.4	7.7	7.1	6.6	6.8	6.5	6.8	6.1
Min	6.7	6.7	6.0	4.4	5.5	3.5	5.8	4.0
Max	8.8	9.4	7.9	8.0	8.0	7.9	8.0	7.3

pH				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	8.32	8.17	7.71	7.30	7.53	6.99	7.54	6.85
3	8.10	7.82	8.11	7.49	6.96	7.29	7.68	6.65
5	8.29	8.37	8.58	8.22	7.79	8.50	8.28	8.52
7	8.36	8.15	8.20	7.63	7.87	8.24	8.31	8.33
Average	8.27	8.13	8.15	7.66	7.54	7.76	7.95	7.59
Min	8.10	7.82	7.71	7.30	6.96	6.99	7.54	6.65
Max	8.36	8.37	8.58	8.22	7.87	8.50	8.31	8.52

Ammonia (ppm)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	0.073	0.067	0.213	14.186	15.744	12.890	14.365	2.746
4	<0.063	0.067	0.218	15.990	16.057	13.808	15.205	2.594
Average	0.052	0.067	0.216	15.088	15.901	13.349	14.785	2.670
Min	<0.063	0.067	0.213	14.186	15.744	12.890	14.365	2.594
Max	0.073	0.067	0.218	15.990	16.057	13.808	15.205	2.746

Alkalinity (mg/L CaCO3)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	70.0	158.8	120.0	113.2	206.0	218.8	115.2	174.4
5	56.4	171.6	132.0	132.0	216.0	228.4	132.0	196.0
Average	63.2	165.2	126.0	122.6	211.0	223.6	123.6	185.2
Min	56.4	158.8	120.0	113.2	206.0	218.8	115.2	174.4
Max	70.0	171.6	132.0	132.0	216.0	228.4	132.0	196.0

Hardness (mg/L CaCO3)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1		208.0	312.4	179.2	255.2	248.0	185.6	
5	54.0	220.0	312.0	184.0	280.0	212.0	196.0	
Average	54.0	214.0	312.2	181.6	267.6	230.0	190.8	
Min	54.0	208.0	312.0	179.2	255.2	212.0	185.6	
Max	54.0	220.0	312.4	184.0	280.0	248.0	196.0	

Conductivity (umhos/cm)				Treatments				
Day	Lab water	OGC	OG1	OG2	OG3	OG4	OG5	OG6
1	147.7	387.0	799.0	635.0	699.0	724.0	635.0	594.0
5	149.0	417.0	798.0	622.0	685.0	690.0	628.0	534.0
Average	148.4	402.0	798.5	628.5	692.0	707.0	631.5	564.0
Min	147.7	387.0	798.0	622.0	685.0	690.0	628.0	534.0
Max	149.0	417.0	799.0	635.0	699.0	724.0	635.0	594.0

Appendix Table 2. Survival of *Pimephales promelas* Exposed to Water Samples From Oak Grove, MN.

Treatment	Rep.	Survial	Average Survival (%)	Standard Deviation
Lab Water	1	10		
Lab Water	2	8		
Lab Water	3	10		
Lab Water	4	8	90.0	1.2
OGC	1	7		
OGC	2	9		
OGC	3	7		
OGC	4	8	77.5	1.0
OG1	1	7		
OG1	2	10		
OG1	3	10		
OG1	4	9	90.0	1.4
OG2	1	0		
OG2	2	0		
OG2	3	0		
OG2	4	0	0.0	0.0
OG3	1	0		
OG3	2	0		
OG3	3	0		
OG3	4	0	0.0	0.0
OG4	1	0		
OG4	2	0		
OG4	3	0		
OG4	4	1	2.5	0.5
OG5	1	0		
OG5	2	0		
OG5	3	0		
OG5	4	0	0.0	0.0
OG6	1	Spilled		
OG6	2	8		
OG6	3	7		
OG6	4	8	76.7	0.6

Appendix Table 3. Survival of *C. dilutus* Exposed to Water Samples From Oak Grove, MN.

Treatment	Rep.	Survial	Average Survival (%)	Standard Deviation
Lab Water	1	10		
Lab Water	2	10		
Lab Water	3	10		
Lab Water	4	10	**100.0**	0.0
OGC	1	11		
OGC	2	10		
OGC	3	10		
OGC	4	10	**102.5**	0.5
OG1	1	9		
OG1	2	10		
OG1	3	10		
OG1	4	10	**97.5**	0.5
OG2	1	6		
OG2	2	7		
OG2	3	5		
OG2	4	7	**62.5**	1.0
OG3	1	11		
OG3	2	9		
OG3	3	8		
OG3	4	10	**95.0**	1.3
OG4	1	9		
OG4	2	11		
OG4	3	11		
OG4	4	7	**95.0**	1.9
OG5	1	4		
OG5	2	6		
OG5	3	5		
OG5	4	6	**52.5**	1.0
OG6	1	8		
OG6	2	10		
OG6	3	10		
OG6	4	10	**95.0**	1.0

Appendix Table 4. Survival and Reproduction of Ceriodaphnia dubia Exposed to Water Samples From Oak Grove, MN.

Treatment	Rep.	Survival	Average Survival (%)	Standard Deviation	Reproduction	Average Reproduction	Standard Deviation
Lab Water	1	1			10		
Lab Water	2	1			18		
Lab Water	3	1			15		
Lab Water	4	1			21		
Lab Water	5	1			24		
Lab Water	6	1			27		
Lab Water	7	1			21		
Lab Water	8	1			6		
Lab Water	9	1			18		
Lab Water	10	1	100.0	0.0	13	18.3	7.7
OGC	1	1			12		
OGC	2	0			0		
OGC	3	1			9		
OGC	4	1			17		
OGC	5	1			12		
OGC	6	1			11		
OGC	7	1			16		
OGC	8	0			13		
OGC	9	1			12		
OGC	10	0	70.0	0.5	0	10.2	5.8
OG1	1	1			20		
OG1	2	1			26		
OG1	3	1			17		
OG1	4	1			22		
OG1	5	0			0		
OG1	6	1			21		
OG1	7	1			19		
OG1	8	1			6		
OG1	9	1			20		
OG1	10	1	90.0	0.3	4	15.5	8.8
OG2	1	0			0		
OG2	2	0			0		
OG2	3	0			0		
OG2	4	0			0		
OG2	5	0			0		
OG2	6	0			0		
OG2	7	0			0		
OG2	8	0			0		
OG2	9	0			0		
OG2	10	0	0.0	0.0	0	0.0	0.0
OG3	1	0			0		
OG3	2	0			0		
OG3	3	1			0		
OG3	4	0			0		
OG3	5	0			0		
OG3	6	0			0		
OG3	7	0			0		
OG3	8	1			0		
OG3	9	0			0		
OG3	10	0	20.0	0.4	0	0.0	0.0
OG4	1	0			0		
OG4	2	0			0		
OG4	3	0			0		
OG4	4	0			0		
OG4	5	0			0		
OG4	6	0			0		
OG4	7	1			0		
OG4	8	0			0		
OG4	9	0			0		
OG4	10	0	10.0	0.3	0	0.0	0.0
OG5	1	0			0		
OG5	2	0			0		
OG5	3	0			0		
OG5	4	0			0		
OG5	5	0			0		
OG5	6	0			0		
OG5	7	0			0		
OG5	8	0			0		
OG5	9	0			0		
OG5	10	0	0.0	0.0	0	0.0	0.0
OG6	1	1			3		
OG6	2	1			0		
OG6	3	1			0		
OG6	4	1			4		
OG6	5	1			3		
OG6	6	1			0		
OG6	7	1			5		
OG6	8	1			0		
OG6	9	1			0		
OG6	10	1	100.0	0.0	0	1.5	2.0

APPENDIX L

LSRI REPORT, OCTOBER 2006

Toxicity Reduction Evaluation of Water From Tire Shreds, In Oak Grove, Minnesota.

By

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Final Report

To

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395 John Ireland Boulevard
St. Paul, Minnesota 55155-1899

(Robert Edstrom, Project Officer)

October 20th, 2006

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INTRODUCTION

The Lake Superior Research Institute (LSRI), University of Wisconsin-Superior, Superior, WI, contracted with the Minnesota Department of Transportation (MNDOT) to evaluate the toxicity of well water samples collected from Oak Grove, Minnesota. The study area groundwater maybe contaminated by exposure to tire shreds. The study site has been previously sampled for chemical analysis and toxicity evaluation of the groundwater. Sampling sites, identified by MNDOT, served as either a reference (OG1) or contaminated (OGC, OG2-5) site. LSRI was contracted to perform water-only toxicity tests using larval fathead minnows (*Pimephales promelas*) and the cladoceran *Ceriodaphnia dubia*. Assessment methods for toxicity have been utilized for many years and more recently, techniques to reduce or identify the cause of toxicity in wastewaters, ambient waters, and sediments have been developed and applied. A toxicity reduction evaluation (TRE) is a site-specific study conducted in a stepwise process designed to identify the causative agents of toxicity in an attempt to isolate the sources of toxicity and evaluate the effectiveness of toxicity control options (Norberg-King et al., 2001). A limited TRE approach was applied to the samples collected from the Oak Grove, Minnesota site.

METHODS

Sample Collection and Preparation

Water samples were collected on 25th of September 2006 and then again on 29th of September 2006 by MNDOT staff. The water samples were transported to LSRI in coolers on ice. Samples were received with minimal head-space. Prior to the collection of water samples, preliminary chemistry (temperature, dissolved oxygen, conductivity, and pH) field measurements were conducted by MNDOT staff at all sites. The morning after receipt of the water samples at LSRI, water chemistry was measured again on all of the samples. Water characteristics were measured for temperature, dissolved oxygen, conductivity, pH, alkalinity, and hardness (Appendix Table 1). The dissolved oxygen at all of the sites was below the initial acceptable criterion (U.S. EPA, 1993) of 4.0 mg/L except for OGC.

Each morning during the study, the cubitainers containing the water samples were removed from the refrigerator and shaken to homogenize the sample. Approximately 3.5 L of water was poured from the cubitainer into a 4 L glass jar. The jars containing the samples were placed into a water bath to bring the temperature of the samples to 25 ± 2.0°C. While the temperature was being adjusted to the temperature of the water used in the toxicity testing, the samples were aerated to bring the dissolved oxygen level to at least a minimum of 4 mg/L. The initial water samples that were received were used for the first four days (days 0 – 3) of the toxicity testing. New water samples from the same sample sites was received at LSRI on day 3. That water was used for the daily renewals starting on day 4 and through the remainder of the test.

Approximately 2.2 L of each water sample that had been temperature adjusted and aerated was vacuum filtered through glass fiber filters (Pall Corporation Type A/E, 1.0 µm retention). The water was filtered to remove particulates from the water samples. The majority of particles present in most of the samples were due to the formation of iron oxides/hydroxides formed when the water samples were exposed to air. Half of the filtered water was used in the toxicity tests and the other half was treated with zeolite to remove a portion of the ammonia present in the water samples. The zeolite treatment involved passing approximately 1.1 L of filtered water through a chromatography column (19 x 300 mm) containing 40 g of zeolite (Ammo Ammonia Remover, Aquarium Pharmaceuticals, Inc.). The zeolite was rinsed thoroughly with deionized water to remove the fine dust from the larger particles before transferring it into the chromatography column. A small plug of glass wool was added to the chromatography column before the zeolite was added to keep smaller zeolite particles from being washed from the column and into the treated water sample. After the zeolite was added to the column, deionized water was added and the column was tapped to remove trapped air bubbles. The flow rate through the column was adjusted to about 30 mL per minute using deionized water. The column was drained of deionized water, a small aliquot of the filtered water sample was used to rinse the column and then the filtered sample was added to the column. The column was again tapped to remove trapped air and the 1.1 L sample was passed through the zeolite column. The zeolite treated samples were used in another portion of the toxicity tests.

Samples were collected from each of the three fractions (aerated/baseline, filtered and zeolite treated) of the water samples for analysis of total iron and total ammonia daily. A 10 mL sample was collected and preserved with 1% nitric and 1% hydrochloric acids for analysis of total iron. The total ammonia samples were 25 mL preserved by the addition of sulfuric acid to a pH of less than 2. The preserved ammonia samples were refrigerated until they were analyzed. After the aeration, warming, and treatment of samples pH, total alkalinity, total hardness, and conductivity were measured (Appendix Table 1).

Sample Analysis

Sample analysis was conducted for the parameters listed below on samples collected from the daily renewal solutions before they were split and added to the *C. dubia* and fathead minnow exposure chambers. After counting and transferring the organisms to the renewal water, the "old" exposure solutions were composited by pouring the replicate exposure solutions from each site into pre-cleaned glass containers for the respective species. Samples were then collected from the composite samples for the analyses indicated below.

Total ammonia was analyzed using a gas sensing electrode (Orion ammonia electrode Model 95-12). Water samples were made basic (pH >11) by the addition of an ISA solution (ionic strength adjustor). The ISA solution contains sodium hydroxide, disodium EDTA and a trace amount of methanol. Addition of the ISA converts any ionized ammonia (NH_4^+) present in the sample to unionized ammonia (NH_3). The unionized ammonia diffuses through the gas permeable membrane of the ammonia electrode and changes the pH of the internal filling solution. An ammonia calibration curve was generated using six ammonium chloride standards. The concentration of total ammonia in the samples was calculated based on the ammonia calibration curve.

Total iron samples were analyzed by atomic absorption (AA) on a Varian SpectrAA 200 in the flame analysis mode. The analysis was conducted at the 248.3 nm wavelength. A calibration curve was developed utilizing five analytical standards containing known concentrations of iron and a reagent blank. Concentrations of total iron in the samples were determined by the AA instrument using this calibration curve.

Total alkalinity (as $CaCO_3$) was measured by adding a 25.0 mL sample to a 125 mL Erlenmeyer flask. The content of a Bromcresol Green-Methyl Red Indicator packet was added to the flask containing the sample. The sample was titrated with 0.020 N sulfuric acid. Total hardness (as $CaCO_3$) was measured by adding a 25.0 mL sample to be analyzed to a 125 mL Erlenmeyer flask. One mL (20 drops) of Hardness 1 Buffer Solution was added to the sample in the flask. The contents of a ManVer 2 Indicator packet was also added to the flask containing the sample. The sample was titrated with TitraVer (EDTA) titrant.

Static-Renewal Water-Only Toxicity Tests

Static-renewal water only tests were performed with two freshwater organisms; the larval fish *Pimephales promelas*, and the cladoceran *Ceriodaphnia dubia*. The objectives of these tests were to determine if the contaminants in the water were harmful to these organisms and if the treatments (filtering and zeolite) would decrease the toxicity when compared to the baseline test. Survival and growth were the endpoints for the fathead minnow while survival and reproduction were the endpoints for the *C. dubia* test. The LSRI Standard Operating Procedures, "Conducting a 48-hour and 96-hour Renewal Test with Fathead Minnows (AT/4)," "Conducting Early-Life Stage Toxicity Tests with a Fathead Minnow *Pimephales promelas* (AT/1)," and "Conducting Renewal Chronic Toxicity Tests with *Daphnia magna* (AT/3)," are based upon EPA methods (U.S. EPA, 2000) and adapted for use in this project. Briefly, the tests were initiated with juvenile life-stage organisms. *Pimephales promelas* were 7 days old, and the *Ceriodpahnia dubia* were <24 hours-old. The tests were performed at nominal temperatures of 25.0 ± 2.0 °C and the test water was renewed daily (See Appendix Table 1).

The fathead minnow tests daily renewal occurred by gently pouring off 80% of overlying water into a composite container from each replicate. Surviving adults were counted and data recorded on study data sheets. New exposure water was added by gently pouring the water down the side of the exposure beaker that was tipped slightly. This ensured that the animals were not damaged during the renewal process.

The *C. dubia* tests daily renewal occurred by first counting surviving adult and young produced. Data was recorded on project data sheets. Adults were transferred by a large bore pipette to corresponding exposure cups containing the renewal solution.

The replicate beakers (3 for fatheads and 10 for *C. dubia*) were fed equal volumes of food. *C. dubia* received 0.1 mL daily of a yeast, Cerophyll®, and trout chow mixture containing 1800 mg/L total suspended solids and 0.1 mL *Selenastrum* algae at $1.0* 10^8$ cells/mL. Fathead minnows were fed twice daily, six hours apart, 0.15 g (1000-1500 nauplii) of newly hatched (less than 24-h old) brine shrimp nauplii.

During the tests, measurements were taken for temperature and dissolved oxygen daily on the renewal solutions and the composited "old" exposure solutions. The pH was measured on days 1, 3, 5, and 7 in the renewal solutions and composited "old" exposure solutions. Alkalinity, hardness, and conductivity were measured on day 0 and 4 on the renewal water samples (Appendix Table 1) and then on day 4 and 7 for the composited "old" exposure water (Appendix Table 1).

Statistical Analysis

Analysis of variance (ANOVA) procedures were used to make comparisons between the control and treatment survival. SigmaStat® software procedures were used to perform all the statistical computations. If the data met assumptions of normality and homogeneity of variance, then parametric procedures were used. First, an ANOVA was performed followed by mean comparisons using Tukey's test. Non-normal data were transformed using the arc-sine transformation (U.S. EPA, 1993) to meet the normality and homogeneity of variance requirements. If transformed data did not meet the normality and homogeneity of variance assumptions, analysis on ranks was conducted. Mean percent survivals and mean reproduction were analyzed with a statistical significance level of α=0.05.

Quality Assurance/Quality Control (QA/QC)

Toxicity tests were initiated with healthy, vigorous animals. Reference toxicant tests were performed with test species prior to the start of the definitive test and data is available upon request. In the toxicity test, percent survival in the laboratory controls were compared to published test acceptability criteria (U.S. EPA, 1993) to determine overall performance of the animals and the test system. Test conditions were monitored daily for parameters that might affect the outcome of the test (i.e., temperature and dissolved oxygen). Daily and weekly calibration of test meters ensured optimal performance. Reference standards and duplicate samples were used in the analysis of iron, ammonia, alkalinity, and hardness. Any deviations were discussed with the principal investigator and documented in the study notebook. The studies were conducted with a high degree of quality assurance/quality control criteria. The QC/QA documentation was noted on the raw data sheets and study notebooks.

RESULTS

Pimephales promelas 7-day Static-Renewal Water-Only Toxicity Test

Mean percent survival during the 7 days of exposure was high (93.3, 86.7-96.7, and 96.7-100 percent, respectively) for animals exposed to the performance control, the reference water, and the method blanks (Table 1) and met published acceptance criteria of greater than 80 percent survival (U.S. EPA 1993). Animals exposed to the treatments had a mean survival range of 0-93.3 percent (Table 1). Treatments OG2 baseline, OG2 filtered, OG5 baseline, and OG5 filtered had zero percent survival by the second day (Table 3). Toxicity was reduced in the OG2 and OG5 zeolite treatments; however, by the end of the seventh day survival was significantly ($p < 0.05$) reduced when compared to the performance control and reference site OG1 (Table 1 and 3). Survival was significantly ($p < 0.05$) reduced in treatments OG3 filtered, OG3 zeolite, OG4 baseline, and OG4 filtered when compared to the performance water control (Table 1). OG4 zeolite survival was not significantly reduced when compared to the performance control and reference site. OG4 zeolite showed a reduction in toxicity when compared to the OG4 baseline and OG4 filtered treatments.

The growth endpoint met the published acceptance criteria of dry weight greater than 0.25 mg in the performance control. Growth was significantly ($p < 0.05$) reduced when compared to the performance control and OG1 baseline in treatments OG3 baseline, OG4 filtered, and OG5 zeolite (Table 1).

Ceriodaphnia dubia Survival and Reproduction Static-Renewal Water-Only Toxicity Test

Mean percent survival during the 7 days of exposure was high (90 percent) for animals exposed in the performance control (Table 2). The performance control met the published acceptance criteria of greater than 80% survival (U.S. EPA, 2000). The reference site OG1 baseline had poor survival of 30% (Table 2). Animals exposed to the treatments had a range of mean survivals from 0-100 percent (Table 2). Sites OG2 (filtered and zeolite) and OG5 (all treatments) had complete mortality by the end of seven days (Table 2 and 4). Survival was significantly ($p < 0.05$) reduced in sites OG2 baseline, OG2 filtered, OG2 zeolite, OG3 baseline, OG3 filtered, OG3 zeolite, OG4 baseline, OG5 baseline, OG5 filtered, and OG5 zeolite when compared to the performance control (Table 2). It appears that treatments OG4 filtered and OG4 zeolite reduced the toxicity when compared to the baseline (Table 4).

Reproduction was an average total of 8.9 young in the performance ~~lab~~ control while the reference site OG1 baseline had an average total of 6.7 young (Table 2). Treatments OG3 baseline, OG3 filtered, and OG3 zeolite had 30-50 percent survival but had no reproduction (Table 2). Site OG4 filtered and OG4 zeolite also had no reproduction but had 90 and 80 percent survival, respectively (Table 2).

Analytical results for Iron and Ammonia

The exposure of most of the samples (OG2 – OG6) to air caused the formation of a large amount of orangish-brown colored precipitate. Based on the iron content of these samples, the majority of the precipitate was presumably due to oxides of iron being formed. As part of the treatment of samples in preparation for the toxicity exposures, an aliquot of all samples was filtered through glass fiber filters to remove particles present in the aerated samples. During the filtering process, several of the samples (OG2 and OG5) were noted to have produced a foamy layer on top of the filtered sample being collected in the filtration flask. The filtered water from site OG4 also produced some foaming but less than was noted for site OG2 and OG5.

The aerated samples that contained a significant amount of the orangish-brown colored precipitate were found to have a major reduction (97.0 – 99.7%) in the average total iron content of the filtered samples as compared to their mean baseline iron content (Table 5). The two samples that didn't have an obvious orangish-brown colored precipitate (OG1 and OGC) had lower average total iron contents in the baseline samples but also had significant amounts (88.3 – 96.6%) of total iron removed by the filtration process. The zeolite treatment of the filtered water was used to remove ammonia from the filtered water. Zeolite, because of its ion exchange capability, removed some additional iron from the filtered samples (Table 5).

Comparing the mean total iron content of the "new" samples for each treatment type with the average total iron present in the composited "old" samples indicates that iron was lost over the 24 hour exposure period for which each of the solutions was used (Table 5). This loss was greatest in the fathead baseline samples. A majority of this loss can be explained in how the "old" samples were obtained. Approximately 80% of the 24 hour old solutions were carefully poured out of the exposure beakers and into the compositing container so as not to remove any of the larval fish. This careful siphoning allowed the iron oxide precipitate that had formed upon aeration to remain in the bottom of the exposure beaker. The composite "old" samples from the *C. dubia* exposures were prepared by pouring the water from the cup in which the organism had been exposed into the compositing beaker. This transfer allowed some of the iron oxide to be transferred to the composite "old" sample. This difference in the way the "old " composite samples were prepared resulted in the "old" baseline samples from the *C. dubia* exposures having higher total iron contents than those from the fathead exposures for most of the samples. The values obtained for the "old" fathead samples are probably more accurate in regard to the amount of total iron present in the water column.

Following filtering of the samples, a 1.1 L aliquot was treated by passing the water through a chromatography column containing zeolite. The zeolite treatment reduced the mean total ammonia content of the filtered samples by 45.1 – 80.7% (Table 5). The percent reduction in the total ammonia content was greatest (73.0 – 80.7%) for the samples with the lowest total ammonia content (OG1, OG6 and OGC). Sites OG2 and OG5 had the highest total ammonia contents and had the smallest percentage reduction (50.4 and 45.1%, respectively) in ammonia due to the zeolite treatment.

Sites with lowest total ammonia content (OG1 and OGC) showed similar ammonia concentrations in the "new" and "old" samples for *C.dubia* for all treatments. The "old" samples from the fathead exposures tended to be slightly elevated in ammonia content probably due to the waste products produced by the larval fish. Sites with higher total ammonia contents were found to have reduced ammonia levels in the "old" samples as compared to the "new" samples for most treatments.

Duplicate and spiked samples were analyzed for total ammonia and total iron content for a number of samples (Appendix Table 4). The results for the total iron analysis were good for both the duplicates (RPD = 6.1 ± 10.0%) and the spike recovery (90.6 ± 8.0%). The relative percent difference (RPD) was not able to be calculated (NC) for a number of samples because either one or both of the samples had a value less than the detection limit. For the spiked samples, if the original sample had a value of less than the detection limit, a value of 0.02 mg/L was used for the original sample in the calculation of spike recovery. The duplicate ammonia samples had a mean RPD of 10.9 ± 17.4% and a mean spike recovery of 132.8 ± 67.7% (Appendix Table 4). During the ammonia analysis, it was noted that the samples from sites OG2 and OG5 took much longer to give a complete response than for the other samples. These sites had the highest reported total ammonia contents. Several of the QC samples from site OG2 and OG5 gave results that were much different from the other QC samples. These poor QC results and the much longer response time for samples from these sites cause some uncertainty about the accuracy of the total ammonia results for sites OG2 and OG5.

CONCLUSIONS

contracted with Minnesota Department of Transportation to evaluate the toxicity of water collected from sites in Oak Grove, MN. The study sites were designated as a reference (Site OG1) or contaminated (OG2-OG6 and OGC) sites. A toxicity reduction evaluation (TRE) is a site-specific study conducted in a stepwise process designed to identify the causative agents of toxicity, in an attempt to isolate the sources of that toxicity (Norberg-King et al., 2001). A TRE approach was used here. Based on previous chemistry samples (results provided by MNDOT) and results from earlier toxicity testing (February, 2006) it was decided that ammonia and iron maybe the likely constituents causing toxicity. The treatments as described above were selected to remove or reduce those chemical components in an attempt to reduce toxicity.

The TRE treatments employed were effective in reducing both the iron and ammonia concentrations of the treated samples. Filtration of the samples removed more than 88% of the total iron present in all of the study samples. Based on the previous toxicity study (February, 2006) with waters from these sites, it was believed that the iron oxide precipitate may have been causing or at least contributing to the observed toxicity in those samples exhibiting large amounts of precipitate. Some of the precipitate seemed to adhere to the organisms and it was felt that this might interfere with some normal biological functions. Based on the results of this study, that idea would not seem to be supported except for possibly the *C. dubia* exposure to water from site OG4. The percent survival in the baseline sample was 0%; whereas the survival in the filtered water exposure was 90%. For most of the fathead and *C.dubia* exposures the survival in the baseline and filtered samples were similar. The survival of fatheads in the OG3 filtered sample (6.7%) was substantially lower than in the baseline sample (63.3%). In this sample it would appear that the iron in the baseline sample may have provided some protection for the organisms.

Filtering did not have a significant impact on the total ammonia concentrations of the samples. Treatment of the filtered samples with zeolite was effective in removing between 45 and 81% of the total ammonia. The zeolite treatment also resulted in an increase in the pH of the treated samples. Toxicity of ammonia to aquatic organisms is mainly due to the presence of unionized ammonia (NH_3). The unionized ammonia LC_{50} for larval fathead minnows ranges from 0.75 to 1.5 mg/L (Ambient Water Quality Criteria for Ammonia – 1984). The percentage of ammonia that exists in the unionized form is determined mainly by the pH of the solution. As the pH increases, so does the percentage of ammonia that is present in the unionized form. Temperature also impacts the form in which ammonia exists in water. An increase in temperature also increases the percent of unionized ammonia present. Even though several of the tested sites (OG2, OG3, OG4, OG5 and OG6) had high levels of total ammonia, the unionized ammonia concentrations of many of the exposure solutions were not likely high enough to cause acute toxicity (Table 6).

The short-term chronic tests used here to measure effects are relatively sensitive and are designed to evaluate the toxicity of mixtures entering surface water ecosystems. These tests provide representative estimates of the potential effects on fish and invertebrates (Sheehan et al., 2006).

With the *Pimephales promelas* test species, survival was significantly reduced in the OG2 baseline, OG2 filtered, and OG2 zeolite samples by the end of the seven day exposure. The iron was below detection in both TRE treatments in the renewal samples and the "old" exposures. No reduction of ammonia was noticed in the filtered samples; however, ammonia was reduced by almost half in these samples using the zeolite treatment. It was also observed at the 24 hour time period that the fathead minnow survival was 10.0 percent in the baseline test, zero percent in the filtered test and 73.3 percent in the zeolite treated sample. A possible reason for this increase in survival at 24 hours may be due to the reduction of the ammonia concentration. Similar observations were also noted in well samples OG3, OG4, and OG5. While the above ground sample, OGC, and wells OG1 and OG6 exhibited no significant reduction in survival at the end of seven days.

A significant reduction in survival was observed in the *Ceriodaphnia dubia* test species at sites OG1 (reference site), OG2, OG3, and OG5 when compared to the performance control. No difference in survival was detected between the baseline samples and the TRE treated samples for those sites. OG4 baseline had zero percent survival at the end of seven days while OG4 filtered and OG4 zeolite had survival greater than 80 percent. It was interesting to observe that treatments OG4 filtered and OG4 zeolite had survival greater than 80% but no reproduction. Well OG6 and above ground site, OGC, had high survival and reproduction.

The results of this study indicate that the removal of significant amounts of iron and/or ammonia from the waters provided for the study didn't provide significantly increased survival at any of the sites except OG4. This suggests that there are other contaminants present in the samples that are contributing to the toxicity and reduction in reproduction noted in this study. The two sites with the lowest survival for both fatheads and *C. dubia* and displayed no reproduction for *C. dubia* were site OG2 and OG5. These were the two sites that had noted foaming of the samples when the filtering process was conducted. The chemicals responsible for this foaming may have been significant contributors to the reduction in survival and reproduction. Additional TRE treatments may be successful in helping to identify the class of chemicals not removed by the treatments used in this study that are causing the remaining toxicity and reduction in reproduction.

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Table 1. Mean survival and dry weight of *Pimephales promelas* exposed to water from Oak Grove, MN. Standard deviations are in ( ).

Treatment	Average Percent Survival	Average Dry Weight (mg)
Performance Control	93.3 (5.8)	0.594 (0.102)
Method Blank Baseline	96.7 (5.8)	0.624 (0.015)
Method Blank Filtered	100 (0.0)	0.597 (0.046)
Method Blank Zeolite	96.7 (5.8)	0.606 (0.067)
OG1 Baseline	96.7 (5.8)	0.576 (0.041)
OG1 Filtered	86.7 (11.5)	0.633 (0.088)
OG1 Zeolite	96.7 (5.8)	0.500 (0.077)
OG2 Baseline	0.0 (0.0)[ab]	
OG2 Filtered	0.0 (0.0)[ab]	
OG2 Zeolite	0.0 (0.0)[ab]	
OG3 Baseline	63.3 (15.3)	0.340 (0.057)[ab]
OG3 Filtered	6.7 (11.5)[ab]	0.300 (undefined)
OG3 Zeolite	40.0 (26.5)[b]	0.463 (0.092)
OG4 Baseline	30.0 (20.0)[ab]	0.369 (0.030)
OG4 Filtered	16.7 (5.8)[ab]	0.250 (0.050)[ab]
OG4 Zeolite	70.0 (36.1)	0.416 (0.044)
OG5 Baseline	0.0 (0.0)[ab]	
OG5 Filtered	0.0 (0.0)[ab]	
OG5 Zeolite	3.3 (5.8)[ab]	0.200 (undefined)[ab]
OG6 Baseline	86.7 (23.1)	0.434 (0.047)
OG6 Filtered	76.7 (5.8)	0.601 (0.068)
OG6 Zeolite	50.0 (36.1)	0.630 (0.132)
OGC Baseline	90.0 (10.0)	0.500 (0.046)
OGC Filtered	86.7 (11.5)	0.612 (0.134)
OGC Zeolite	93.3 (11.5)	0.560 (0.017)

[a] Survival or growth significantly ($p < 0.05$) reduced relative to the performance control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

[b] Survival or growth significantly ($p < 0.05$) reduced relative to the OG1 reference by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

Table 2. Mean survival and reproduction of *Ceriodaphnia dubia* exposed to water from Oak Grove, MN. Standard deviations are in ().

Treatment	Average Percent Survival	Average Young
Performance Control	90.0 (31.6)	8.9 (6.3)
Method Blank Baseline	80 (42.2)	6.7 (7.3)
Method Blank Filtered	80 (42.2)	5.5 (7.7)
Method Blank Zeolite	90.0 (31.6)	11.0 (7.8)
OG1 Baseline	30 (48.3)[a]	6.7 (5.1)
OG1 Filtered	10 (31.6)[a]	0.3 (0.7)[a]
OG1 Zeolite	10 (31.6)[a]	2.8 (3.6)
OG2 Baseline	10 (31.6)[a]	0.0 (0.0)[a]
OG2 Filtered	0.0 (0.0)[a]	
OG2 Zeolite	0.0 (0.0)[a]	
OG3 Baseline	30 (48.3)[a]	0.0 (0.0)[a]
OG3 Filtered	50 (52.7)[a]	0.0 (0.0)[a]
OG3 Zeolite	30 (48.3)[a]	0.0 (0.0)[a]
OG4 Baseline	0.0 (0.0)[a]	
OG4 Filtered	90.0 (31.6)	0.0 (0.0)[a]
OG4 Zeolite	80 (42.2)	0.0 (0.0)[a]
OG5 Baseline	0.0 (0.0)[a]	
OG5 Filtered	0.0 (0.0)[a]	
OG5 Zeolite	0.0 (0.0)[a]	
OG6 Baseline	80 (42.2)	2.0 (1.9)
OG6 Filtered	100 (0.0)	7.2 (7.1)
OG6 Zeolite	100 (0.0)	3.7 (3.8)
OGC Baseline	70 (48.3)	7.1 (4.8)
OGC Filtered	90.0 (31.6)	5.5 (6.4)
OGC Zeolite	90.0 (31.6)	15.7 (9.8)

[a] Survival or reproduction significantly ($p < 0.05$) reduced relative to the performance control by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

[b] Survival or reproduction significantly ($p < 0.05$) reduced relative to the OG1 reference by one-way ANOVA and Tukey's pairwise comparisons of the mean responses.

Table 3. Mean (standard deviation) percent survival for larval fatheads exposed to Oak Grove, MN. Tire shred well samples over 7 days.

		Day						
		1	2	3	4	5	6	7
Performance Control		100 (0.0)	100 (0.0)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	93.3 (5.8)	93.3 (5.8)
Method Blank Control	**Baseline**	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)
	Filtered	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)
	Baseline	100 (0.0)	100 (0.0)	100 (0.0)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)
	Filtered	93.3 (11.5)	90.0 (10.0)	90.0 (10.0)	90.0 (10.0)	86.7 (11.5)	86.7 (11.5)	86.7 (11.5)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	96.7 (5.8)	96.7 (5.8)
OG2	**Baseline**	10.0 (10.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Filtered	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Zeolite	73.3 (20.8)	20.0 (17.3)	10.0 (10.0)	10.0 (10.0)	6.7 (5.8)	3.3 (5.8)	0.0 (0.0)
OG3	**Baseline**	73.3 (15.3)	70.0 (10.0)	66.7 (11.5)	66.7 (11.5)	66.7 (11.5)	63.3 (15.3)	63.3 (15.3)
	Filtered	76.7 (15.3)	66.7 (25.2)	63.3 (25.2)	63.3 (25.2)	46.7 (28.9)	30.0 (36.1)	6.7 (11.5)
	Zeolite	100 (0.0)	100 (0.0)	93.3 (5.8)	90.0 (0.0)	50.0 (26.5)	46.7 (30.6)	40.0 (26.5)
OG4	**Baseline**	43.3 (15.3)	33.3 (20.8)	30.0 (20.0)	30.0 (20.0)	26.7 (15.3)	26.7 (15.3)	30.0 (20.0)
	Filtered	43.3 (20.8)	36.7 (15.3)	33.3 (11.5)	30.0 (10.0)	26.7 (11.5)	20.0 (0.0)	16.7 (5.8)
	Zeolite	100 (0.0)	86.7 (23.1)	83.3 (28.9)	83.3 (28.9)	80.0 (26.5)	73.3 (30.6)	70.0 (36.1)
OG5	**Baseline**	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Filtered	3.3 (5.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Zeolite	73.3 (5.8)	23.3 (25.2)	23.3 (25.2)	23.3 (25.2)	23.3 (25.2)	20.0 (26.5)	3.3 (5.8)
	Baseline	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (17.3)	86.7 (23.1)
	Filtered	100 (0.0)	96.7 (5.8)	90.0 (0.0)	90.0 (0.0)	86.7 (5.8)	86.7 (5.8)	76.7 (5.8)
	Zeolite	96.7 (5.8)	96.7 (5.8)	93.3 (5.8)	93.3 (5.8)	83.3 (5.8)	70.0 (26.5)	50.0 (36.1)
OG6	**Baseline**	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	96.7 (5.8)	90.0 (10.0)	90.0 (10.0)	90.0 (10.0)
	Filtered	100 (0.0)	93.3 (5.8)	93.3 (5.8)	93.3 (5.8)	90.0 (10.0)	90.0 (10.0)	86.7 (11.5)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	96.7 (5.8)	96.7 (5.8)	93.3 (11.5)	93.3 (11.5)

Table 4. Mean (standard deviation) percent survival for *C. dubia* exposed to Oak Grove, MN. tire shred well samples over 7 days.

		Day						
		1	2	3	4	5	6	7
Performance Control		100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)
Method Blank Control	**Baseline**	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)	90.0 (31.6)	80 (42.2)	80 (42.2)
	Filtered	90.0 (31.6)	90.0 (31.6)	90.0 (31.6)	90.0 (31.6)	80 (42.2)	80 (42.2)	80 (42.2)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)
OG1	**Baseline**	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	60 (51.6)	40 (51.6)	30 (48.3)
	Filtered	100 (0.0)	90.0 (31.6)	80 (42.2)	50 (52.7)	20 (42.2)	20 (42.2)	10 (31.6)
	Zeolite	100 (0.0)	100 (0.0)	80 (42.2)	60 (51.6)	30 (48.3)	20 (42.2)	10 (31.6)
OG2	**Baseline**	40 (51.6)	10 (31.6)	10 (31.6)	10 (31.6)	10 (31.6)	10 (31.6)	10 (31.6)
	Filtered	60 (51.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Zeolite	50 (52.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
OG3	**Baseline**	100 (0.0)	80 (42.2)	50 (52.7)	40 (51.6)	30 (48.3)	30 (48.3)	30 (48.3)
	Filtered	80 (42.2)	70 (48.3)	70 (48.3)	60 (51.6)	60 (51.6)	50 (52.7)	50 (52.7)
	Zeolite	100 (0.0)	90.0 (31.6)	40 (51.6)	40 (51.6)	40 (51.6)	30 (48.3)	30 (48.3)
OG4	**Baseline**	70 (48.3)	50 (52.7)	40 (51.6)	30 (48.3)	30 (48.3)	0.0 (0.0)	0.0 (0.0)
	Filtered	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)	90.0 (31.6)
	Zeolite	100 (0.0)	80 (42.2)	80 (42.2)	80 (42.2)	80 (42.2)	80 (42.2)	80 (42.2)
OG5	**Baseline**	70 (48.3)	20 (42.2)	10 (31.6)	10 (31.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Filtered	70 (48.3)	10 (31.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	Zeolite	70 (48.3)	20 (42.2)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
OG6	**Baseline**	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	80 (42.2)
	Filtered	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)
OGC	**Baseline**	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	80 (42.2)	70 (48.3)
	Filtered	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)
	Zeolite	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	100 (0.0)	90.0 (31.6)	90.0 (31.6)

Table 5. Mean and standard deviation (std) of total iron and total ammonia analysis.

Sample ID	Mean Total Iron (mg/L)	Std	Mean Total Ammonia (mg/L)	Std
PC Baseline-New	<0.04	<0.04	<0.063	<0.063
PC Baseline-Old *C. dubia*	<0.04	<0.04	0.19	0.08
PC Baseline-Old Fathead	<0.04	<0.04	0.55	0.13
MBC Baseline-New	<0.04	<0.04	<0.063	<0.063
MBC Baseline-Old *C. dubia*	<0.04	<0.04	0.47	0.10
MBC Baseline-Old Fathead	<0.04	<0.04	0.51	0.20
MBC Filtered-New	<0.04	<0.04	<0.063	<0.063
MBC Filtered-Old *C. dubia*	0.07	0.12	0.45	0.65
MBC Filtered-Old Fathead	<0.04	<0.04	0.51	0.19
MBC Zeolite-New	<0.04	<0.04	<0.063	<0.063
MBC Zeolite-Old *C. dubia*	0.05	0.06	0.20	0.15
MBC Zeolite-Old Fathead	<0.04	<0.04	0.53	0.29
OG1 Baseline-New	1.48	1.25	0.31	0.04
OG1 Baseline-Old *C. dubia*	0.31	0.17	0.36	0.12
OG1 Baseline-Old Fathead	0.39	0.20	0.67	0.14
OG1 Filtered-New	0.05	<0.04	0.30	0.03
OG1 Filtered-Old *C. dubia*	0.05	0.06	0.31	0.13
OG1 Filtered-Old Fathead	0.05	0.04	0.77	0.15
OG1 Zeolite-New	0.04	<0.04	0.08	0.02
OG1 Zeolite-Old *C. dubia*	<0.04	<0.04	0.15	0.14
OG1 Zeolite-Old Fathead	<0.04	<0.04	0.49	0.07
OG2 Baseline-New	12.96	7.21	33.34	18.38
OG2 Baseline-Old *C. dubia*	7.63	6.70	23.70	10.21
OG2 Baseline-Old Fathead	3.28	0.47	22.65	11.24
OG2 Filtered-New	0.05	0.05	30.20	16.15
OG2 Filtered-Old *C. dubia*	<0.04	<0.04	24.15	11.24
OG2 Filtered-Old Fathead	<0.04	<0.04	23.90	Undefined
OG2 Zeolite-New	<0.04	<0.04	14.98	10.46
OG2 Zeolite-Old *C. dubia*	<0.04	<0.04	10.62	4.22
OG2 Zeolite-Old Fathead	<0.04	<0.04	9.66	2.61
OG3 Baseline-New	49.96	24.99	16.73	5.05
OG3 Baseline-Old *C. dubia*	30.65	27.56	8.62	2.67
OG3 Baseline-Old Fathead	2.77	1.27	12.17	2.46
OG3 Filtered-New	1.43	2.39	14.56	2.60
OG3 Filtered-Old *C. dubia*	0.19	0.12	9.49	2.52
OG3 Filtered-Old Fathead	0.46	0.49	11.21	1.65
OG3 Zeolite-New	0.79	1.28	4.67	0.69
OG3 Zeolite-Old *C. dubia*	0.13	0.08	2.48	0.56
OG3 Zeolite-Old Fathead	0.28	0.29	4.25	0.53

Table 5 continued. Mean and standard deviation (std) of total iron and total ammonia analysis

Sample ID	Mean Total Iron (mg/L)	Std	Mean Total Ammonia (mg/L)	Std
OG4 Baseline-New	40.47	13.11	13.77	1.22
OG4 Baseline-Old C. dubia	19.45	14.30	9.42	1.89
OG4 Baseline-Old Fathead	1.36	0.87	11.03	1.60
OG4 Filtered-New	0.31	0.42	14.24	2.16
OG4 Filtered-Old C. dubia	0.11	0.08	9.29	2.80
OG4 Filtered-Old Fathead	0.17	0.17	11.94	1.02
OG4 Zeolite-New	0.25	0.25	5.96	2.39
OG4 Zeolite-Old C. dubia	0.10	0.06	3.36	
OG4 Zeolite-Old Fathead	0.14	0.10	4.58	
OG5 Baseline-New	14.41	3.88	28.79	15.61
OG5 Baseline-Old C. dubia	5.44	7.25	26.70	15.18
OG5 Baseline-Old Fathead	11.30	Undefined	25.40	Undefined
OG5 Filtered-New	0.04	<0.04	28.03	
OG5 Filtered-Old C. dubia	<0.04	<0.04	33.70	25.46
OG5 Filtered-Old Fathead	<0.04	<0.04	22.56	11.81
OG5 Zeolite-New	0.04	<0.04	15.38	
OG5 Zeolite-Old C. dubia	<0.04	<0.04	14.74	16.35
OG5 Zeolite-Old Fathead	0.05	0.06	8.99	4.94
OG6 Baseline-New	93.49	26.94	4.39	0.88
OG6 Baseline-Old C. dubia	36.66	22.85	2.42	0.67
OG6 Baseline-Old Fathead	1.97	1.07	3.66	
OG6 Filtered-New	0.55	0.83	3.93	0.68
OG6 Filtered-Old C. dubia	0.11	0.13	2.36	0.76
OG6 Filtered-Old Fathead	0.49	0.18	3.42	0.62
OG6 Zeolite-New	0.33	0.49	1.06	0.25
OG6 Zeolite-Old C. dubia	0.07	0.08	0.64	0.31
OG6 Zeolite-Old Fathead	0.11	0.13	1.46	0.23
OGC Baseline-New	2.65	1.94	0.57	0.11
OGC Baseline-Old C. dubia	1.31	1.33	0.32	0.14
OGC Baseline-Old Fathead	0.39	0.13	0.46	0.34
OGC Filtered-New	0.31	0.04	0.57	0.11
OGC Filtered-Old C. dubia	0.23	0.06	0.83	0.14
OGC Filtered-Old Fathead	0.21	0.06	0.76	0.12
OGC Zeolite-New	0.32	0.03	0.11	0.02
OGC Zeolite-Old C. dubia	0.24	0.04	0.93	0.55
OGC Zeolite-Old Fathead	0.22	0.07	0.50	0.08

Table 6. Calculated unionized ammonia concentrations for "old" exposure solutions.

Sample ID	Mean Total NH3 (mg/L)	% Unionized	Unionized NH3 (mg/L)*
OG1 Baseline-Old Fathead	0.678	7.3	0.05
OG1 Filtered-Old Fathead	0.766	8.1	0.06
OG1 Zeolite-Old Fathead	0.493	8.4	0.04
OG2 Baseline-Old Fathead	22.7	3.5	0.79
OG2 Filtered-Old Fathead	23.9	-	-
OG2 Zeolite-Old Fathead	9.66	4.0	0.39
OG3 Baseline-Old Fathead	12.2	6.4	0.78
OG3 Filtered-Old Fathead	11.2	7.7	0.86
OG3 Zeolite-Old Fathead	4.25	8.6	0.37
OG4 Baseline-Old Fathead	11.0	6.6	0.62
OG4 Filtered-Old Fathead	11.9	7.3	0.87
OG4 Zeolite-Old Fathead	4.58	8.1	0.37
OG5 Baseline-Old Fathead	25.4	-	-
OG5 Filtered-Old Fathead	22.6	5.7	1.29
OG5 Zeolite-Old Fathead	8.99	4.5	0.40
OG6 Baseline-Old Fathead	3.66	6.2	0.23
OG6 Filtered-Old Fathead	3.42	9.0	0.31
OG6 Zeolite-Old Fathead	1.46	9.3	0.14
OGC Baseline-Old Fathead	0.461	6.2	0.03
OGC Filtered-Old Fathead	0.763	7.4	0.06
OGC Zeolite-Old Fathead	0.503	6.8	0.03
OG1 Baseline-Old C. dubia	0.358	12.7	0.05
OG1 Filtered-Old C. dubia	0.308	11.5	0.04
OG1 Zeolite-Old C. dubia	0.148	12.7	0.02
OG2 Baseline-Old C. dubia	23.7	6.2	1.47
OG2 Filtered-Old C. dubia	24.2	9.5	2.29
OG2 Zeolite-Old C. dubia	10.6	9.7	1.03
OG3 Baseline-Old C. dubia	8.62	11.3	0.97
OG3 Filtered-Old C. dubia	9.49	12.7	1.21
OG3 Zeolite-Old C. dubia	2.46	15.2	
OG4 Baseline-Old C. dubia	9.42	11	1.04
OG4 Filtered-Old C. dubia	9.29	13	1.21
OG4 Zeolite-Old C. dubia	3.36	15.5	0.52
OG5 Baseline-Old C. dubia	26.7	10.4	2.78
OG5 Filtered-Old C. dubia	33.7	10.4	3.50
OG5 Zeolite-Old C. dubia	14.7	12.0	1.77
OG6 Baseline-Old C. dubia	2.42	12.5	0.30
OG6 Filtered-Old C. dubia	2.36	14.3	0.34
OG6 Zeolite-Old C. dubia	0.636	15.8	0.10
OGC Baseline-Old C. dubia	0.318	14	0.04
OGC Filtered-Old C. dubia	0.326	16.4	0.05
OGC Zeolite-Old C. dubia	0.331	14.9	0.05

* Unionized ammonia calculated based on mean pH of "old" solutions and using a mean temperature of 23°C.

Appendix Table 1

Daily Water Characteristic Measurements

Appendix Table 1. Daily water characteristic measurements (temperature, dissolved oxygen, pH, conductivity, alkalinity, and hardness).

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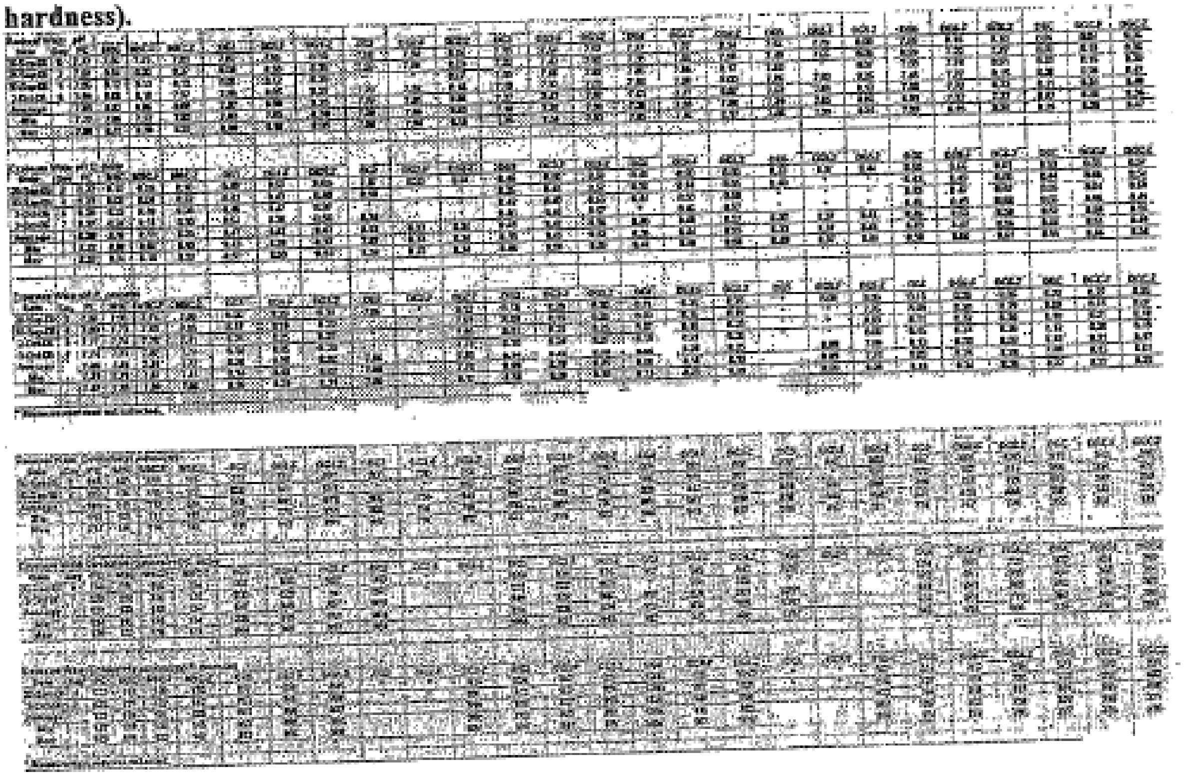
Appendix Table 1 continued. Daily water characteristic measurements (temperature, dissolved oxygen, pH, conductivity, alkalinity, and hardness).



Appendix Table 1 continued. Daily water characteristic measurements (temperature, dissolved oxygen, pH, conductivity, alkalinity, and hardness).

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Appendix 2

Daily Ammonia Measurements

Appendix Table 2. Total ammonia measurements for *C. dubia* and *P. promelas* exposed to tire shred water samples from Oak Grove, MN.

Sample ID	Day 0 (mg/L)	Day 1 (mg/L)	Day 2 (mg/L)	Day 3 (mg/L)	Day 4 (mg/L)	Day 5 (mg/L)	Day 6 (mg/L)	Day 7 (mg/L)	Mean	Std. Dev.	Min	Max
PC Baseline-New	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063		<0.063	<0.063	<0.063	<0.063
MBC Baseline-New	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063		<0.063	<0.063	<0.063	<0.063
MBC Filtered-New	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063		<0.063	<0.063	<0.063	<0.063
MBC Zeolite-New	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063	<0.063		<0.063	<0.063	<0.063	<0.063
OG1 Baseline-New	0.279	0.352	0.267	0.324	0.309	0.330	0.312		0.326	0.035	0.267	0.352
OG1 Filtered-New	0.288	0.308	0.299	0.293	0.304	0.328	0.346		0.321	0.020	0.294	0.346
OG1 Zeolite-New	0.071	0.069	0.079	0.091	0.069	0.110	<0.063		0.078	0.016	<0.063	0.110
OG2 Baseline-New	62.6	27.6	28.8	19.9	18.7	18.0	25.3		28.3	16.2	18.7	65.0
OG2 Filtered-New	57.1	33.5	19.2	23.0	16.2	49.5	24.8		30.9	16.2	16.2	57.1
OG2 Zeolite-New	34.3	17.4	5.78	5.79	11.0	22.4	7.67		15.0	10.6	5.78	34.3
OG3 Baseline-New	24.0	21.6	10.3	16.0	12.4	10.8	12.3		15.7	5.05	10.3	24.0
OG3 Filtered-New	14.3	17.9	10.6	13.3	15.3	17.30	12.6		14.5	2.60	10.6	17.9
OG3 Zeolite-New	5.00	5.27	3.37	4.4	3.62	5.40	4.30		4.57	0.820	3.37	5.40
OG4 Baseline-New	15.3	14.7	12.1	12.8	14.5	15.9	12.9		13.6	1.22	12.1	15.9
OG4 Filtered-New	17.1	15.50	12.0	12.3	14.7	15.70	14.4		14.5	2.16	12.0	17.1
OG4 Zeolite-New	11.2	5.76	4.85	4.92	5.83	6.40	5.66		6.38	2.30	4.85	11.2
OG5 Baseline-New	51.7	45.1	14.5	15.5	17.2	37.7	18.5		28.6	16.0	14.5	51.7
OG5 Filtered-New	29.6	36.5	15.4	15.2	21.9	35	30.2		26.0	8.61	15.4	36.5
OG5 Zeolite-New	32.6	13.8	5.12	5.56	10.8	23.6			15.4	10.7	5.12	32.6
OG6 Baseline-New	5.02	5.27	3.01	3.20	2.87	2.77	4.16		4.39	0.980	3.01	5.27
OG6 Filtered-New	4.00	3.72	2.93	3.10	4.61	4.38	4.41		3.93	0.676	2.93	4.61
OG6 Zeolite-New	0.980	0.939	0.748	0.893	1.18	1.47	1.36		1.08	0.259	0.748	1.47
OGC Baseline-New	0.714	0.761	0.515	0.697	0.480	0.608	0.462		0.577	0.114	0.480	0.761
OGC Filtered-New	0.785	0.718	0.511	0.610	0.463	0.491	0.463		0.580	0.138	0.463	0.785
OGC Zeolite-New	0.131	0.156	0.100	0.123	0.100	0.106	0.083		0.113	0.023	0.083	0.156
PC Baseline-Old Filtered		0.349	0.634	0.491	0.640	0.596	0.820	0.996	0.563	0.135	0.349	0.996

Appendix Table 2 continued. Total ammonia measurements for *C. dubia* and *P. promelas* exposed to tire shred water samples from Oak Grove, MN.

	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7				
Sample ID	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	Mean	Std. Dev.	Min	Max
MBC Baseline-Old Fathead		0.251	0.25	0.459	0.554	0.594	0.659	0.801	0.508	0.205	0.250	0.801
MBC Filtered-Old Fathead		0.312	0.298		0.430	0.589	0.643	0.776	0.506	0.195	0.288	
MBC Zeolite-Old Fathead		0.468	0.464	0.576	<0.063	0.595	1.01	0.582	0.528	0.287	<0.063	
OG1 Baseline-Old Fathead		0.441	0.626	0.919	0.640	0.743	0.688	0.632	0.670	0.144	0.441	
OG1 Filtered-Old Fathead		0.480	0.922	0.867	0.589	0.796	0.770	0.840	0.766	0.146	0.480	0.922
OG1 Zeolite-Old Fathead		0.458	0.470	0.450	0.411	0.604	0.504	0.407	0.493	0.072		0.604
OG2 Baseline-Old Fathead		30.6	14.7						22.7	11.2	14.7	30.6
OG2 Filtered-Old Fathead		23.9							23.9		23.9	23.9
OG2 Zeolite-Old Fathead		10.3	6.70	6.68	9.06	12.7	12.9	10.3	9.81	2.61	6.68	12.9
OG3 Baseline-Old Fathead		13.4	8.76	10.0	11.7	15.2	11.6	15.0	12.2	2.46	8.76	15.2
OG3 Filtered-Old Fathead		10.9	8.52	10.5	10.29	14.3	9.77	13.30	11.2	1.85	8.52	14.3
OG3 Zeolite-Old Fathead		3.61	3.96	4.17	4.10	5.29	4.58	4.34	4.26	0.534	3.61	5.29
OG4 Baseline-Old Fathead		9.03	11.1	12.0	13.2	11.6	11.0	10.4	11.0	1.60	9.03	13.2
OG4 Filtered-Old Fathead		12.6	10.4	11.8	13.50	11.8	11.4	12.4	11.9	1.02	10.4	13.5
OG4 Zeolite-Old Fathead		5.03	4.26	4.12	4.99	4.75	4.95	4.63	4.68	0.365	4.12	5.03
OG5 Baseline-Old Fathead		25.4							25.4		25.4	25.4
OG5 Filtered-Old Fathead		30.9	14.2						22.6	11.8	14.2	30.9
OG5 Zeolite-Old Fathead		18.2	9.21	2.61	6.89	11.5	7.73	9.76	9.41	4.94	2.61	18.2
OG6 Baseline-Old Fathead		4.16	2.70	3.22	3.06	4.06	3.53	4.82	3.66	0.735	2.70	4.82
OG6 Filtered-Old Fathead		2.95	2.87	3.21	3.00	3.95	3.43	4.56	3.42	0.619	2.87	4.56
OG6 Zeolite-Old Fathead		1.18	1.32	1.61	1.29	1.56	1.55	1.81	1.46	0.233	1.18	1.81
OGC Baseline-Old Fathead		0.822	0.761	0.626	0.419	0.177	0.136	0.093	0.461	0.306	0.093	0.826
OGC Filtered-Old Fathead		0.876	0.810		0.700	0.749	0.881	0.564	0.763	0.120	0.564	0.881
		0.534	0.537	0.612	0.441	0.481	0.547	0.364	0.503	0.090	0.364	0.612
		0.098	0.197	0.289	0.222	0.264	0.250	0.074	0.184	0.084	0.074	0.289
		0.094	0.145	0.198	0.144	0.257	0.310	<0.063	0.167	0.096	<0.063	0.310
		0.152	0.148	1.07	0.172	0.266	0.433	0.207	0.446	0.546	0.148	
		0.136	<0.063	0.489	0.090	0.165	0.207	0.352	0.198	0.153	<0.063	

Appendix Table 2 continued. Total ammonia measurements for *C. dubia* and *P. promelas* exposed to tire shred water samples from Oak Grove, MN.

Sample ID	Day 0 (mg/L)	Day 1 (mg/L)	Day 2 (mg/L)	Day 3 (mg/L)	Day 4 (mg/L)	Day 5 (mg/L)	Day 6 (mg/L)	Day 7 (mg/L)	Mean	Std. Dev.	Min	Max
OGT Baseline-Old C. dubia		0.565	0.382	0.491	0.210	0.427	0.360	<0.250	0.358	0.110	0.105	0.491
OGT Filtered-Old C. dubia		0.525	0.430	0.309	0.211	0.267	0.500	0.270	0.329	0.128	0.125	0.500
OGT Zeolite-Old C. dubia		0.092	<0.053	0.339	<0.053	0.307	0.139	0.430	0.168	0.139	<0.053	0.432
		21.3	12.1				37.7		23.7	10.2	12.1	37.7
		33.1	16.2						24.7	11.7	16.2	33.1
		13.6	7.63						10.6	4.23	7.63	13.6
		8.00	6.39	13.9	4.71	12.3	7.02	10.4	8.92	3.57	4.71	12.5
		12.40	5.93	8.53	6.26	19.0	7.38	10.50	9.89	4.62	5.93	19.0
		2.79	1.70	1.80	2.23	3.15	2.85	2.36	2.41	0.556	1.70	3.15
		12.8	9.8	8.38	9.07	12.1	0.53		9.69	1.89	6.92	12.8
		12.6	8.22	3.36	6.07	8.08	6.25	11.3	8.19	3.00	6.95	12.6
		4.20	2.53	3.09	3.14	3.98	3.24	3.10	3.38	0.536	2.38	4.25
		42.7	24.9	12.6					26.7	15.2	12.5	42.3
		51.7	15.7						33.7	25.5	15.7	51.7
		33.5	5.93	4.65					14.7	16.5	4.08	33.5
		1.93	1.90	1.98	2.41	2.79	2.6	3.73	2.42	0.657	1.90	3.75
		2.27	1.86	1.84	1.89	3.29	1.96	3.38	2.35	0.760	1.12	3.49
		0.454	0.339	0.557	0.541	0.859	1.34	0.357	0.636	0.340	0.357	1.34
		0.371	0.353	0.409	0.350	0.427	0.252	<0.053	0.315	0.128	<0.053	0.427
		0.486	0.259	0.326	0.071	0.302	0.350	0.415	0.326	0.137	0.071	0.486
		0.102	<0.053	0.098	1.57	0.171	0.246	0.050	0.321	0.560	<0.053	1.57

Appendix Table 3

Daily Iron Measurements

Appendix Table 3. Total iron measurements for *C. dubia* and *P. promelas* exposed to tire shred water samples from Oak Grove, MN.

Sample ID	Day 0 (mg/L)	Day 1 (mg/L)	Day 2 (mg/L)	Day 3 (mg/L)	Day 4 (mg/L)	Day 5 (mg/L)	Day 6 (mg/L)	Day 7 (mg/L)	Mean	Std. Dev.	Min	Max
PC Baseline-New	<0.04	0.09	<0.04	<0.04	0.05	<0.04	<0.04		<0.04		<0.04	0.09
MBC Baseline-New	<0.04	<0.04	<0.04	0.04	<0.04	0.05	0.05		<0.04		<0.04	0.05
MBC Filtered-New	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04		<0.04		<0.04	<0.04
MBC Sedim-New	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04		<0.04	-	<0.04	<0.04
OG1 Baseline-New	4.29	1.40	1.10	1.31	0.29	0.54	0.05		1.29	1.25	0.02	4.29
OG1 Filtered-New	0.06	<0.04	<0.04	<0.04	0.08	0.30	0.05		0.05	<0.04	<0.04	0.30
OG1 Sedim-New	0.04	0.04	<0.04	<0.04	0.08	0.05	0.04		0.04	<0.04	<0.04	0.08
OG2 Baseline-New	25.4	12.4	6.09	19.7	6.51	12.9	8.29		13.0	7.2	6.09	25.4
OG2 Filtered-New	0.04	<0.04	0.04	<0.04	0.04	<0.04	0.16		0.05	0.05	<0.04	0.16
OG2 Sedim-New	<0.04	0.05	<0.04	<0.04	0.04	<0.04	<0.04		<0.04	<0.04	<0.04	0.05
OG3 Baseline-New	51.9	93.9	29.0	24.5	39.6	35.0	72.8		49.5	25.0	24.5	93.9
OG3 Filtered-New	2.16	6.82	0.49	0.07	0.11	0.10	0.76		1.49	2.39	0.07	6.82
OG3 Sedim-New	0.91	3.61	0.29	0.09	0.10	0.09	0.40		0.79	1.28	0.09	3.61
OG4 Baseline-New	60.6	17.6	36.6	45.8	26.7	45.8	59.6		42.5	15.1	17.6	60.6
OG4 Filtered-New	0.08	1.20	0.08	0.39	0.05	0.30	0.08		0.31	0.43	0.05	1.20
OG4 Sedim-New	0.07	0.74	0.08	0.28	<0.04	0.23	0.39		0.26	0.25	<0.04	0.74
OG5 Baseline-New	12.8	15.0	5.45	20.4	16.6	11.4	18.5		14.4	3.9	5.45	20.4
OG5 Filtered-New	0.04	0.04	0.05	0.04	0.04	<0.04	<0.04		0.04	<0.04	<0.04	0.05
OG5 Sedim-New	0.04	<0.04	0.05	0.04	0.04	<0.04	0.04		0.04	<0.04	<0.04	0.05
OG6 Baseline-New	105	105	63.2	59.3	135.4	59.4	63.3		85.5	29.0	59.4	135.4
OG6 Filtered-New	0.07	2.29	1.35	0.08	<0.04	0.08	0.08		0.56	0.89	<0.04	2.29
OG6 Sedim-New	0.06	1.32	0.73	0.09	0.04	0.06	0.05		0.33	0.49	0.04	1.32
OGC Baseline-New	2.02	1.25	6.09	4.53	1.81	2.01	0.96		2.65	1.84	0.96	6.09
OGC Filtered-New	0.33	0.32	0.37	0.30	0.27	0.22	0.31		0.31	0.04	0.27	0.37
OGC Sedim-New	0.36	0.33	0.35	0.30	0.29	0.29	0.30		0.32	0.03	0.29	0.36
FO Baseline-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

Appendix Table 3 continued. Total iron measurements for *C. dubia* and *P. promelas* exposed to tire shred water samples from Oak Grove, MN.

Sample ID	Day 0 (mg/L)	Day 1 (mg/L)	Day 2 (mg/L)	Day 3 (mg/L)	Day 4 (mg/L)	Day 5 (mg/L)	Day 6 (mg/L)	Day 7 (mg/L)	Mean	Std. Dev.	Min	Max
MSC Baseline-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
MSC Filtered-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
MSC Zeolite-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
OG1 Baseline-Old Fathead		0.32	0.18	0.53	0.22	0.35	0.30	0.74	0.38	0.20	0.18	0.74
OG1 Filtered-Old Fathead		0.04	<0.04	<0.04	<0.04	0.04	0.04	0.14	0.05	0.04	<0.04	0.14
OG1 Zeolite-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.04	<0.04	<0.04	<0.04	0.04
OG2 Baseline-Old Fathead		2.89	3.61						3.25	0.51	2.89	3.61
OG2 Filtered-Old Fathead		<0.04							<0.04		<0.04	<0.04
OG2 Zeolite-Old Fathead		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
OG3 Baseline-Old Fathead		6.29	3.42	1.74	1.53	2.88	2.52	2.42	2.97	1.67	1.53	6.29
OG3 Filtered-Old Fathead		1.25	1.07	0.07	0.30	0.15	0.10	0.52	0.49	0.49	0.07	1.25
OG3 Zeolite-Old Fathead		0.54	0.25	0.14	0.05	0.05	0.06	0.26	0.20	0.18	0.05	0.54
OG4 Baseline-Old Fathead		2.55	1.36	0.63	0.81	0.63	2.16	1.25	1.38	0.67	0.41	2.55
OG4 Filtered-Old Fathead		0.08	0.64	0.07	0.28	0.06	0.72	0.07	0.12	0.17	0.06	0.64
		0.05	0.31	0.08	0.14	0.05	0.04	0.25	0.14	0.10	0.05	0.31
		11.3							11.3		11.3	11.3
		0.04	<0.04						<0.04	<0.04	<0.04	0.04
		<0.04	<0.04	0.38	<0.04	<0.04	<0.04	<0.04	0.05	0.05	<0.04	0.13
		0.04	3.29	0.27	1.08	1.87	1.55	2.26	1.57	1.07	0.04	3.29
		0.04	0.51	0.38	0.05	0.55	0.07	0.19	0.19	0.19	0.04	0.51
		0.04	0.30	0.17	0.05	<0.04	<0.04	0.05	0.11	0.10	<0.04	0.30
		0.57	0.37	0.26	0.34	0.36	0.55	0.30	0.39	0.13	0.26	0.57
		0.32	0.25	0.18	0.18	0.18	0.25	0.19	0.22	0.05	0.18	0.32
		0.39	0.25	0.19	0.15	0.21	0.21	0.29	0.22	0.08	0.13	0.39
		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
		<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
		<0.04	<0.04	0.35	<0.04	<0.04	<0.04	<0.04	0.07	0.12	<0.04	0.35
		<0.04	<0.04	0.15	<0.04	<0.04	<0.04	0.07	0.05	0.05	<0.04	0.15

Appendix Table 3 continued. Total iron measurements for *C. dubia* and *P. promelas* exposed to fire shred water samples from Oak Grove, MN.

Sample ID	Day 0 (mg/L)	Day 1 (mg/L)	Day 2 (mg/L)	Day 3 (mg/L)	Day 4 (mg/L)	Day 5 (mg/L)	Day 6 (mg/L)	Day 7 (mg/L)	Mean	Std. Dev.	Min.	Max.
OG1 Baseline-Old C. dubia		0.69	0.39	0.29	0.86	0.37	0.70	0.31	0.51	0.17	0.31	0.69
OG1 Filtered-Old C. dubia		0.04	<0.04	<0.04	<0.04	0.14	0.04	0.03	0.06	0.05	<0.04	0.14
OG1 Zeolite-Old C. dubia		<0.04	<0.04	<0.04	<0.04	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
OG2 Baseline-Old C. dubia		15.8	11.8	2.78			1.53	1.38	6.63	6.70	1.35	15.8
OG2 Filtered-Old C. dubia		<0.04	<0.04						<0.04	<0.04	<0.04	<0.04
OG2 Zeolite-Old C. dubia		<0.04	<0.04						<0.04	<0.04	<0.04	<0.04
OG3 Baseline-Old C. dubia		37.5	14.8	8.95	25.8	39.7	7.84	30.1	23.6	27.8	7.84	39.8
OG3 Filtered-Old C. dubia		0.32	0.22	0.34	0.06	0.09	0.07	0.25	0.19	0.12	0.06	0.32
OG3 Zeolite-Old C. dubia		0.19	0.22	0.17	0.06	0.09	0.05	0.21	0.15	0.09	0.04	0.22
OG4 Baseline-Old C. dubia		12.6	24.9	8.98	16.1	24.2	7.90		15.6	14.3	7.9	24.9
		0.04	0.20	0.15	0.18	<0.04	0.09	0.30	0.11	0.09	<0.04	0.21
		<0.04	0.10	0.04	0.12	<0.04	0.07	0.30	0.10	0.09	<0.04	0.30
		16.8	9.98	7.29	0.54				8.44	7.28	0.54	16.5
		<0.04	<0.04	<0.08					<0.04	<0.04	<0.04	<0.04
		<0.04	<0.04	0.04					<0.04	<0.01	<0.04	0.04
		47.9	26.9	28.7	25.8	28.8	35.0	29.1	30.7	22.9	16.5	39.5
		<0.04	0.04	0.04	0.06	<0.04	<0.04	0.04	0.11	0.13	<0.04	0.34
		<0.04	0.21	0.15	0.06	<0.04	<0.04	<0.04	0.07	0.08	<0.04	0.21
		0.56	0.58	2.36	0.62	3.67	0.64	0.41	1.31	1.35	0.24	3.68
		0.27	0.27	0.28	0.31	0.17	0.15	0.19	0.23	0.06	0.17	
		0.24	0.27	0.30	0.32	0.28	0.26	0.24	0.25	0.04	0.18	

Appendix Table 4

Ammonia and Iron QC Samples

Appendix Table 4. Ammonia and iron quality control samples.

Ammonia QC Samples - Tire Shred Project					
	Original	Duplicate	Spiked		Spike
Sample ID	Sample	Sample	Sample	RPD	Recovery
OG5 Z-N Day-0	32.47	16.72		64.04	
GC Z-N Day-0	0.121		4.49		113.6
OG1 B-N Day-1	0.352		4.55		109.9
OG2 F-N Day-1	20.46	31.51		42.52	
OG4 F-O Day-1F	12.62		19.02		166.4
OG6 Z-O Day-1F	1.18	1.20		1.68	
OG1 B-O Day-1C	0.186	0.182		2.17	
OG2 Z-O Day-1C	13.6		27.51		361.7
OG3 F-N Day-2	10.53	10.89		3.36	
OG4 Z-N Day-2	4.05		7.79		97.2
OG1 B-O Day-2F	0.625		4.42		98.7
OG5 F-O Day-2F	14.18	13.88		2.14	
OG1 B-O Day-2C	0.384	0.313		20.37	
OG4 F-O Day-2C	8.22		12.35		107.4
OG4 F-N Day-3	12.35	12.55		1.61	
OG5 Z-N Day-3	6.36		11.24		126.9
OG3 F-O Day-3F	10.48		14.55		105.8
OGC B-O Day-3F	0.826	0.836		1.20	
OG3 Z-O Day-3C	1.86	2.23		18.09	
OG6 B-O Day-3C	1.99		5.76		98.0
OG2 F-N Day-4	20.34		25.70		139.4
OG4 Z-N Day-4	5.88	5.64		4.17	
2 Z-O Day-4F	8.06	8.64		6.95	
OGC B-O Day-4F	0.409		4.83		115.0
OG3 Z-O Day-4C	2.23		6.64		114.7
OG6 B-O Day-4C	2.11	1.97		6.86	
OG5 F-N Day-5	36.04		45.47		245.2
OGC B-N Day-5	0.595	0.595		0.00	
OG4 F-O Day-5F	11.78	12.12		2.85	
OG6 B-O Day-5F	4.06		7.99		102.2
PC B-N Day-6	<0.063	<0.063		NC	
OG1 B-N Day-6	0.312		3.67		87.3
OG2 Z-O Day-6F	12.86	11.97		7.17	
OG3 F-O Day-6F	9.77		13.33		92.6
OG6 B-O Day-6C	2.51	2.52		0.40	
OG1 F-O Day-7F	0.84		5.02		108.7
OGC B-O Day-7F	0.093		4.56		116.1
			Mean	**10.9**	**132.8**
			Std Dev.	**17.4**	**67.7**

Appendix Table 4 continued. Ammonia and iron quality control samples.

Iron QC Samples - Tire Shred Project

Sample ID	Original Sample	Duplicate Sample	Spiked Sample	RPD	Spike Recovery
OG5 Z-N Day-0	0.04	0.04		0.0	
GC Z-N Day-0	0.36		2.19		93.4
OG1 B-N Day-1	1.48		2.93		74.0
OG2 F-N Day-1	<0.04	<0.04		NC	
OG4 F-O Day-1	0.08		1.81		89.3
OG6 Z-O Day-1	0.04	<0.04		NC	
OG1 B-O Day-1	0.59	0.53		10.7	
OG2 Z-O Day-1	<0.04		1.94		98.0
OG3 F-N Day-2	0.50	0.51		1.98	
OG4 Z-N Day-2	0.06		1.75		86.2
OG1 B-O Day-2	0.18		1.68		76.5
OG5 F-O Day-2	<0.04	<0.04		NC	
OG4 F-O Day-2	0.20		1.92		87.8
OG4 F-N Day-3	0.39	0.39		0.0	
OG5 Z-N Day-3	0.04		1.94		96.9
OG3 F-O Day-3	0.27		2.09		92.9
OGC B-O Day-3	0.28	0.28		0.0	
OG3 Z-O Day-3	0.17	0.17		0.0	
OG6 B-O Day-3	2.67		4.56		96.4
OG2 F-N Day-4	0.04		1.94		96.9
OG4 Z-N Day-4	<0.04	0.04		NC	
OG2 Z-O Day-4	<0.04	<0.04		NC	
GC B-O Day-4	0.34		2.19		94.4
OG3 Z-O Day-4	0.04		2.09		
OG6 B-O Day-4	28.8	24.8		14.9	
OG5 F-N Day-5	<0.04		1.95		98.5
OGC B-N Day-5	2.01	2.73		30.4	
OG4 F-O Day-5	0.06	0.06		0.0	
OG6 B-O Day-5	1.67		3.30		83.2
PC B-O Day-5	<0.04		1.77		89.3
PC B-N Day-6	<0.04	0.05		NC	
OG1 B-N Day-6	0.78		2.28		76.5
OG2 Z-O Day-6	<0.04	<0.04		NC	
OG3 F-O Day-6	0.09		1.86		90.3
OG6 B-O Day-6	15.0	15.4		2.63	
OGC Z-O Day-6	0.18		2.07		96.4
OG5 Z-O Day-7	<0.04		1.89		95.4
OG6 Z-O Day-7	<0.04		1.72		86.7
			Mean	**6.1**	**90.6**
			Std. Dev.	**10.0**	**8.0**

APPENDIX M

YEARS 2007 AND 2008, ALL DATA

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
4/19/2007					
Temperature	Celcius	-	16.1	-	17.3
Dissolved Oxygen	mg/L	-	11.7	-	12.8
pH	S.U.	-	7.4	-	7.8
Specific Conductance	uS/cm	-	420	-	432
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT
4/19/2007								
Depth to groundwater	Feet	6.20	4.50	4.97	4.86	4.40	5.85	-
Temperature	Celcius	7.5	4.9	7.8	7.2	7.7	8.3	-
Dissolved Oxygen	mg/L	2.6	1.8	1.9	1.9	1.8	2.0	-
pH	S.U.	7.5	6.6	6.4	6.2	6.8	5.6	-
Specific Conductance	uS/cm	530	1213	1366	1460	1110	1170	-
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
6/27/2007					
Temperature	Celcius	-	22.6	-	24.3
Dissolved Oxygen	mg/L	-	3.3	-	1.2
pH	S.U.	-	6.9	-	7.0
Specific Conductance	uS/cm	-	440	-	455
(1 uS/cm = 1 umhos/cm)					

Field Parameters 6/27/2007	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT
Depth to groundwater	Feet	6.55	4.77	5.90	5.58	4.66	6.42	-
Temperature	Celcius	14.5	13.1	16.8	13.5	11.8	15.0	24.7
Dissolved Oxygen	mg/L	2.2	1.8	2.2	2.0	2.7	2.2	5.5
pH	S.U.	7.2	6.7	6.3	6.2	6.8	6.2	7.2
Specific Conductance (1 uS/cm = 1 umhos/cm)	uS/cm	597	1151	1362	1451	1170	768	434

Field Parameters 11/14/2007	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
Temperature	Celcius	-	5.7	-	5.71
Dissolved Oxygen	mg/L	-	9.6	-	9.0
pH	S.U.	-	6.7	-	6.6
Specific Conductance (1 Us/cm = 1 umhos/cm)	Us/cm	-	415	-	419

Field Parameters 11/14/2007	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT
Depth to groundwater	Feet	6.18	4.08	4.95	4.85	3.98	5.86	-
Temperature	Celcius	13.5	11.6	13.9	12.6	11.7	11.3	-
Dissolved Oxygen	mg/L	2.1	1.4	1.2	2.4	1.6	3.2	-
Ph	S.U.	6.6	6.6	5.9	5.5	6.6	6.2	-
Specific Conductance (1 Us/cm = 1 umhos/cm)	Us/cm	1201	1119	1102	1300	1147	1329	-

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
4/30/2008					
Depth to groundwater	Feet				
Temperature	Celcius	Instrument Failure			
Dissolved Oxygen	mg/L				
pH	S.U.				
Specific Conductance	uS/cm				
(1 uS/cm = 1 umhos/cm)					

Field Parameters	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT
4/30/2008								
Depth to groundwater	Feet	-	5.71	3.81	4.55	4.41	3.70	5.40
Temperature	Celcius	Instrument Failure						
Dissolved Oxygen	mg/L							
pH	S.U.							
Specific Conductance	uS/cm							
(1 uS/cm = 1 umhos/cm)								

Field Parameters	Units	North East Ditch	North Middle Ditch	North West Ditch	South Ditch
6/26/2008					
Depth to groundwater	Feet	-		-	-
Temperature	Celcius	-	17.4	-	16.5
Dissolved Oxygen	mg/L	-	8.8	-	7.6
pH	S.U.	-	7.9	-	7.7
Specific Conductance	uS/cm	-	453	-	456
(1 uS/cm = 1 umhos/cm)					

Field Parameters 6/26/2008	Units	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT
Depth to groundwater	Feet	6.27	3.93	5.11	5.04	3.82	6.04	-
Temperature	Celcius	12.4	11.6	15.2	13.0	12.1	12.4	-
Dissolved Oxygen	mg/L	3.2	1.4	2.2	1.7	1.5	1.7	-
pH	S.U.	7.4	7.6	7.0	6.9	7.4	6.9	-
Specific Conductance (1 uS/cm = 1 umhos/cm)	uS/cm	883	1344	1423	1699	1286	1508	-

Inorganic Parameters	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
4/19/2007												
COD	mg/L	14	13	230	130	110	260	66	23	26	20	5
TSS	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	20	4
Alkalinity	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	10	2
Ammonia-N	mg/L	0.15	NA	NA	NA	NA	NA	NA	0.086	0.066	0.02	0.01
Total Organic Carbon	mg/L	10	6	74	37	31	82	15	11	5	15	3
Gasoline Range Organics	ug/L	<30	NA	NA	NA	NA	NA	NA	<30	NA	30	17

NA = Not analyzed.

Inorganic Parameters	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
6/27/2007												
COD	mg/L	38	<20	240	100	120	250	59	46	40	25	5
TSS	mg/L	9	NA	NA	NA	NA	NA	NA	21	NA	20	4
Alkalinity	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	170	10	2
Ammonia-N	mg/L	0.028	0.17	11	9.2	8.8	11	1.6	<0.02	0.055	0.05	0.01
Total Organic Carbon	mg/L	7.3	11	77	19	16	57	5.7	6.9	13	15	3
Gasoline Range Organics	ug/L	<30	<30	34	21	17	37	<30	<30	NA	85	17

NA = Not analyzed.

Inorganic Parameters	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
11/14/2007												
COD	mg/L	<50	<50	140	<50	<50	140	150	NA	90	25	5
TSS	mg/L	12	12	32	100	98	33	180	NA	6.4	20	4
Alkalinity	mg/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	10	2
Ammonia-N	mg/L	<0.500	<0.500	12.2	6.35	7.88	11.5	7.88	NA	<0.500	0.05	0.01
Total Organic Carbon	mg/L	8.27	1.78	83	52.6	64	71.6	97.8	NA	6.91	15	3
Gasoline Range Organics	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	85	17

NA = Not analyzed.

Metals 4/19/2007	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
Barium	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	10	2
Iron	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	50	10
Manganese	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	25	5
Zinc	ug/L	NA	NA	NA	NA	NA	NA	NA	NA	NA	25	5

NA = Not analyzed.

Metals 6/27/2007	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
Barium	ug/L	NA	68	250	320	340	250	180	79	NA	10	2
Iron	ug/L	NA	660	14000	59000	73000	14000	71000	2300	NA	50	10
Manganese	ug/L	NA	180	290	250	250	160	880	600	NA	25	5
Zinc	ug/L	NA	9	20	53	50	20	40	28	NA	25	5

NA = Not analyzed.

Metals 11/14/2007	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
Barium	ug/L	62	120	290	280	310	300	360	NA	63	10	2
Iron	ug/L	840	2700	17000	65000	56000	20000	180000	NA	900	50	10
Manganese	ug/L	180	310	310	500	290	190	1400	NA	220	25	5

NA = Not analyzed.

Metals 4/30/2008	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
Barium	ug/L	59	75	280	340	350	260	260	NA	56	10	2
Iron	ug/L	1000	1500	17000	47000	58000	16000	54000	NA	820	50	10
Manganese	ug/L	250	210	540	990	1200	240	2600	NA	210	25	5

NA = Not analyzed.

Metals 6/26/2008	Units	UpStream	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	Down Stream	Reporting Limit	MDL
Barium	ug/L	71	100	300	310	330	280	320	NA	83	10	2
Iron	ug/L	1200	820	17000	70000	64000	16000	130000	NA	2000	50	10
Manganese	ug/L	420	260	390	540	480	220	1600	NA	620	25	5

NA = Not analyzed.

Tire Material Related SVOC 4/19/2007	Units	North Ditch	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	CULVERT	South Ditch	Field Blank	Reporting Limit	MDL
Aniline	ug/L	<10	<11	73	15	16	120	<10	<9.3	<10	<10	10	3.2
Benzoic Acid	ug/L	<10	<11	<11	<11	<11	<22	<10	<9.3	<10	<10	10	2.8
Carbazole	ug/L	<10	<11	<11	<11	<11	<22	<10	<9.3	<10	<10	10	1.2
2-Hydroxybenzothiazole (TIC)	ug/L	ND	ND	810	270	430	840	57	ND	ND	ND	NR*	NR*
4(1-Methyl-1-phenylethyl)phenol (TIC)	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NR*	NR*
4(2-Benzothiozolythio)-morpholine (TIC)	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NR*	NR*
4-Acetylmorpholine (TIC)	ug/L	ND	ND	13	7.6	14	19	0.64	ND	ND	ND	NR*	NR*
Benzothiazole (TIC)	ug/L	ND	ND	12	3.2	3.2	8.7	5.3	ND	ND	ND	NR*	NR*

ND= Not detected.

NR* = Not Reported; Sample quantification relative to nearest internal standard.

Tire Material Related SVOC 6/27/2007	Units	North Ditch	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	South Ditch	Field Blank	Reporting Limit	MDL
Aniline	ug/L	ND	<9.3	42	24	35	53	<11	<10	<10	<9.3	10	3.2
Benzoic Acid	ug/L	ND	<9.3	<10	<9.3	<11	<10	<12	<10	<10	<9.3	10	2.8
Carbazole	ug/L	ND	<9.3	<10	<9.3	<11	<10	<13	<10	<10	<9.3	10	1.2
2-Hydroxybenzothiazole (TIC)	ug/L	ND	ND	850	510	720	1000	73	ND	ND	ND	10	5
4(1-Methyl-1-phenylethyl)phenol (TIC)	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	5
4(2-Benzothiozolythio)-morpholine (TIC)	ug/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	5
4-Acetylmorpholine (TIC)	ug/L	ND	ND	15	ND	ND	20	ND	ND	ND	ND	10	5
Benzothiazole (TIC)	ug/L	ND	ND	17	ND	ND	14	ND	ND	ND	ND	10	5

ND = Not detected.

Tire Material Related SVOC
11/14/2007

	Units	North Ditch	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	South Ditch	Field Blank	Reporting Limit	MDL
Aniline	ug/L	<9.3	<10	60	<10	11	95	13	NA	<9.3	<10	10	3.2
2-Hydroxybenzothiazole (TIC)	ug/L	ND	<10	1000	310	700	1300	170	NA	ND	ND	NR*	NR*
Benzothiazole (TIC)	ug/L	ND	<10	15	7	5.8	12	1.8	NA	ND	ND	NR*	NR*

ND= Not detected.

NR* = Not Reported; Sample quantification relative to nearest internal standard.

Tire Material Related SVOC
4/30/2008

	Units	North Ditch	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	South Ditch	Field Blank	Reporting Limit	MDL
Aniline	ug/L	<10	<10	86	<11	<10	86	<10	NA	<10	<10	10	3.2
2-Hydroxybenzothiazole (TIC) #	**ug/L**	**ND**	**ND**	**0.29**	**ND**	**0.57**	**0.065**	**ND**	**NA**	**ND**	**ND**	**NR***	**NR***
Benzothiazole (TIC) #	**ug/L**	**ND**	**ND**	**3.6**	**0.087**	**0.18**	**2.5**	**0.7**	**NA**	**ND**	**ND**	**NR***	**NR***

#: Invalid Data-Extraction procedure changed by lab which effected the recoveries of the TIC compounds. Data excluded from report.

ND= Not detected.

NR* = Not Reported; Sample quantification relative to nearest internal standard.

Tire Material Related SVOC
6/26/2008

	Units	North Ditch	OG 1	OG 2	OG 3	OG 4	OG 5	OG 6	Culvert	South Ditch	Field Blank	Reporting Limit	MDL
Aniline	ug/L	<9.4	<10	100	14	19	110	12	NA	<11	<10	10	1
2-Hydroxybenzothiazole (TIC)	ug/L	ND	ND	620	330	530	690	200	NA	ND	ND	NR*	NR*
Benzothiazole (TIC)	ug/L	ND	ND	11	3.1	4	8.9	8.2	NA	ND	ND	NR*	NR*

ND= Not detected.

NR* = Not Reported; Sample quantification relative to nearest internal standard.

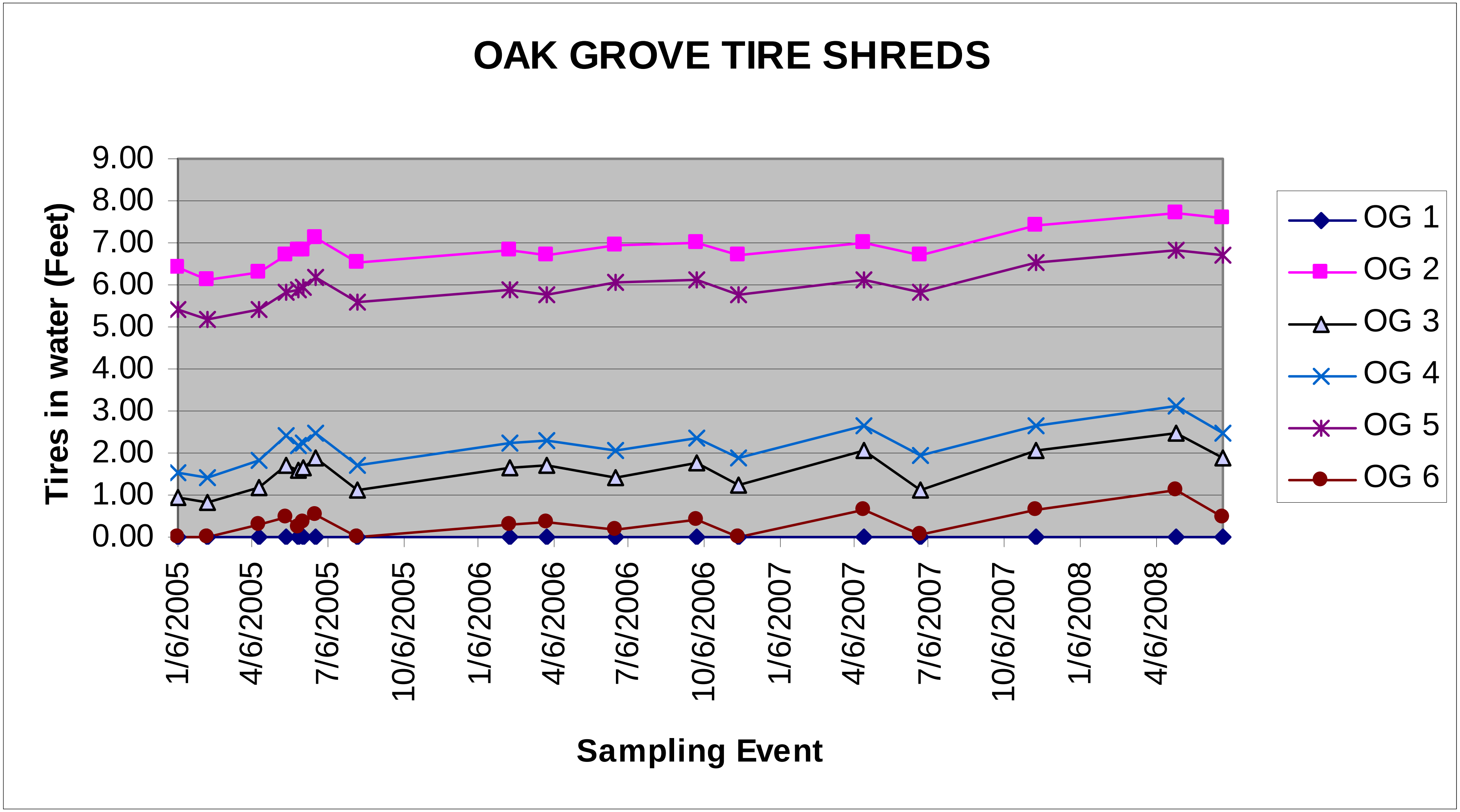
Culvert

		4/19/2007		
PARAMETER	**UNITS**	**Culvert**		MDL
Acenaphthene	ug/L	ND		0.045
Acenaphthylene	ug/L	ND		0.045
Anthracene	ug/L	ND		0.045
Benzo(a)anthracene	ug/L	ND		0.045
Benzo(a)pyrene	ug/L	ND		0.045
Benzo(e)pyrene	ug/L	ND		0.045
Benzo(g,h,i)perylene	ug/L	ND		0.045
Benzofluoranthenes (Total)	ug/L	ND		0.13
Carbazole	ug/L	ND		0.045
2-Chloronaphthalene	ug/L	ND		0.045
Chrysene	ug/L	ND		0.045
Dibenz(a,h)acridine	ug/L	ND		0.045
Dibenz(a,h)anthracene	ug/L	ND		0.045
Dibenz(a,j)acridine	ug/L	ND		0.045
Dibenzo(a,e)pyrene	ug/L	ND		0.045
Dibenzo(a,h)pyrene	ug/L	ND		0.045
Dibenzo(a,I)pyrene	ug/L	ND		0.045
Dibenzo(a,l)pyrene	ug/L	ND		0.045
7H-Dibenzo(c,g)carbazole	ug/L	ND		0.045
Dibenzofuran	ug/L	ND		0.045
7,12-Dimethylbenz(a)anthracene	ug/L	ND		0.045
1,6-Dinitropyrene	ug/L	ND		1.1
1,8-Dinitropyrene	ug/L	ND		1.1
Fluoranthene	ug/L	ND		0.045
Fluorene	ug/L	ND		0.045
Indeno(1,2,3-cd)pyrene	ug/L	ND		0.045
3-Methylcholanthrene	ug/L	ND		0.045
5-Methylchrysene	ug/L	ND		0.045
1-Methylnaphthalene	ug/L	ND		0.045
2-Methylnaphthalene	ug/L	ND		0.045
Naphthalene	ug/L	ND		0.045
5-Nitroacenaphthene	ug/L	ND		0.045
6-Nitrochrysene	ug/L	ND		0.045
2-Nitrofluorene	ug/L	ND		0.045
1-Nitropyrene	ug/L	ND		0.045
4-Nitropyrene	ug/L	ND		0.045
Perylene	ug/L	ND		0.045
Phenanthrene	ug/L	ND		0.045
Pyrene	ug/L	ND		0.045
Nitrobenzene-d5 (S)		75%		
2-Fluorobiphenyl (S)		90%		
Terphenyl-d14 (S)		98%		
Carcinogenic PAHs (ug/L) (BaP Equivalents Worksheet)				
TOTAL PAH	ug/L			
TOTAL COMPDS. DETECTED		0	0	

APPENDIX N

YEARS 2007 AND 2008,

FULL STUDY PLOTS, ALL PARAMETERS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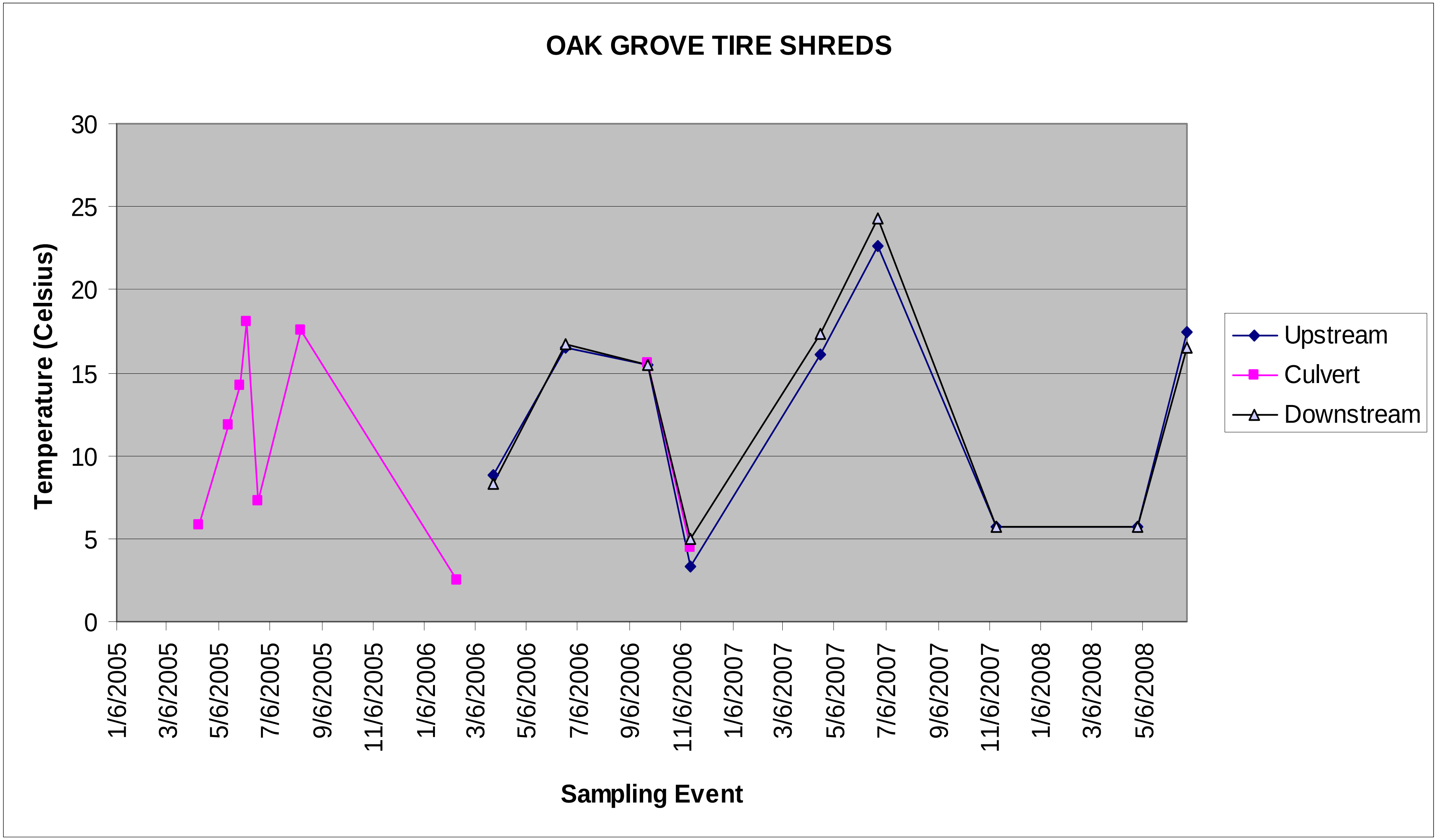
Tires in water (Feet)
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6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25
20
15
10
5
0
1/6/2005
3/6/2005
5/6/2005
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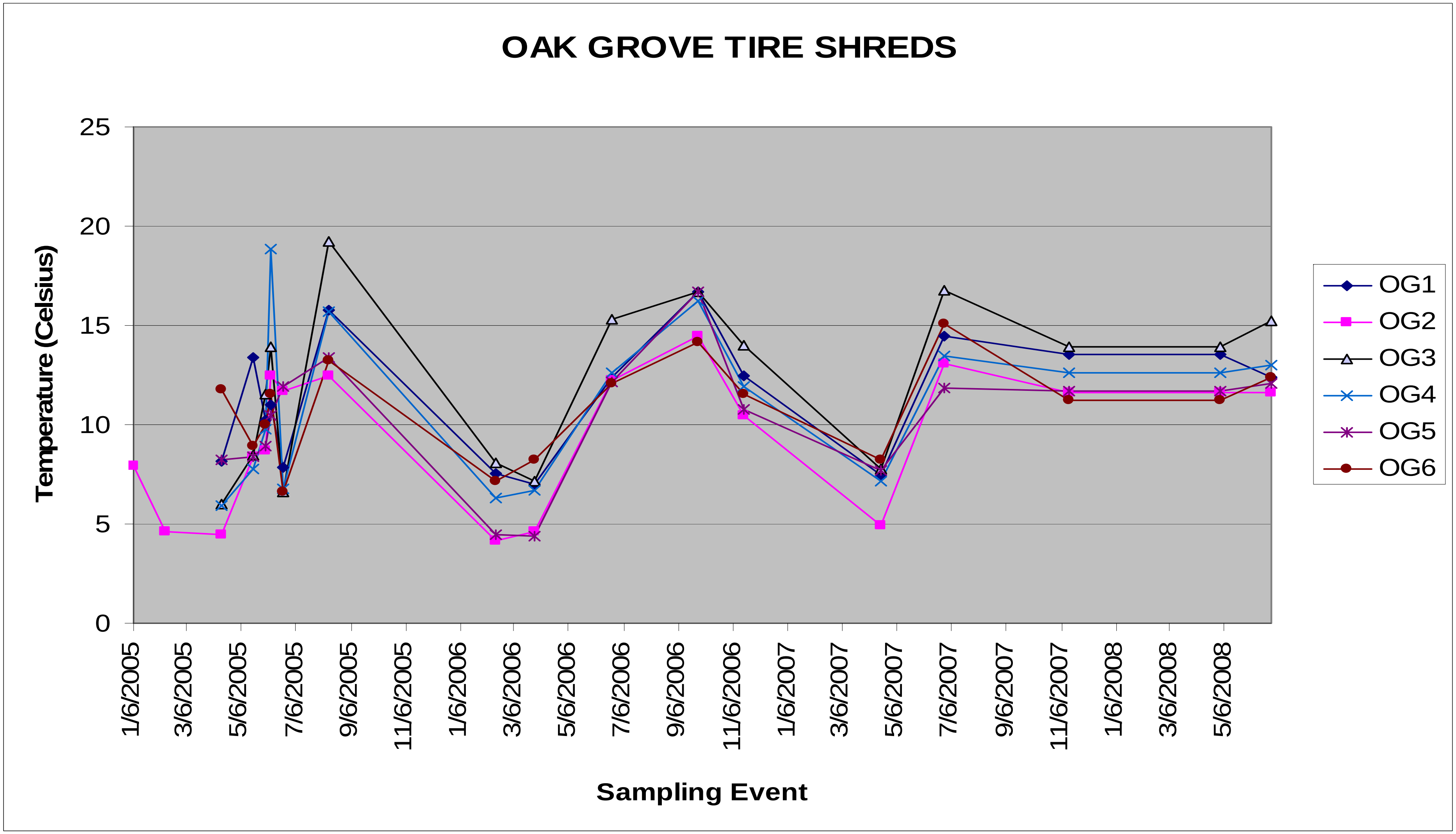
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream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Temperature (Celsius)
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5
10
15
20
25
1/6/2005
3/6/2005
5/6/2005
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3/6/2006
5/6/2006
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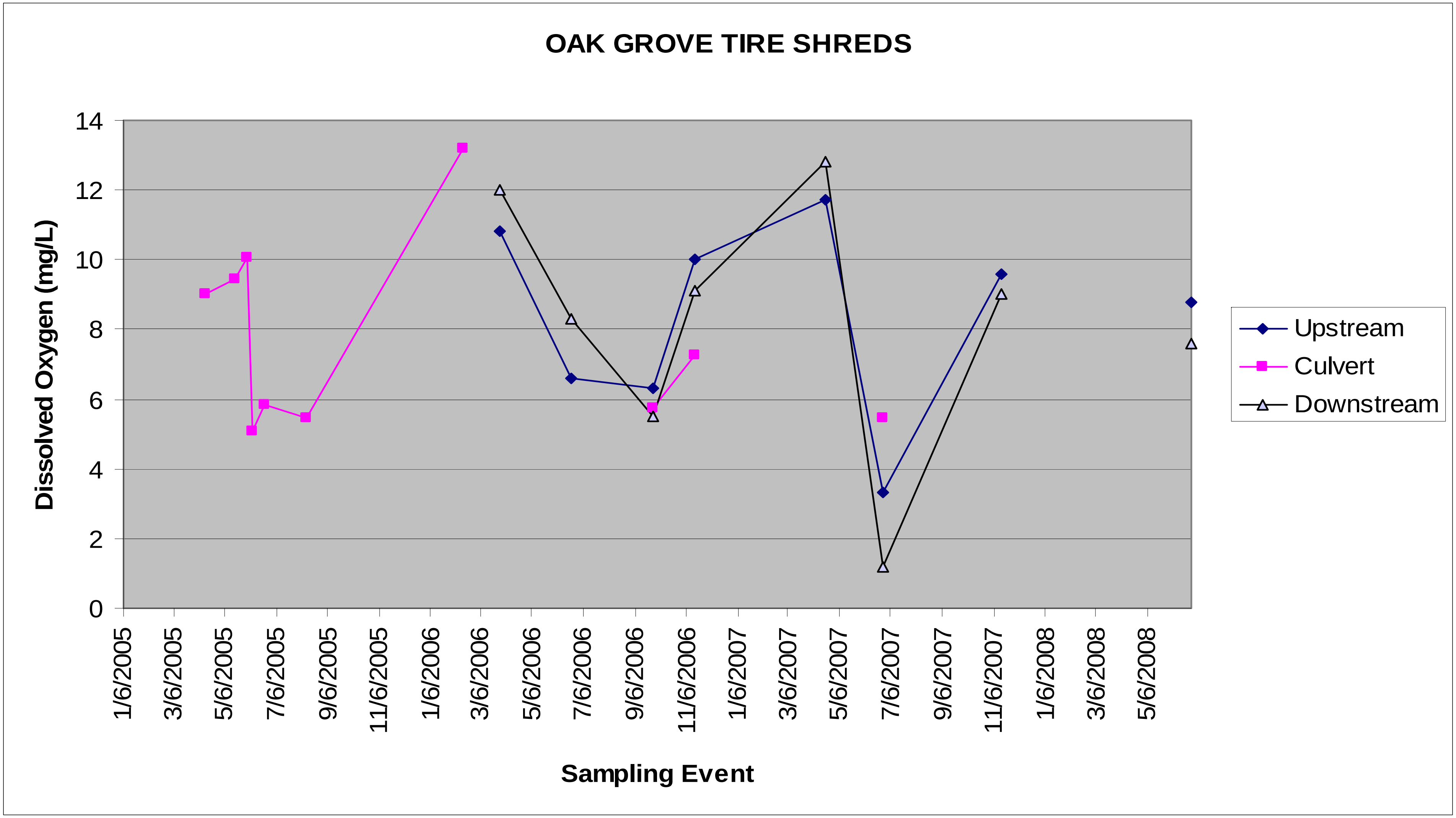
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6


OAK GROVE TIRE SHREDS
Dissolved Oxygen (mg/L)
0
2
4
6
8
10
12
14
1/6/2005
3/6/2005
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7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
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1/6/2007
3/6/2007
5/6/2007
7/6/2007
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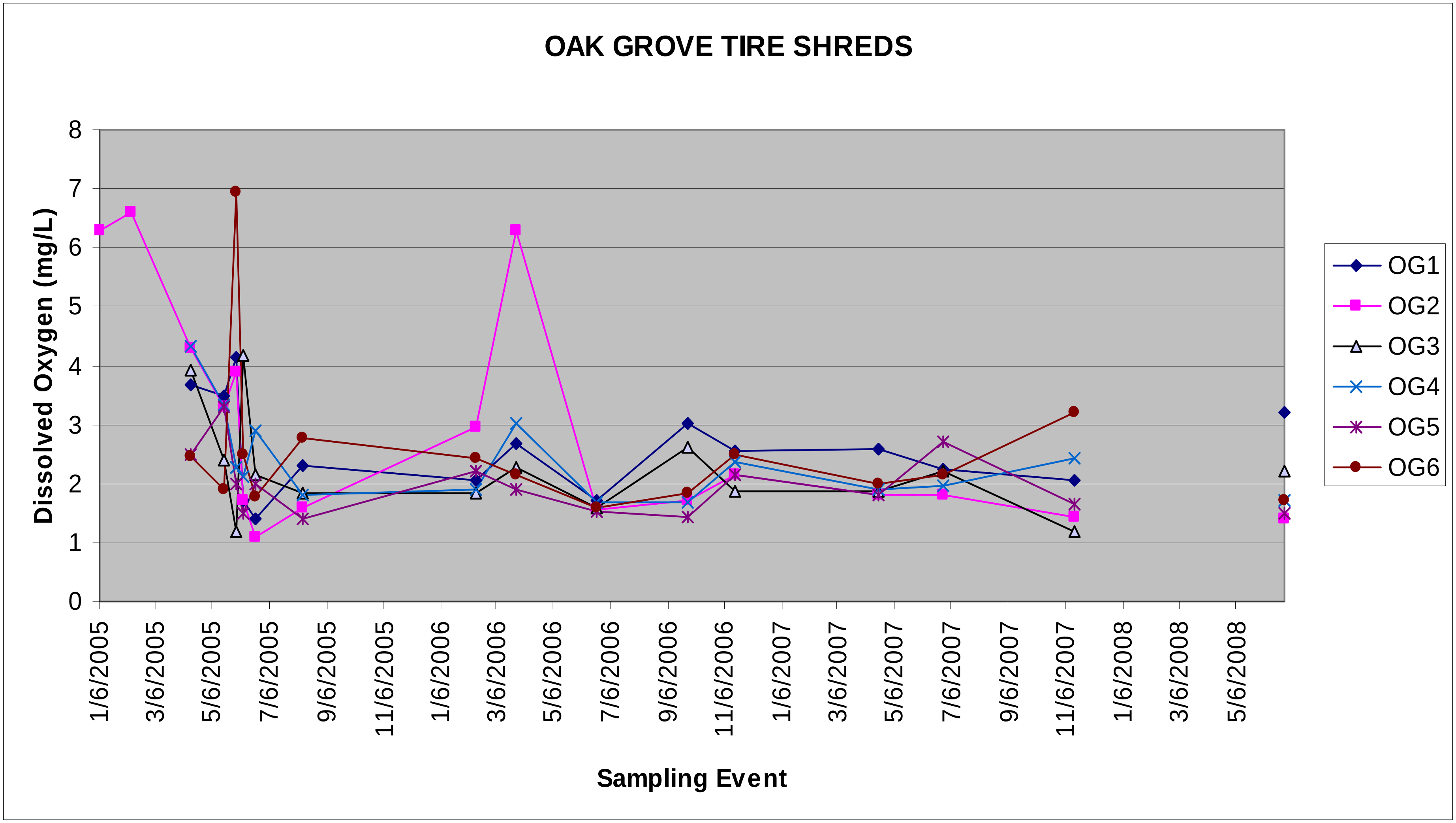
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream


OAK GROVE TIRE SHREDS
Dissolved Oxygen (mg/L)
0
1
2
3
4
5
6
7
8
1/6/2005
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5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
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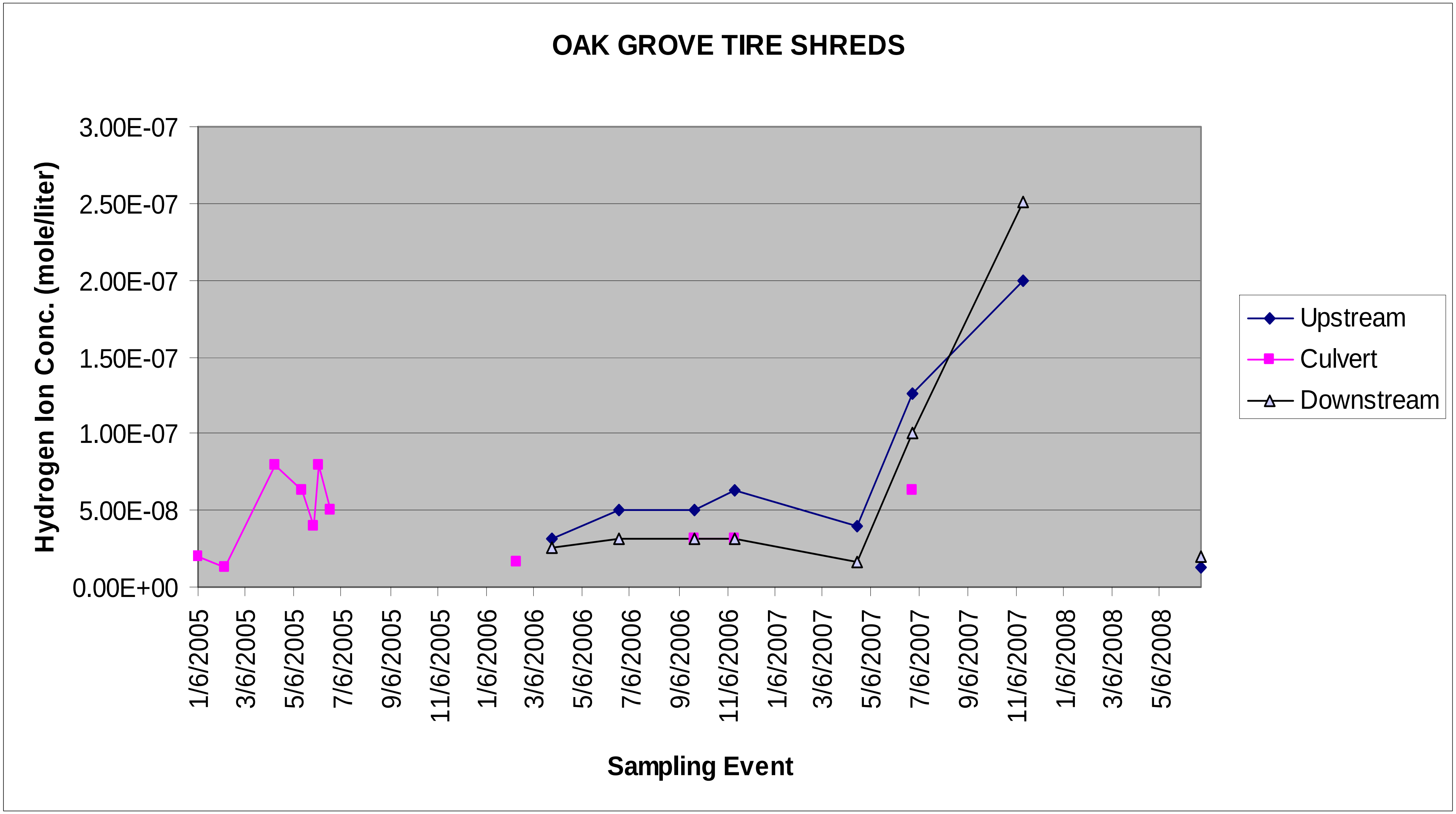
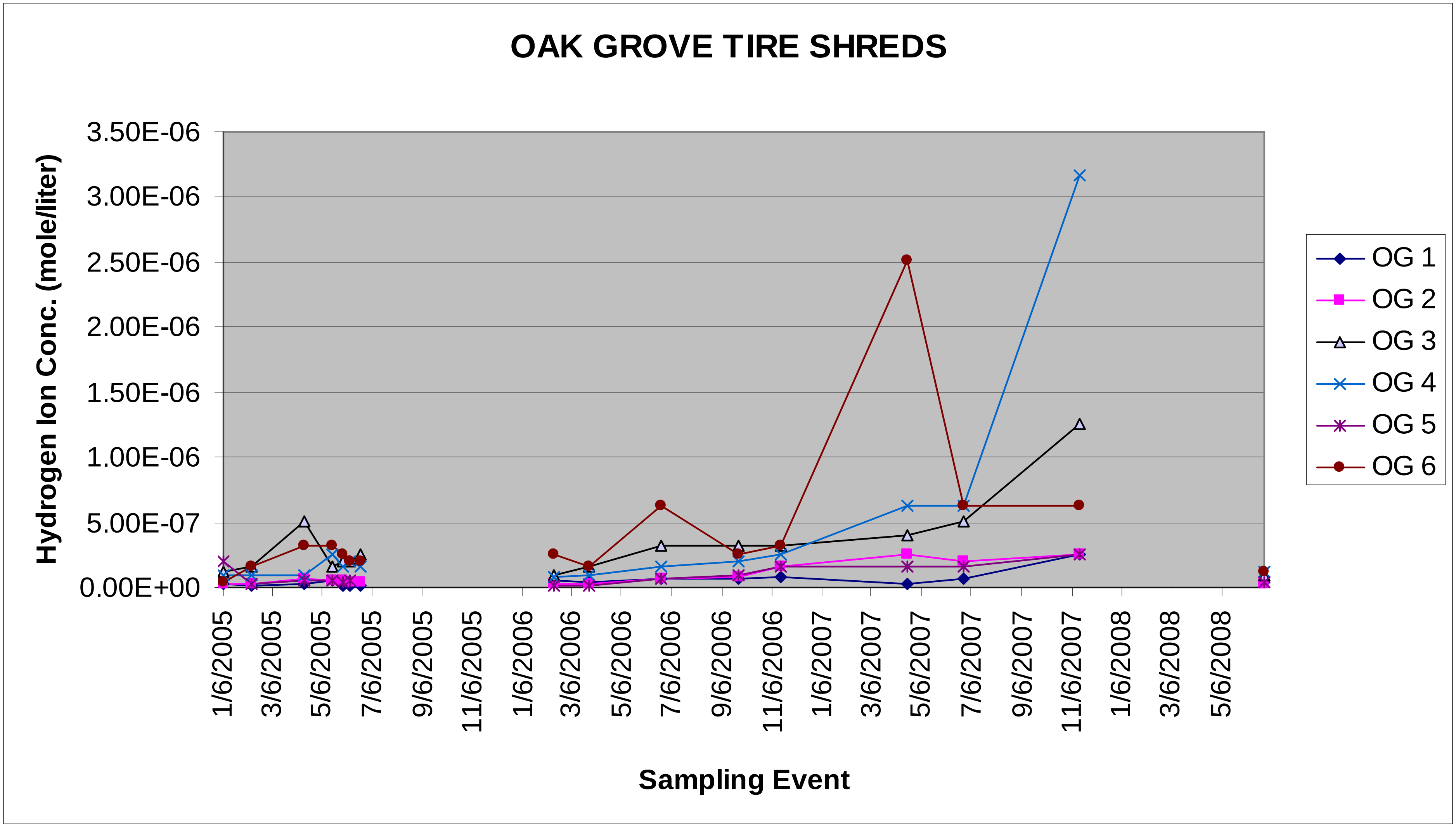
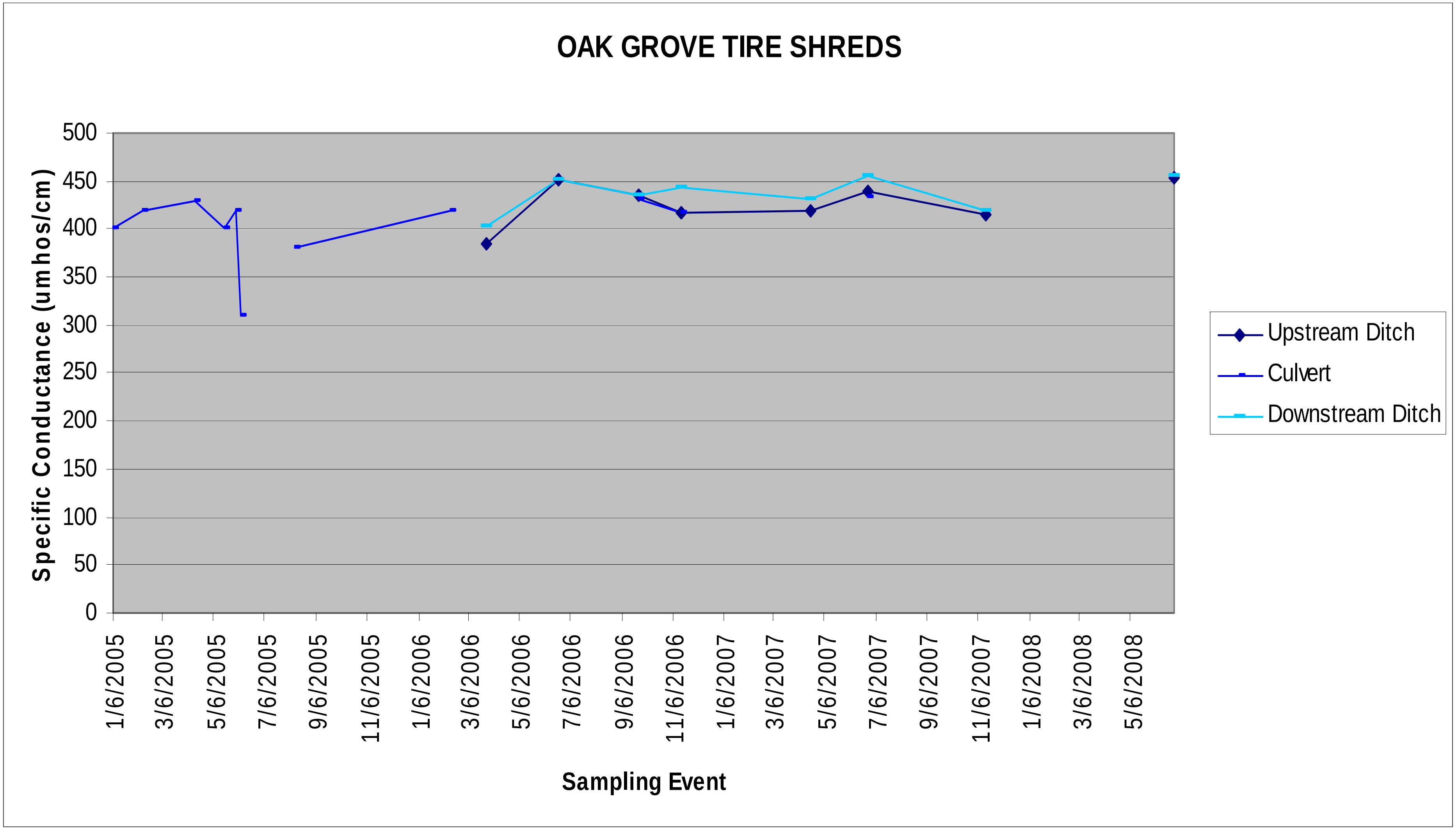
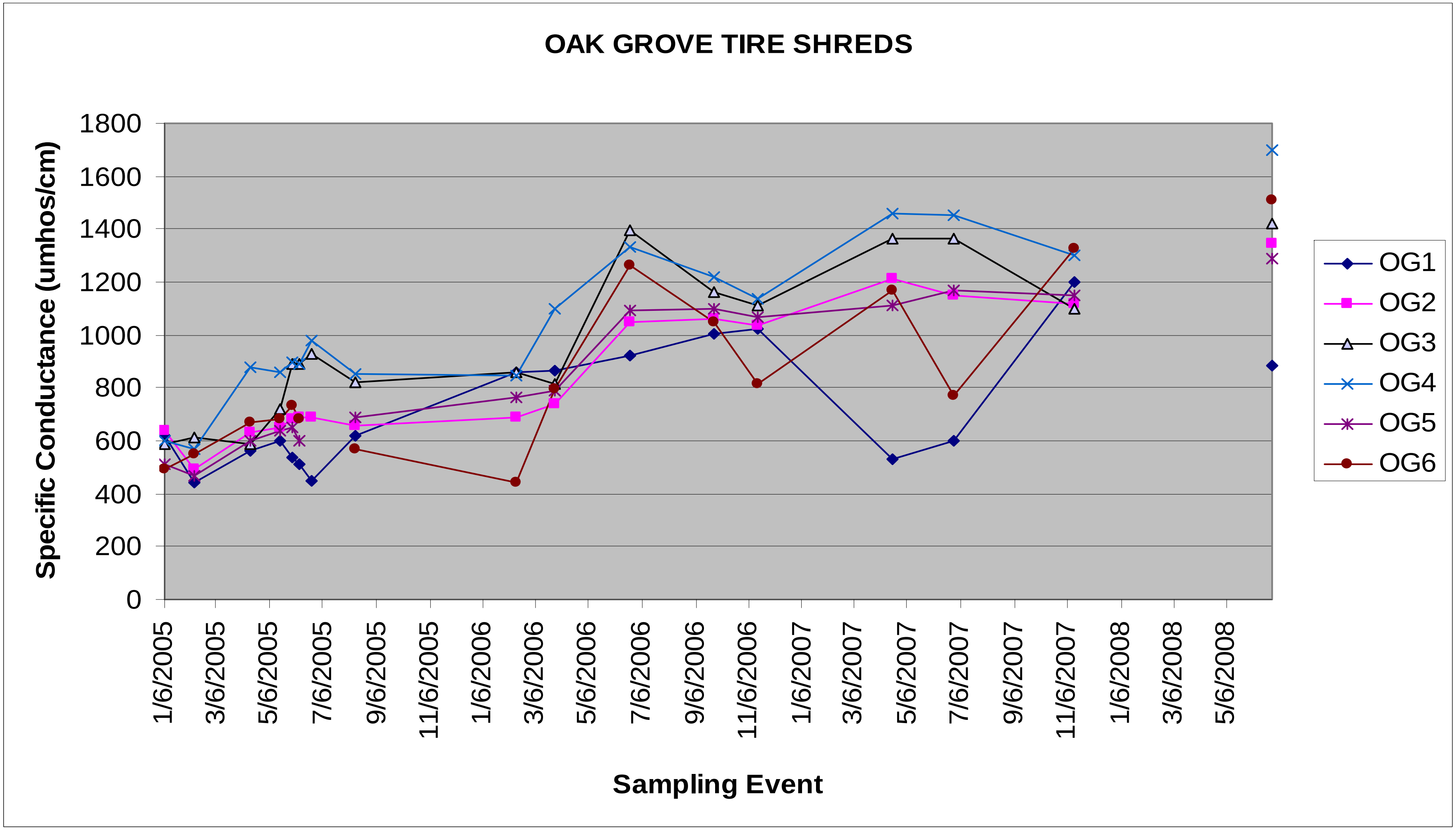
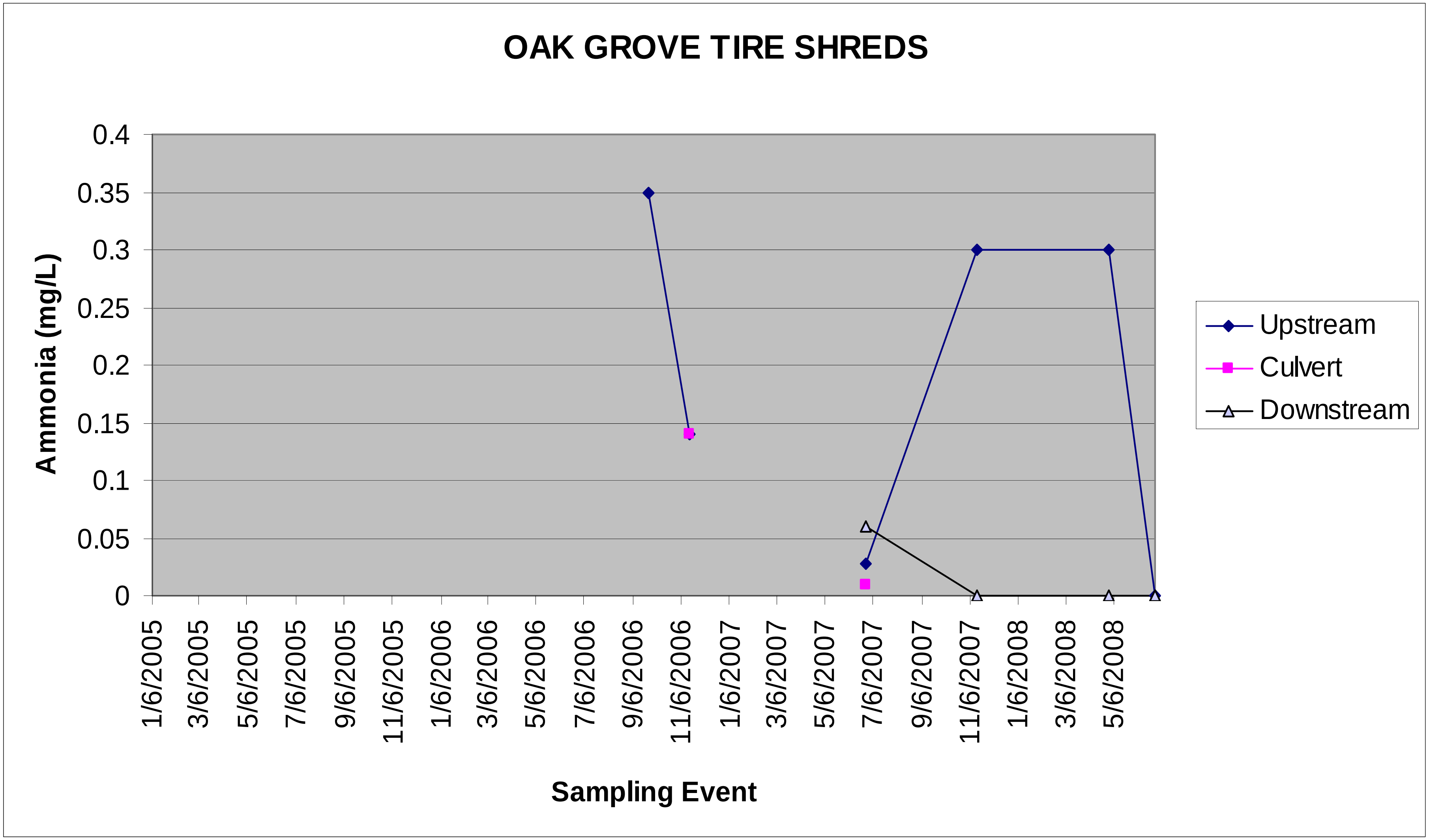
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6

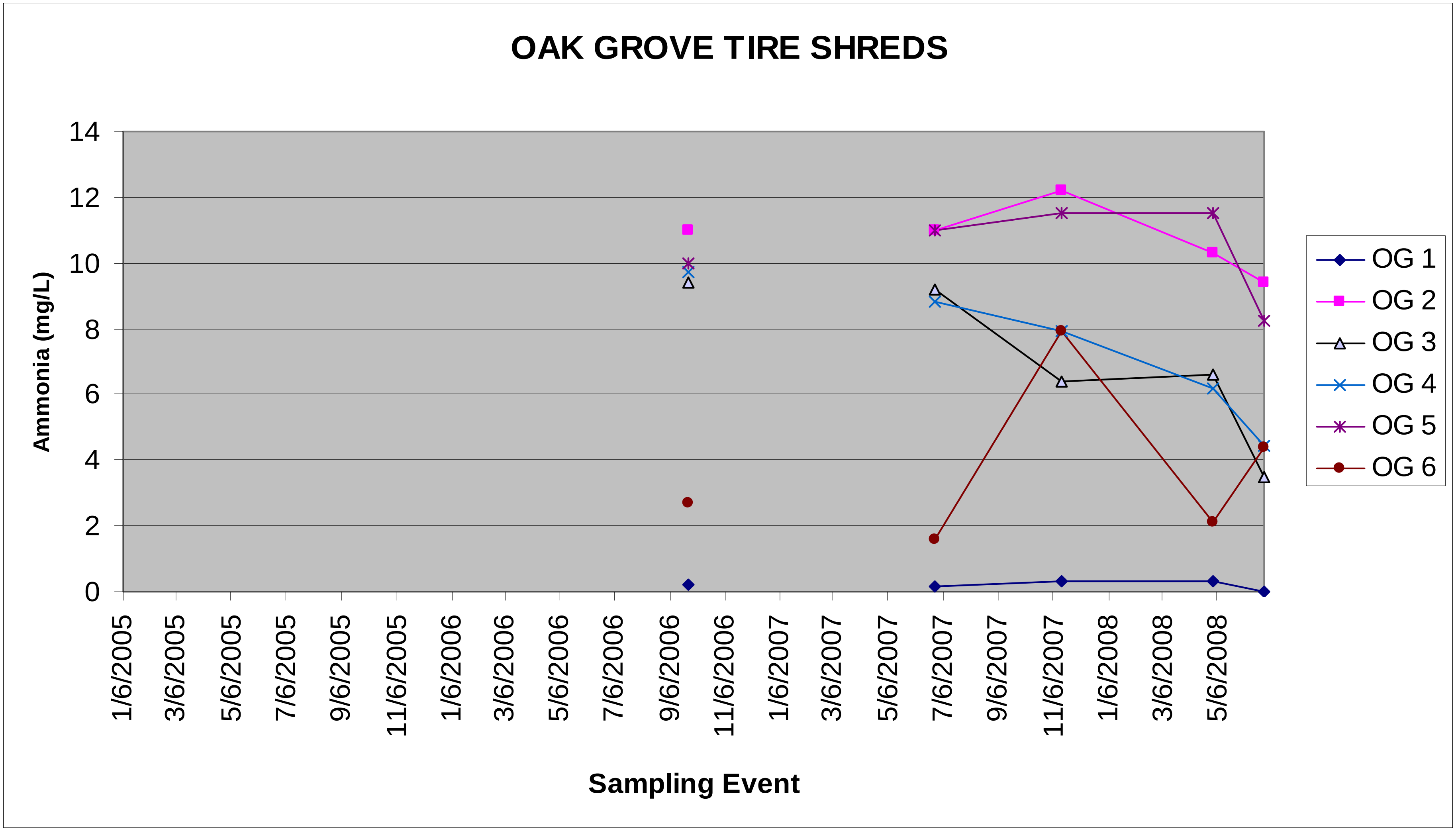

OAK GROVE TIRE SHREDS
Hydrogen Ion Conc. (mole/liter)
3.00E-07
2.50E-07
2.00E-07
1.50E-07
1.00E-07
5.00E-08
0.00E+00
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream

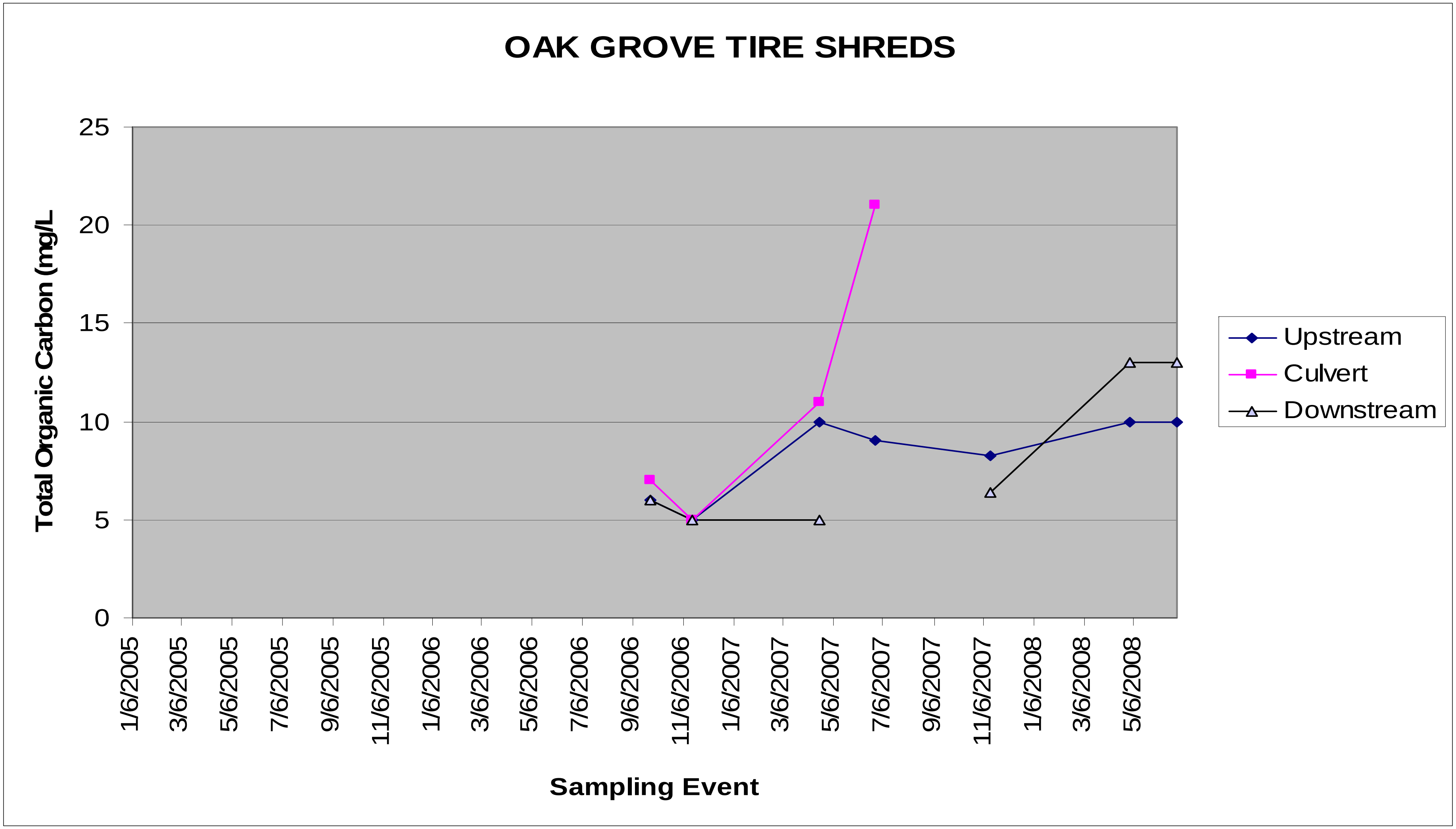

OAK GROVE TIRE SHREDS
Hydrogen Ion Conc. (mole/liter)
3.50E-06
3.00E-06
2.50E-06
2.00E-06
1.50E-06
1.00E-06
5.00E-07
0.00E+00
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

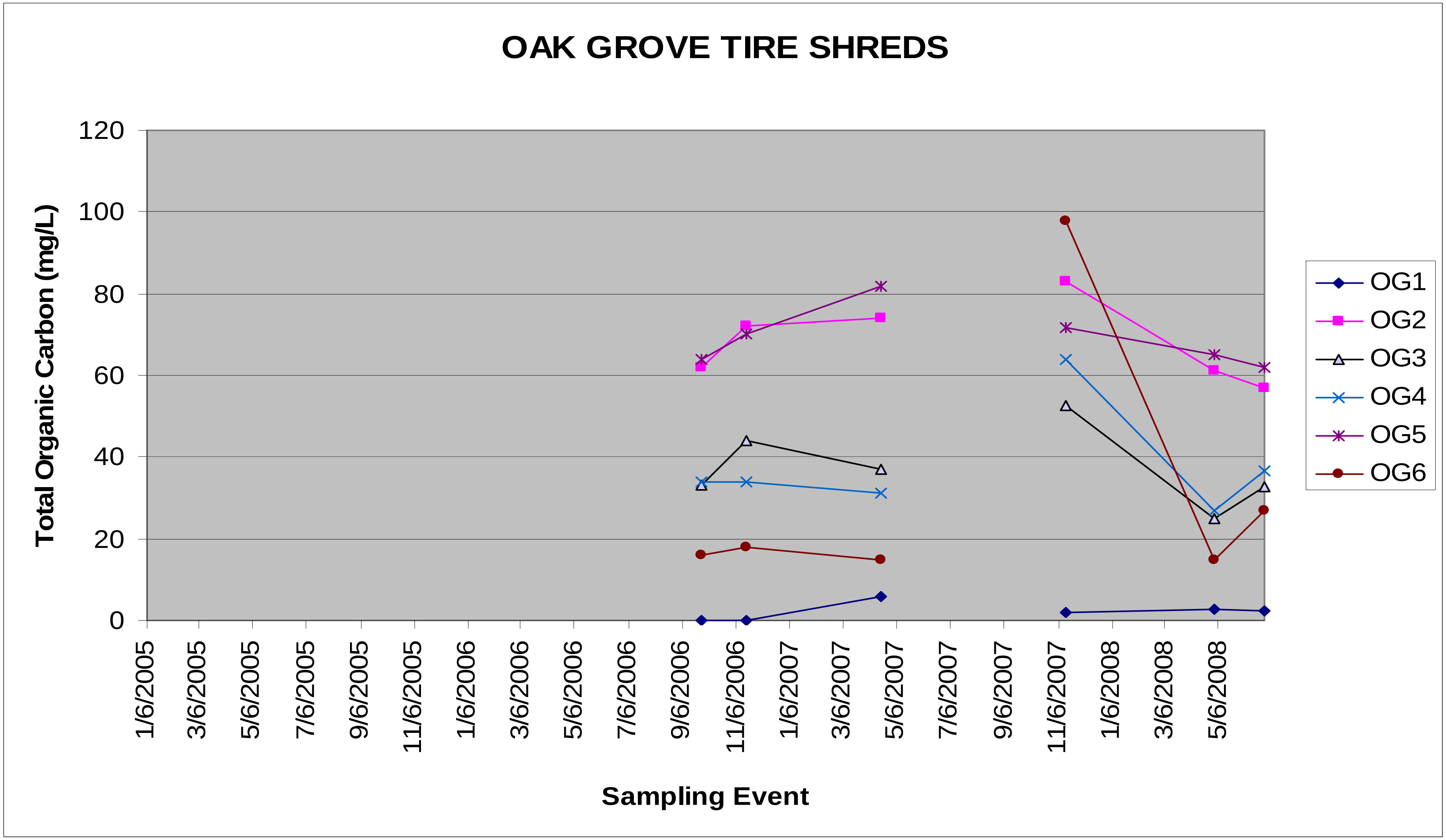

OAK GROVE TIRE SHREDS
Specific Conductance (umhos/cm)
500
450
400
350
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream Ditch
Culvert
Downstream Ditch

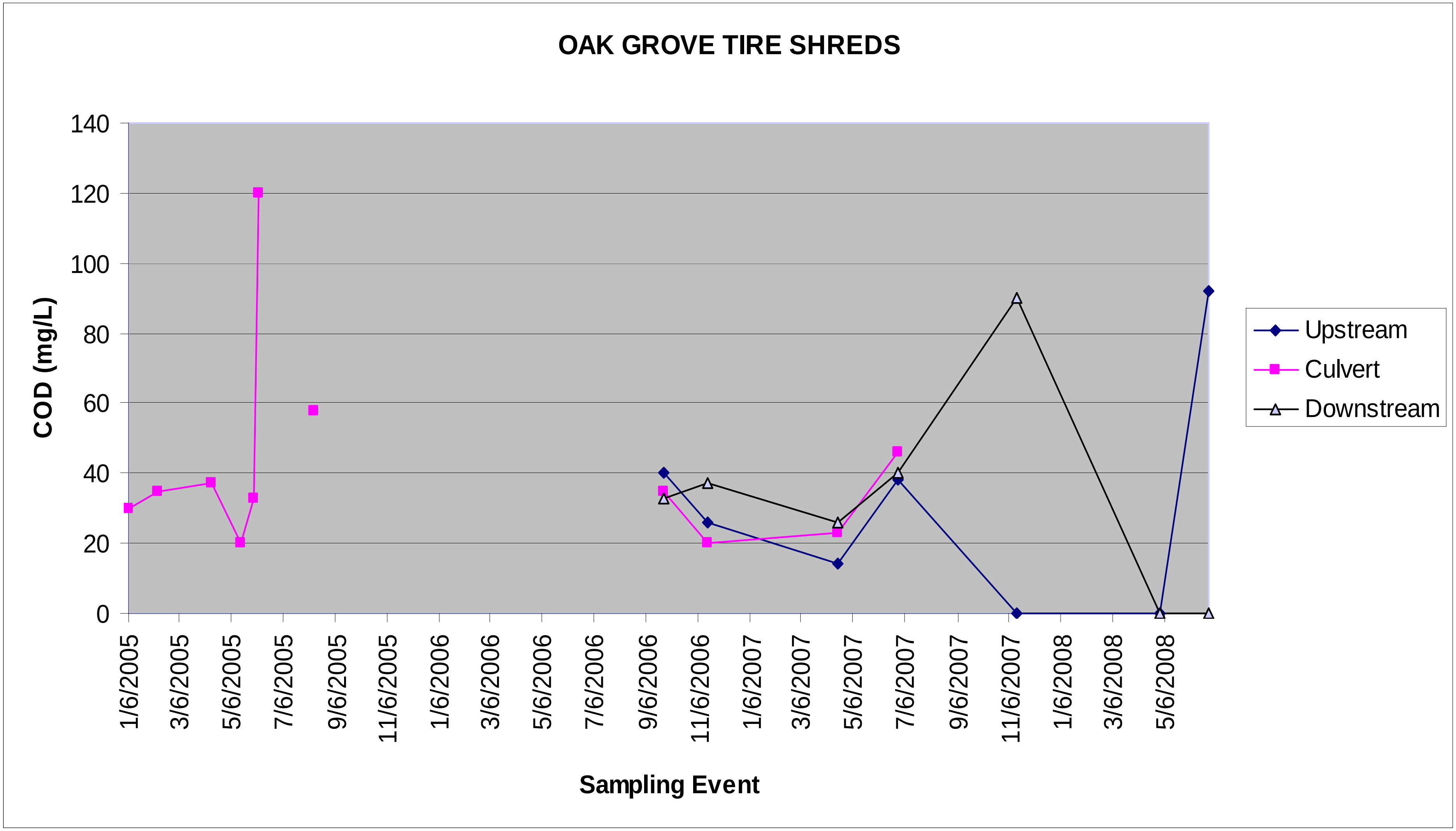

OAK GROVE TIRE SHREDS
Specific Conductance (umhos/cm)
0
200
400
600
800
1000
1200
1400
1600
1800
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6

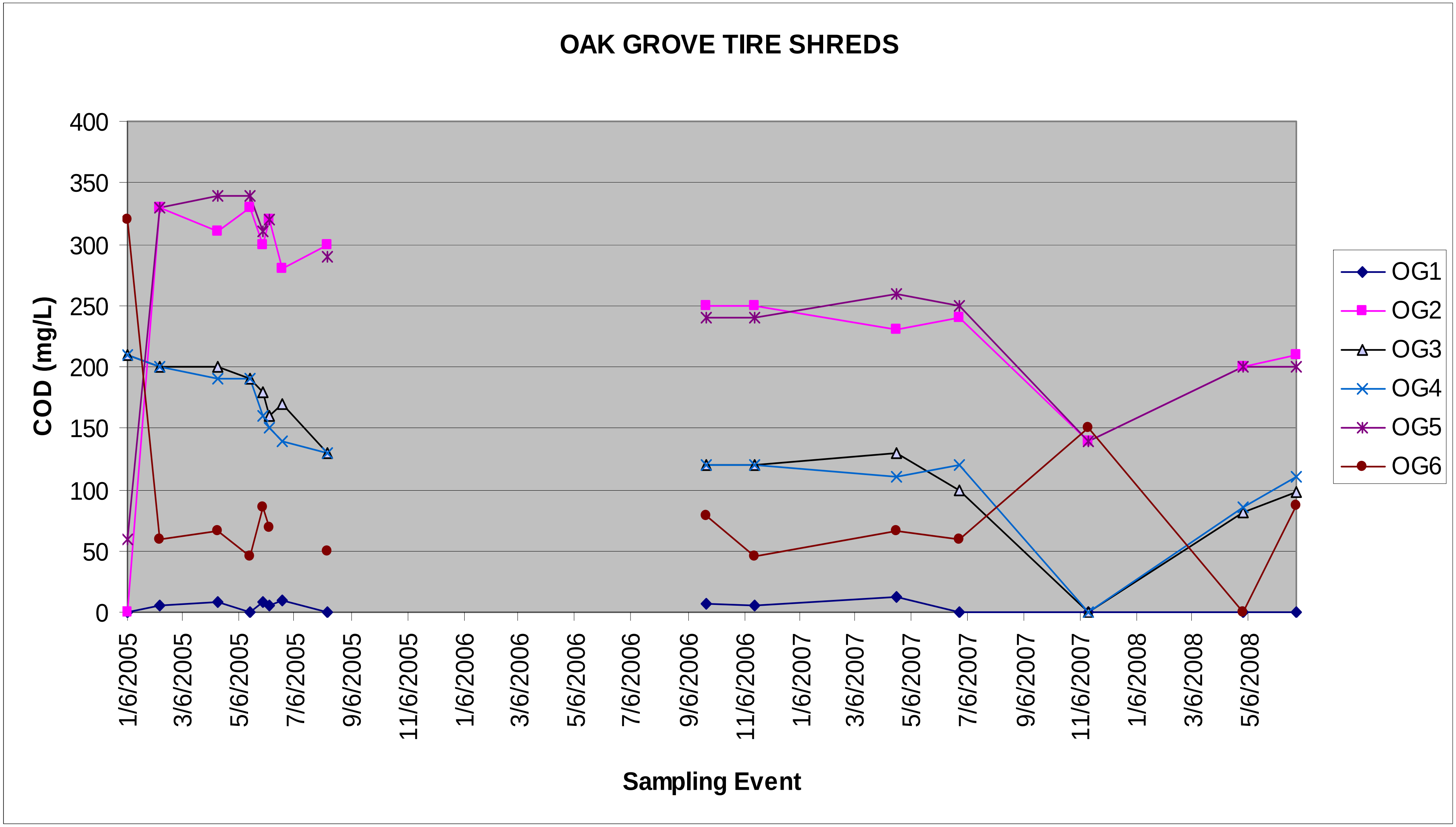

OAK GROVE TIRE SHREDS
Ammonia (mg/L)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream

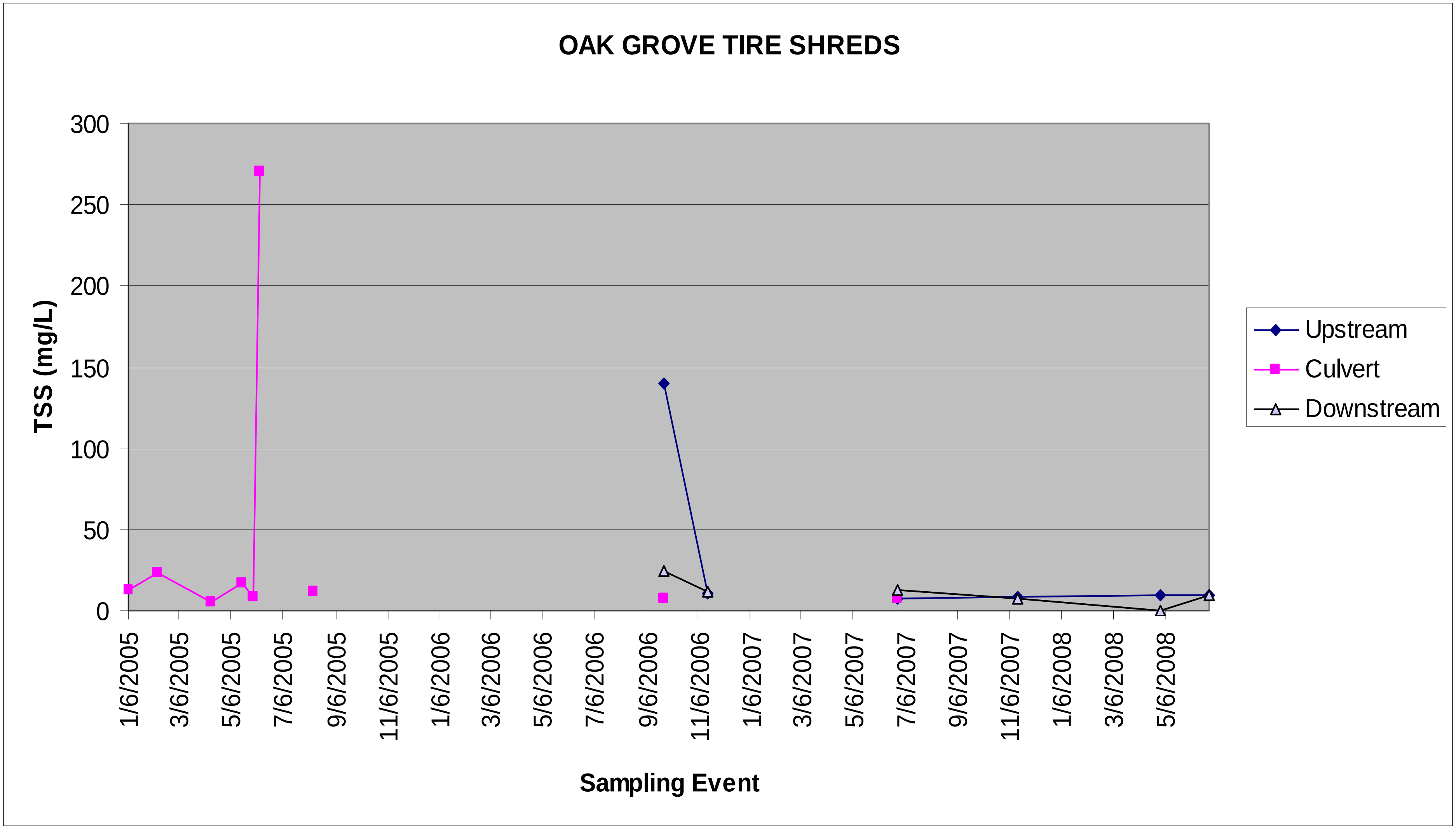

OAK GROVE TIRE SHREDS
Ammonia (mg/L)
14
12
10
8
6
4
2
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

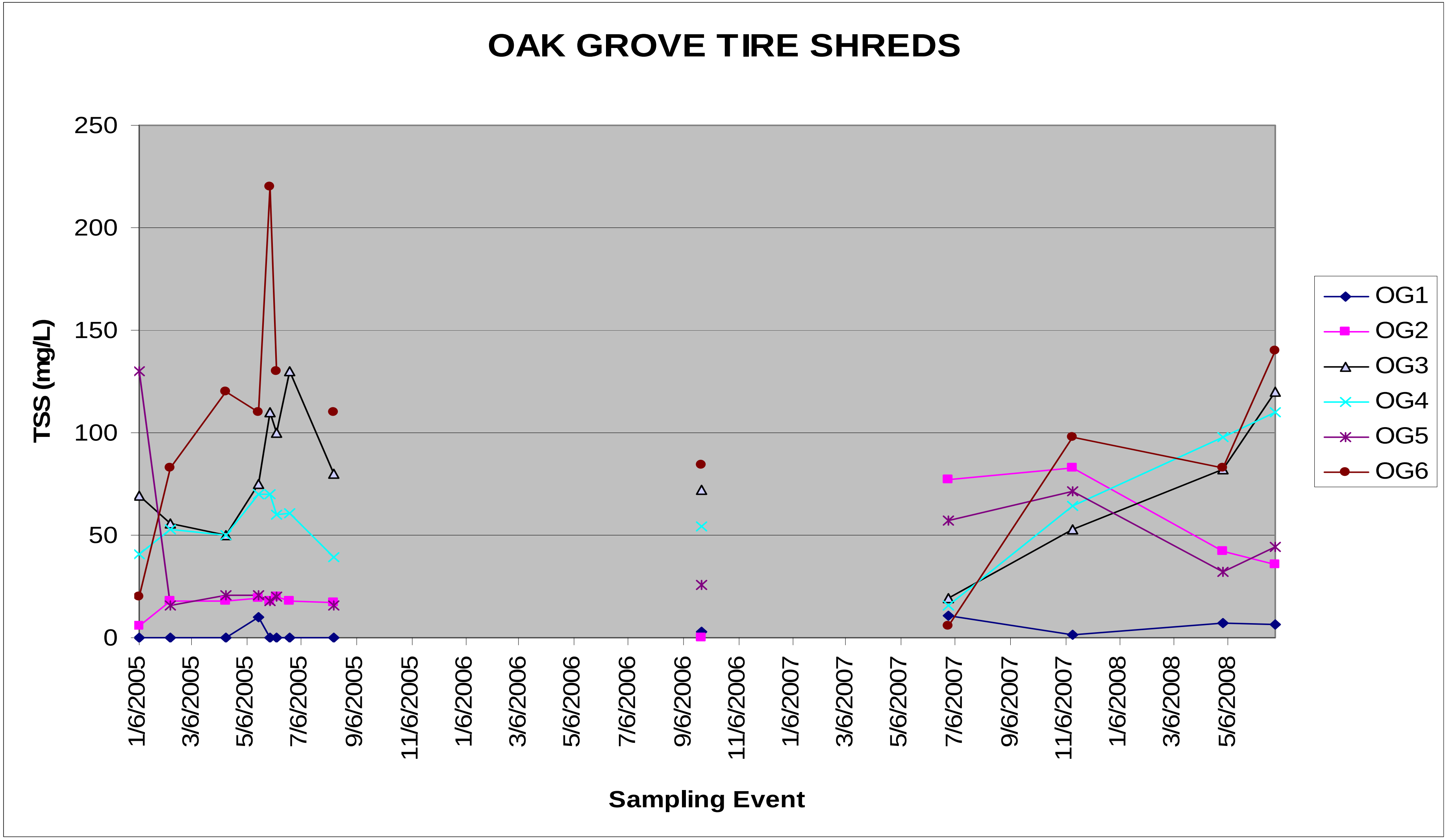

OAK GROVE TIRE SHREDS
Total Organic Carbon (mg/L
0
5
10
15
20
25
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream

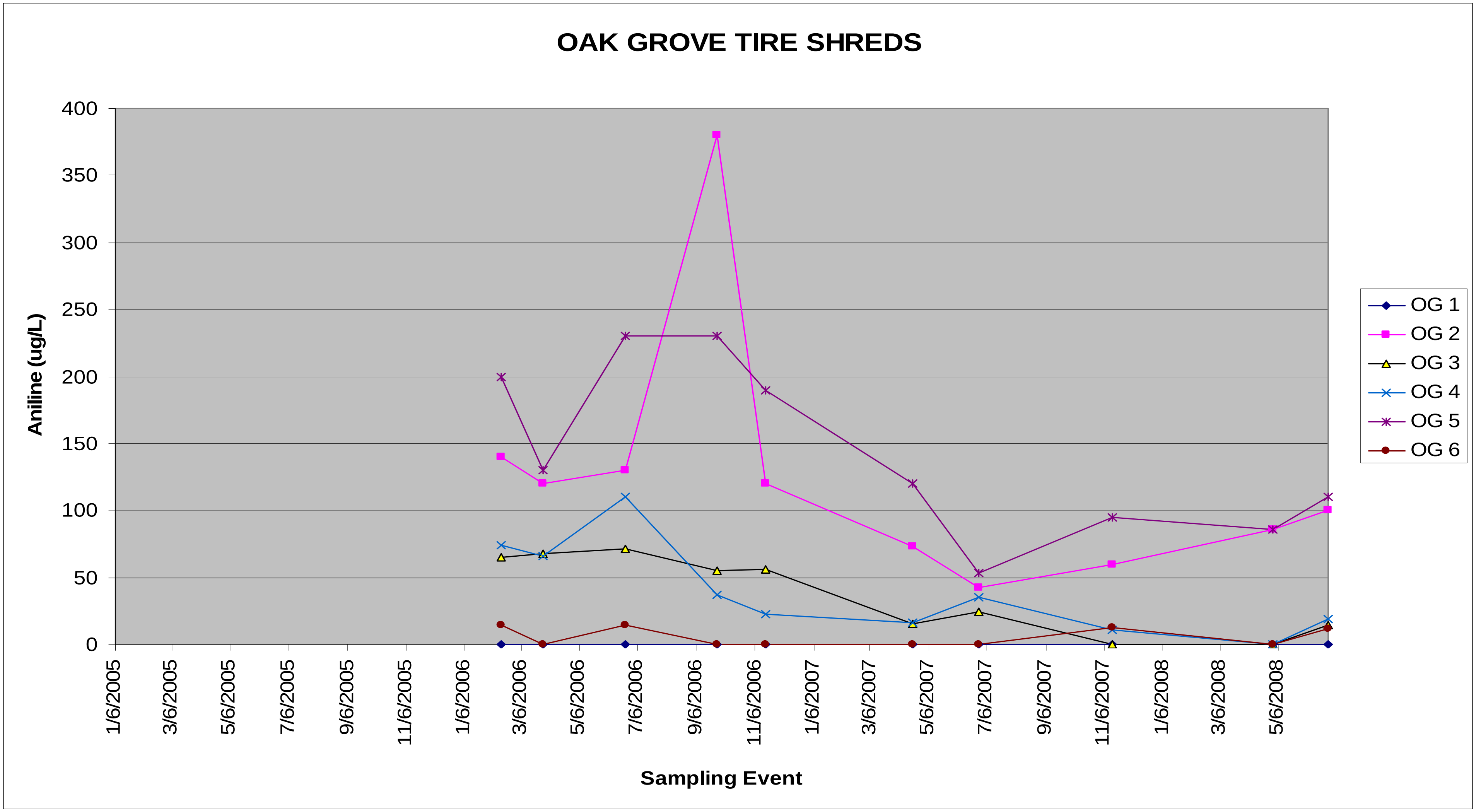

OAK GROVE TIRE SHREDS
Total Organic Carbon (mg/L)
0
20
40
60
80
100
120
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6

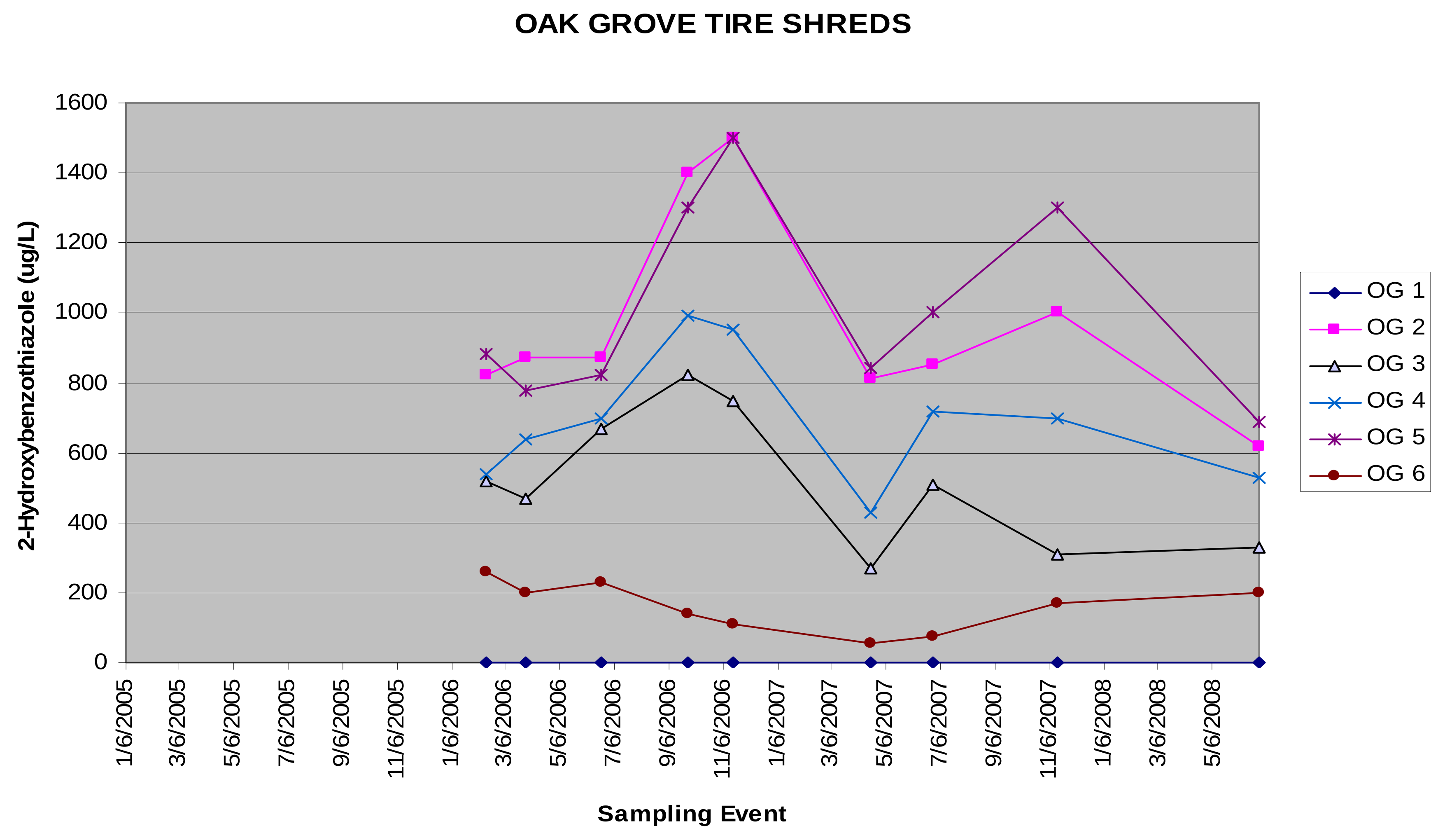

OAK GROVE TIRE SHREDS
COD (mg/L)
140
120
100
80
60
40
20
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream

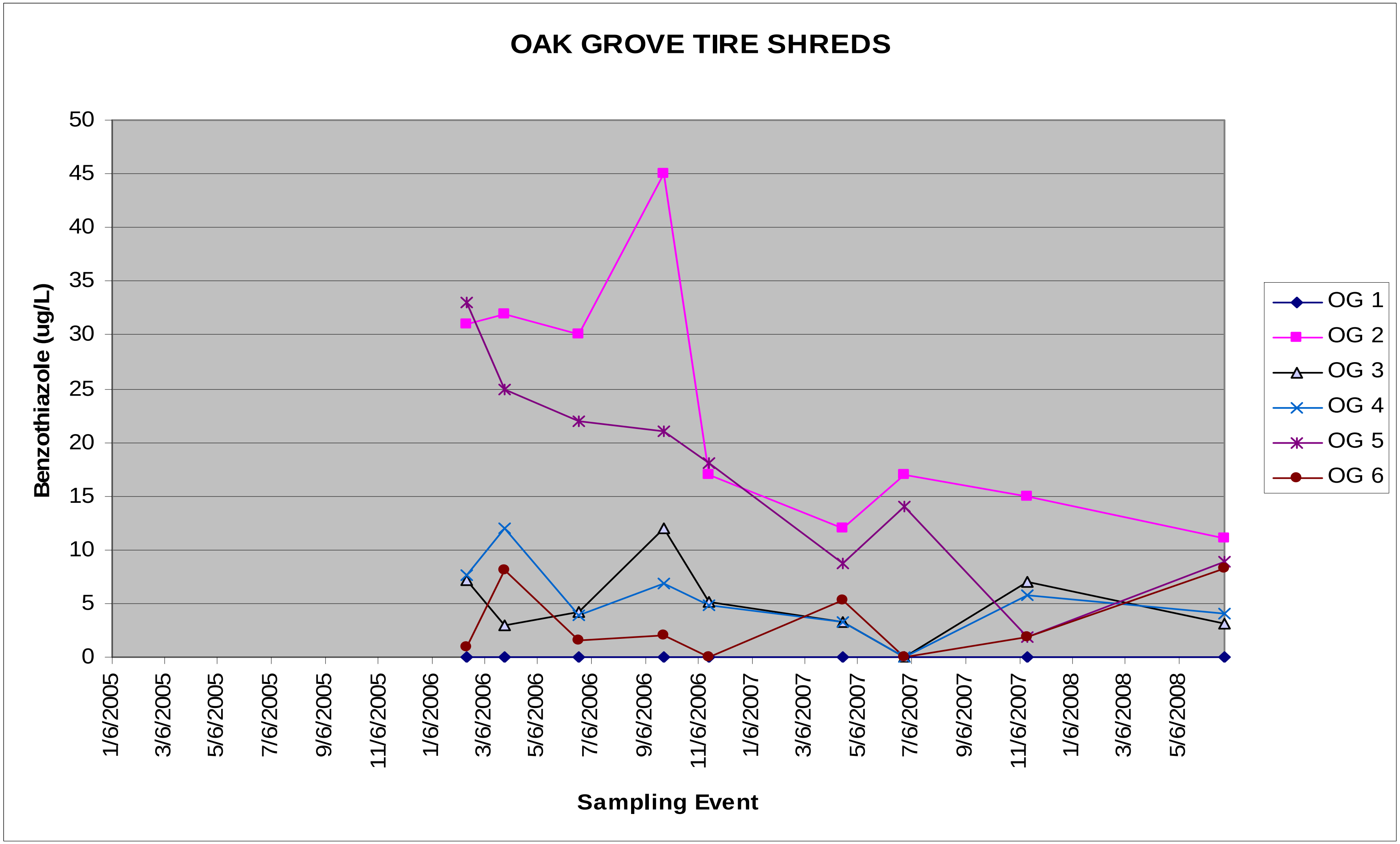

OAK GROVE TIRE SHREDS
COD (mg/L)
400
350
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6

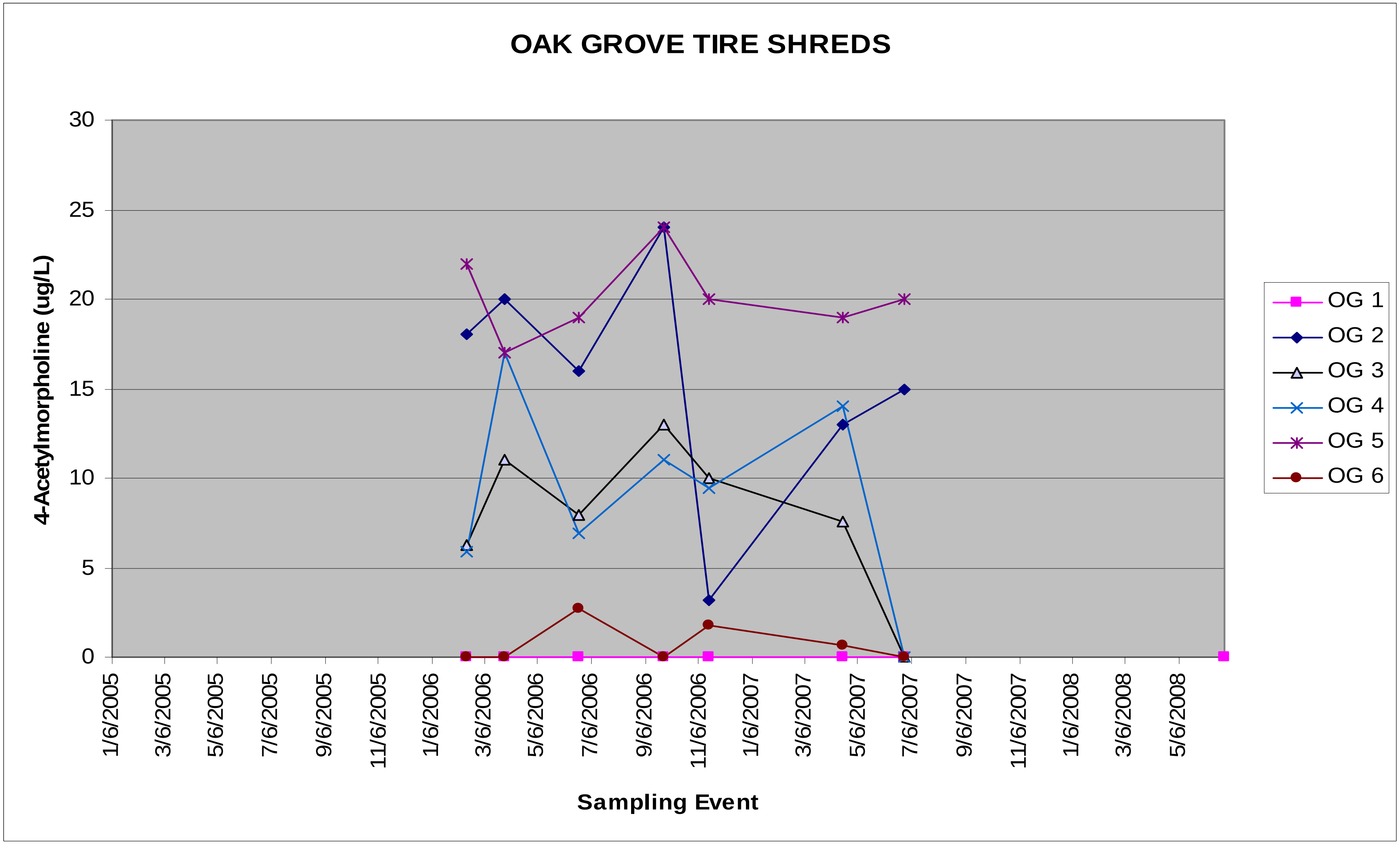

OAK GROVE TIRE SHREDS
TSS (mg/L)
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Upstream
Culvert
Downstream

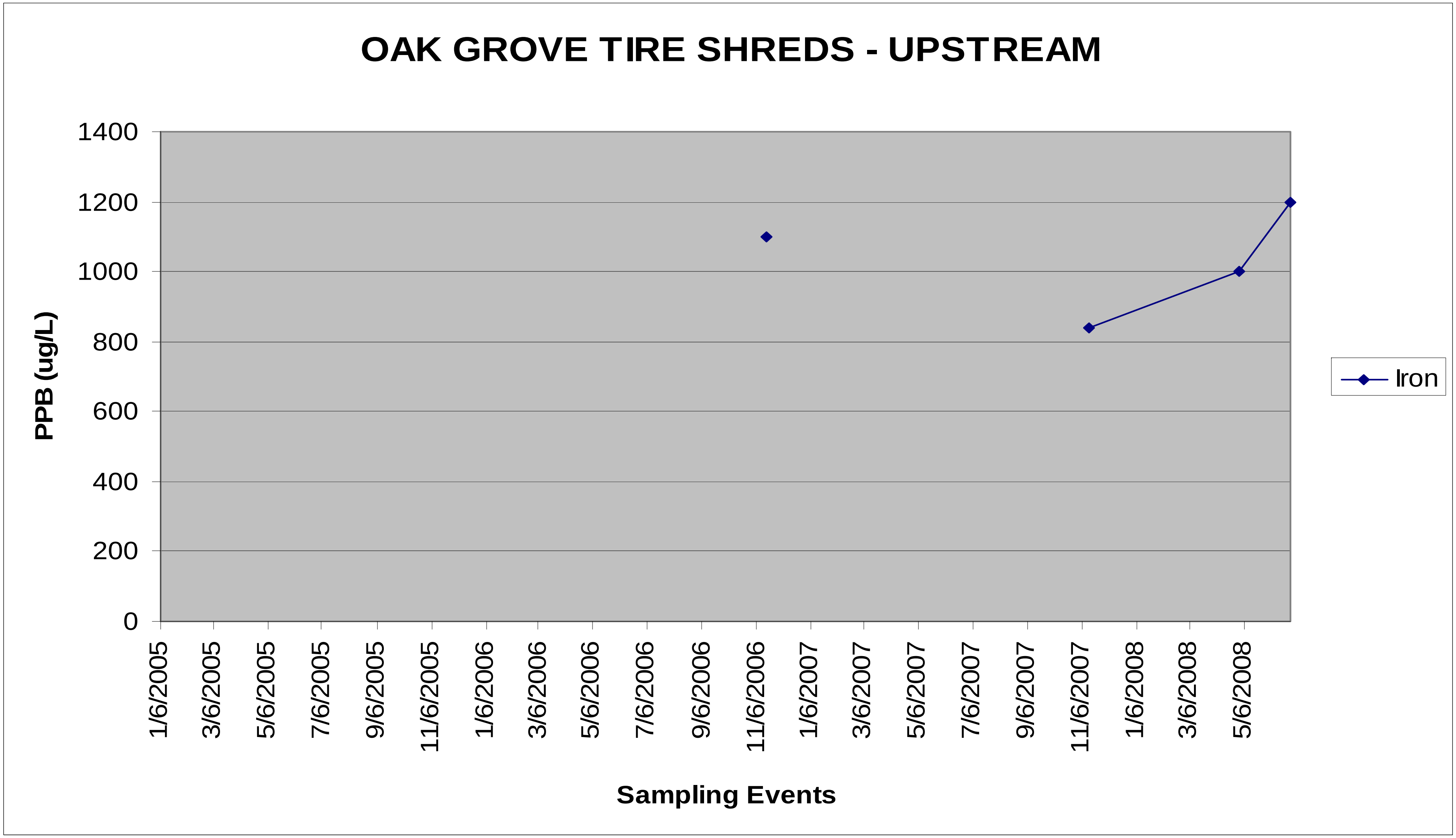

OAK GROVE TIRE SHREDS
TSS (mg/L)
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG1
OG2
OG3
OG4
OG5
OG6

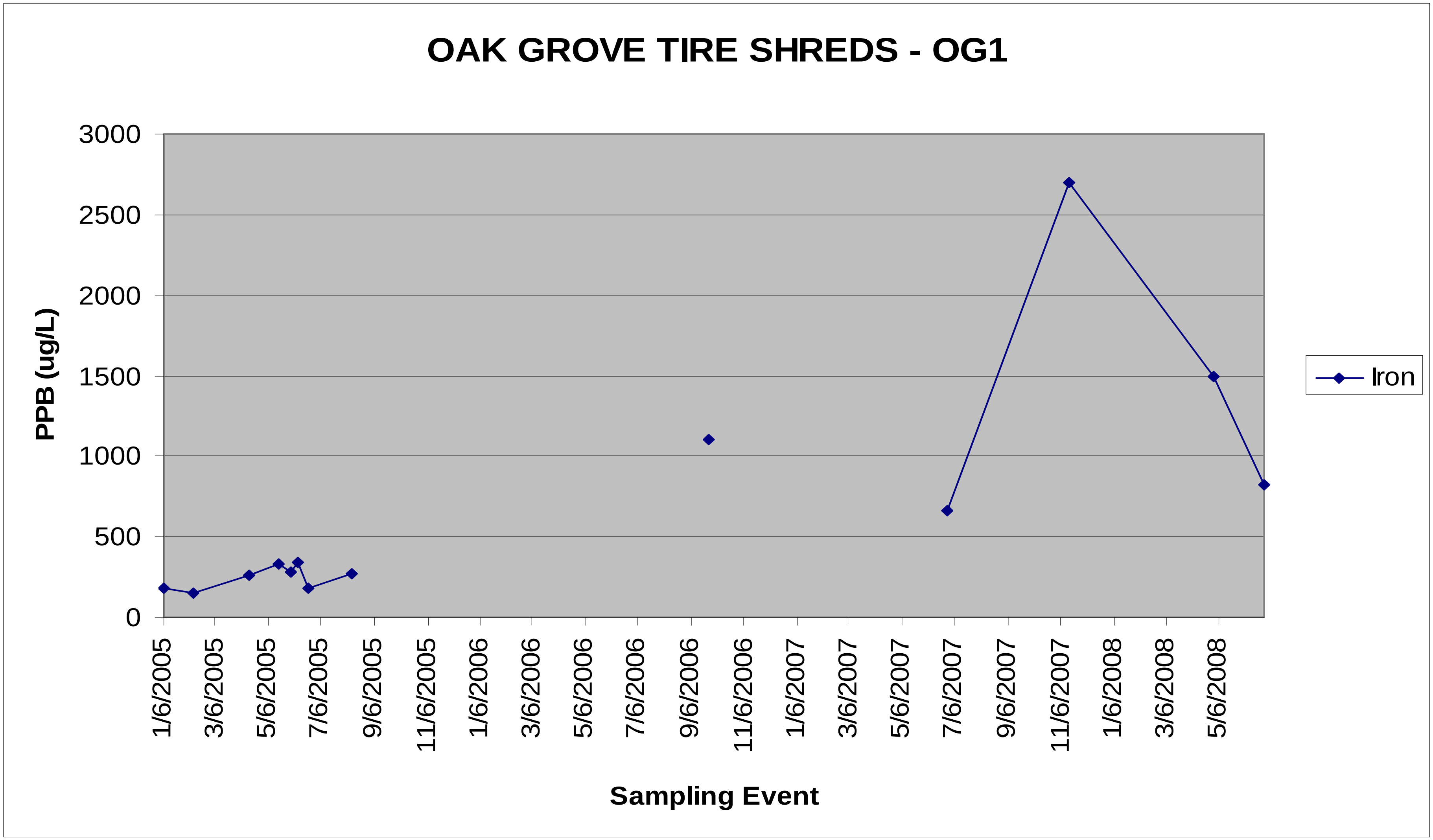

OAK GROVE TIRE SHREDS
Aniline (ug/L)
400
350
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

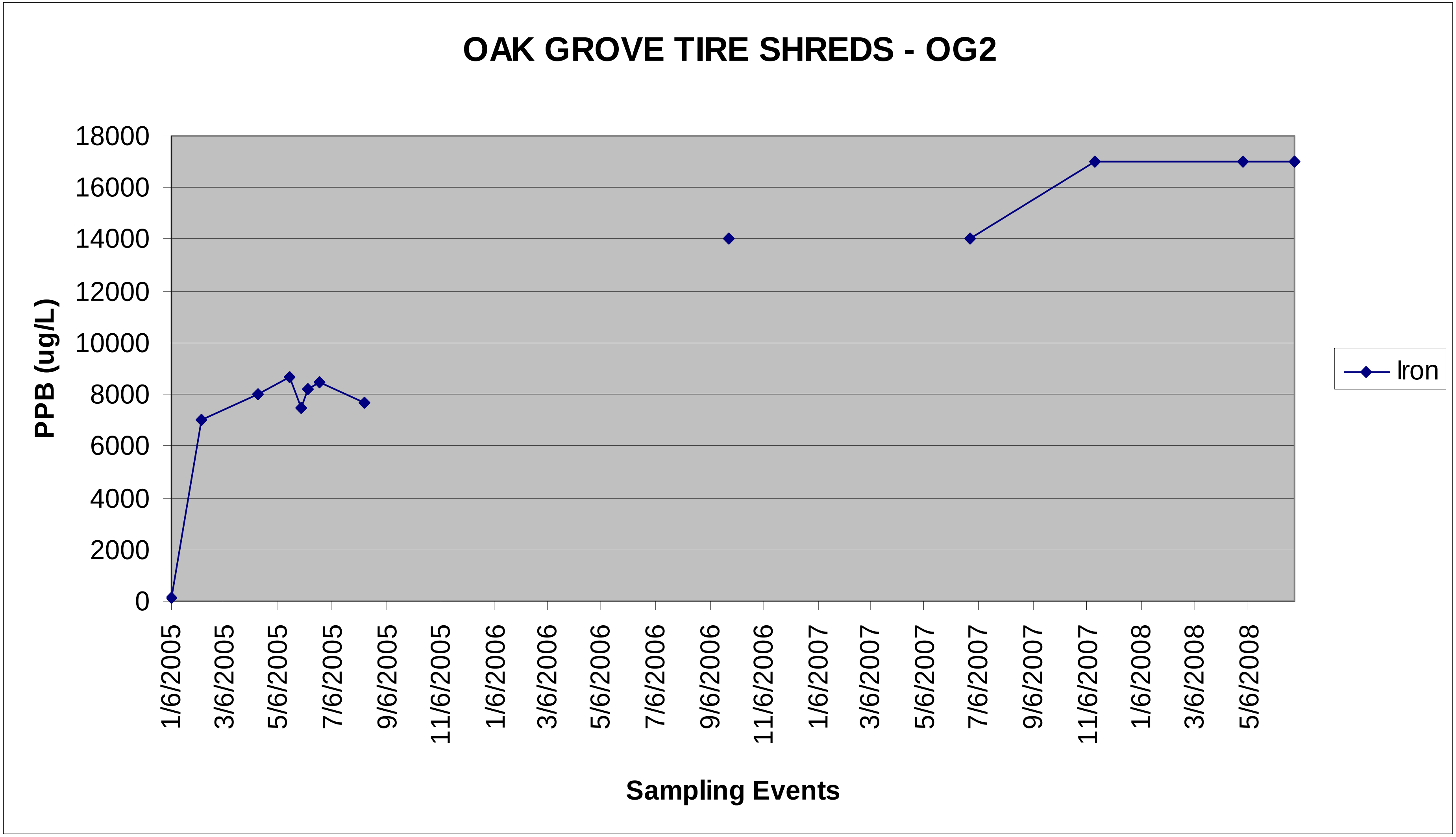

OAK GROVE TIRE SHREDS
2-Hydroxybenzothiazole (ug/L)
0
200
400
600
800
1000
1200
1400
1600
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

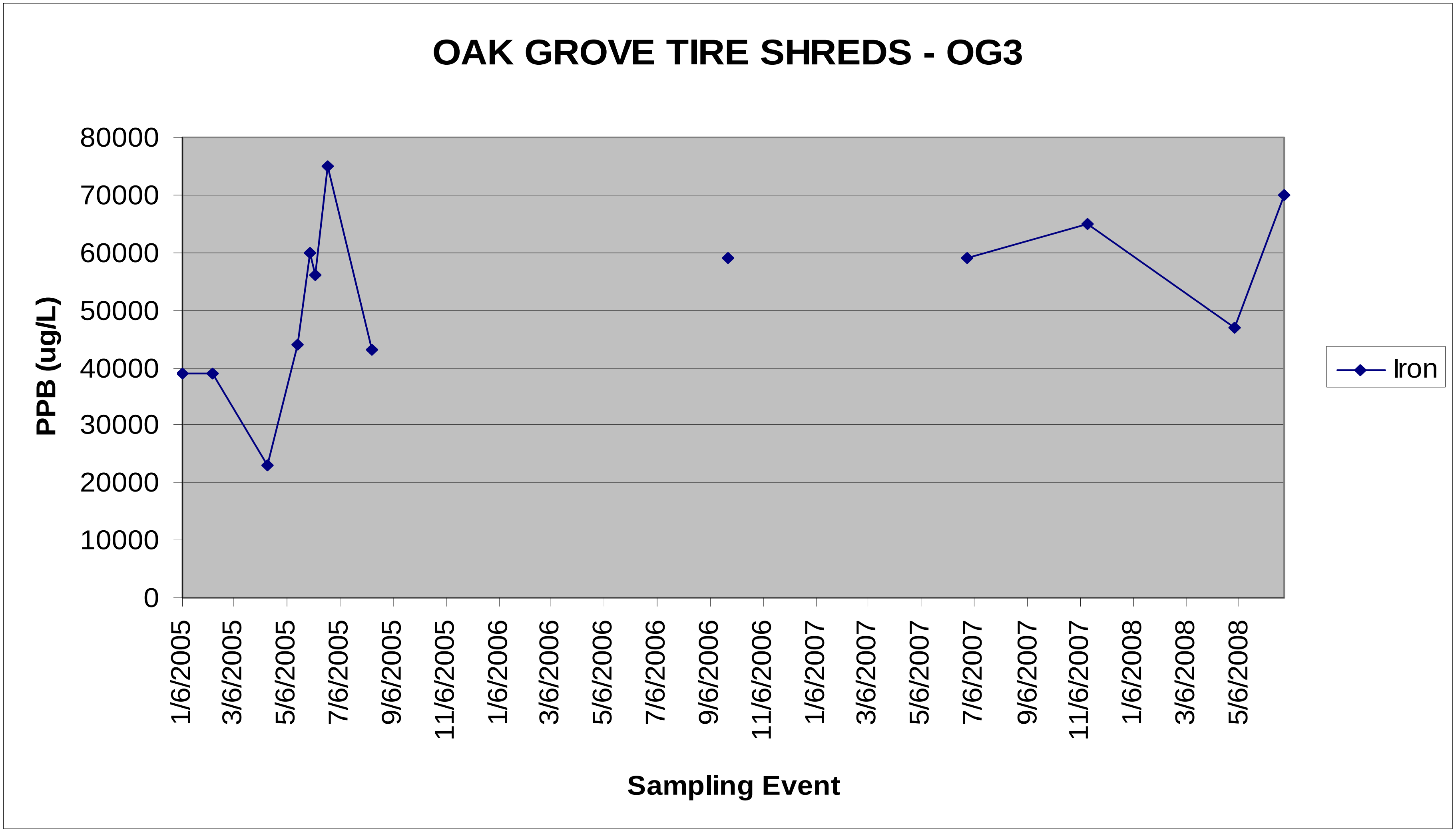

OAK GROVE TIRE SHREDS
Benzothiazole (ug/L)
50
45
40
35
30
25
20
15
10
5
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

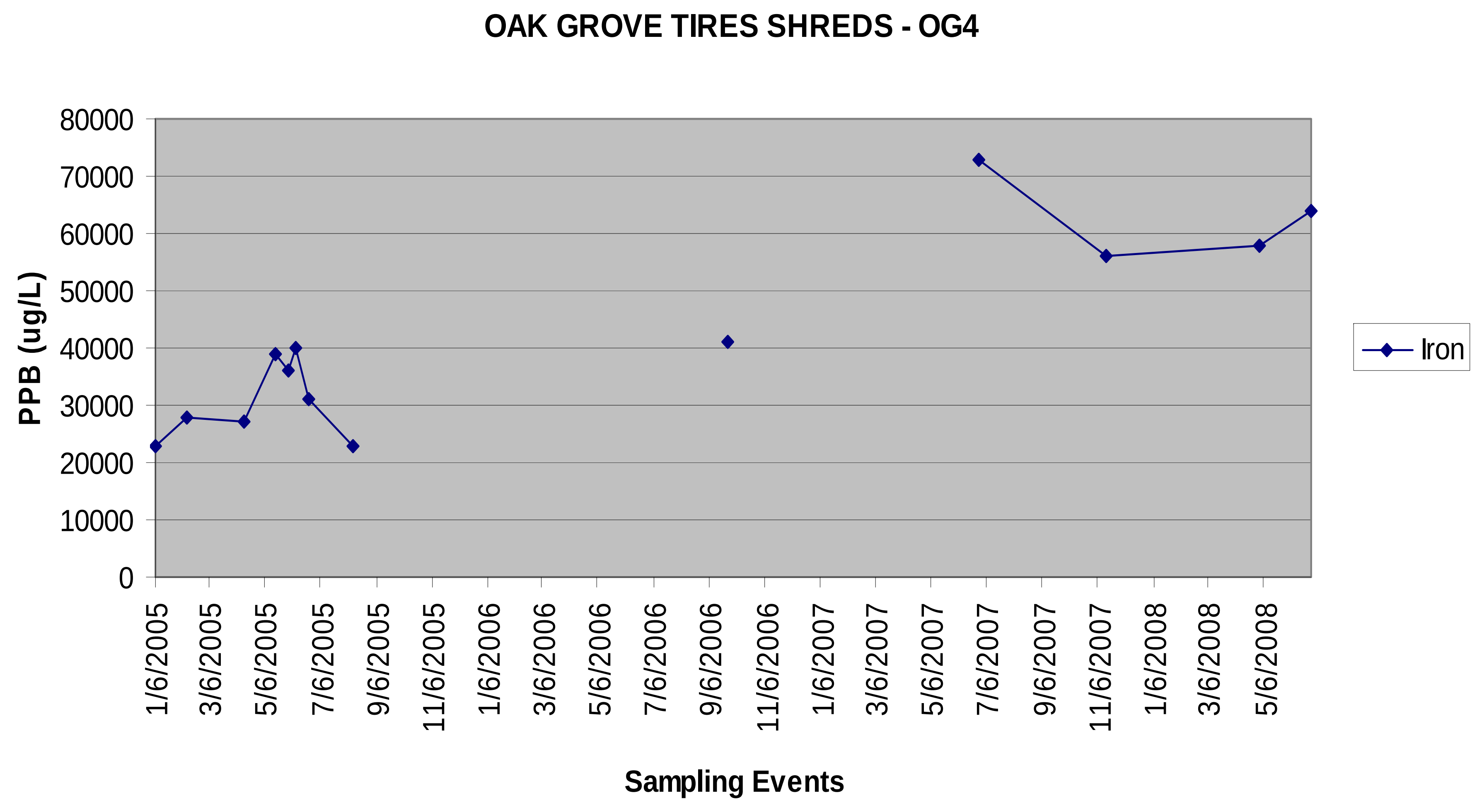

OAK GROVE TIRE SHREDS
4-Acetylmorpholine (ug/L)
30
25
20
15
10
5
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
OG 1
OG 2
OG 3
OG 4
OG 5
OG 6

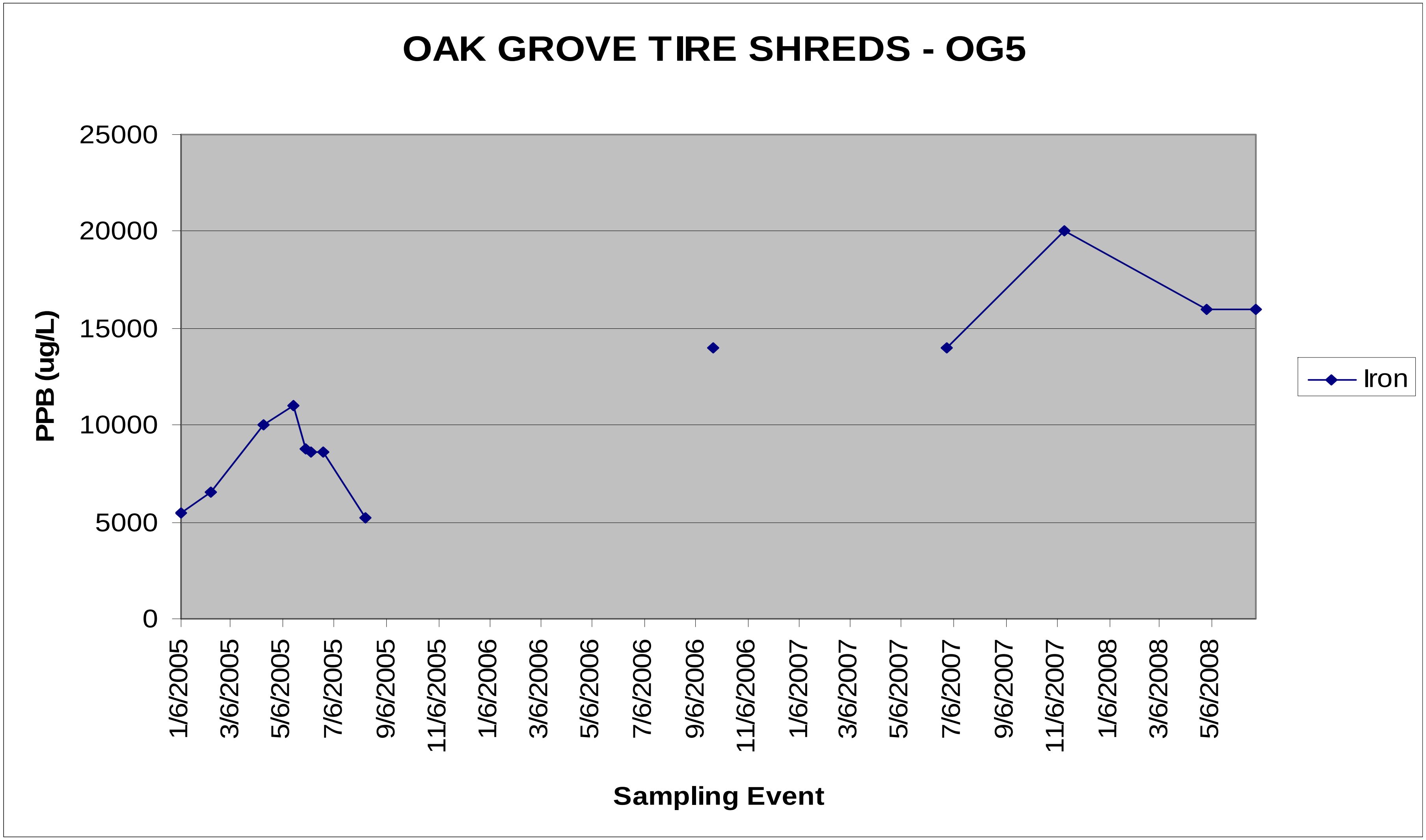

OAK GROVE TIRE SHREDS - UPSTREAM
PPB (ug/L)
1400
1200
1000
800
600
400
200
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Iron

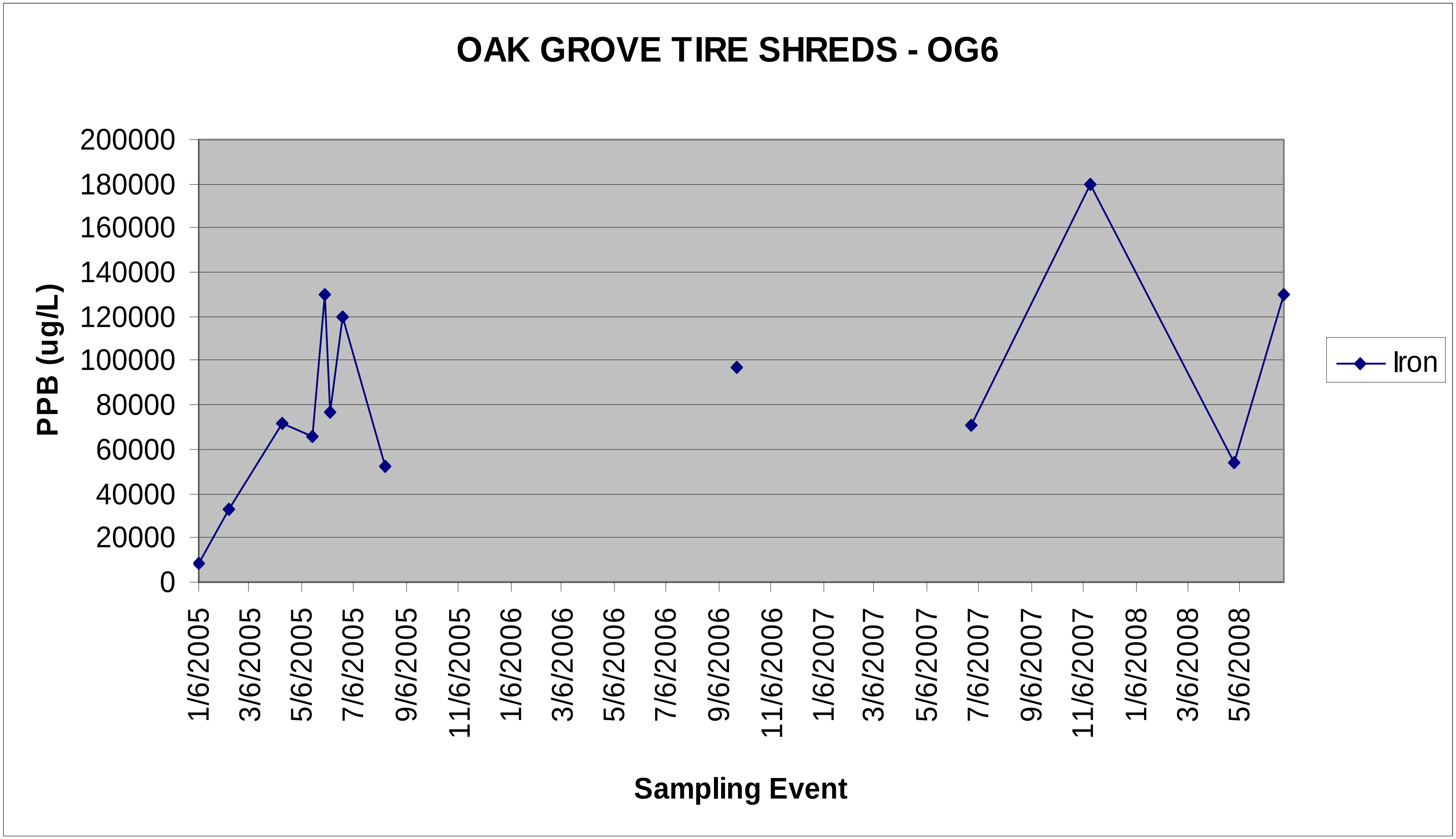

OAK GROVE TIRE SHREDS - OG1
PPB (ug/L)
3000
2500
2000
1500
1000
500
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Iron

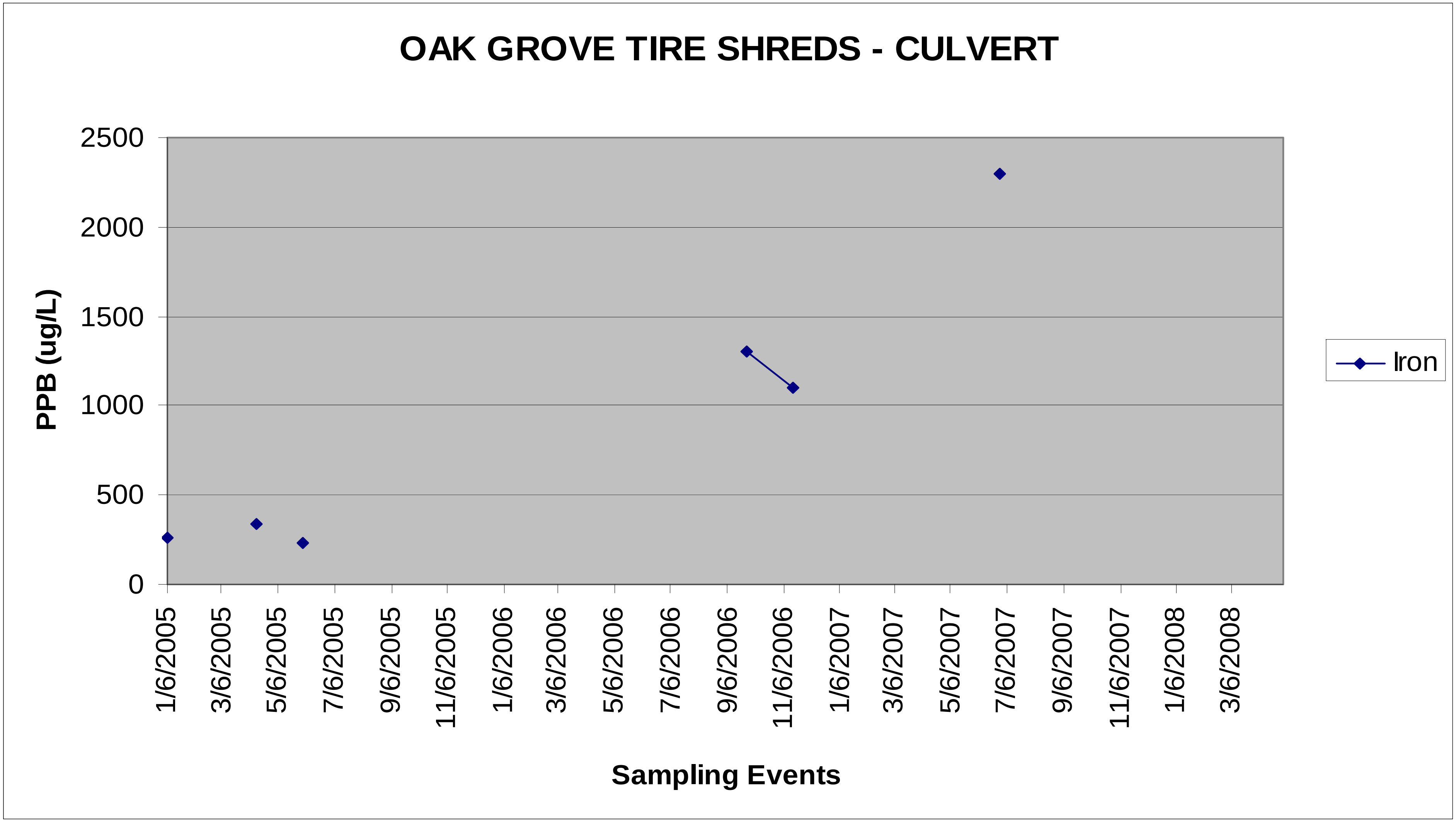

OAK GROVE TIRE SHREDS - OG2
PPB (ug/L)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Iron

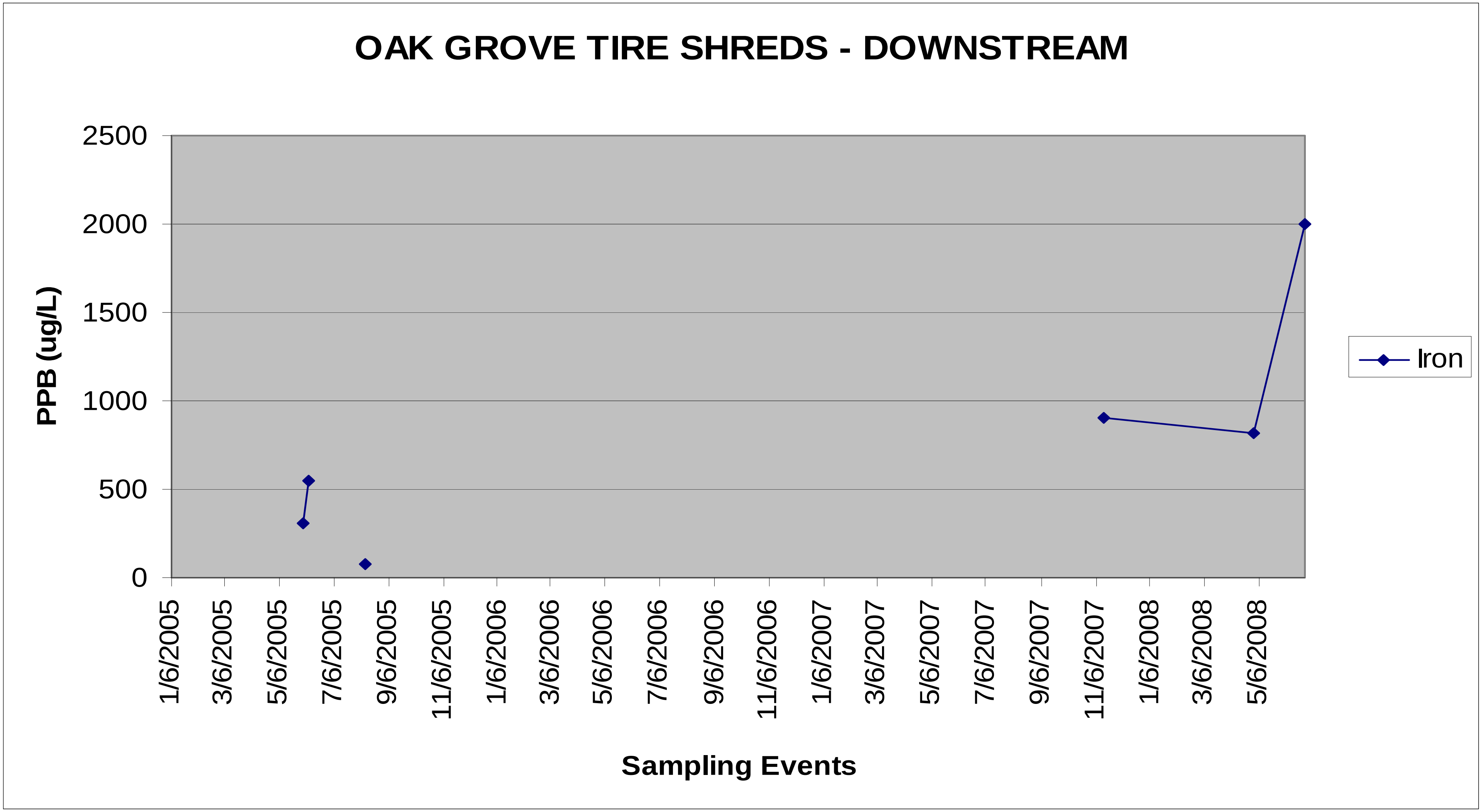

OAK GROVE TIRE SHREDS - OG3
PPB (ug/L)
80000
70000
60000
50000
40000
30000
20000
10000
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Iron

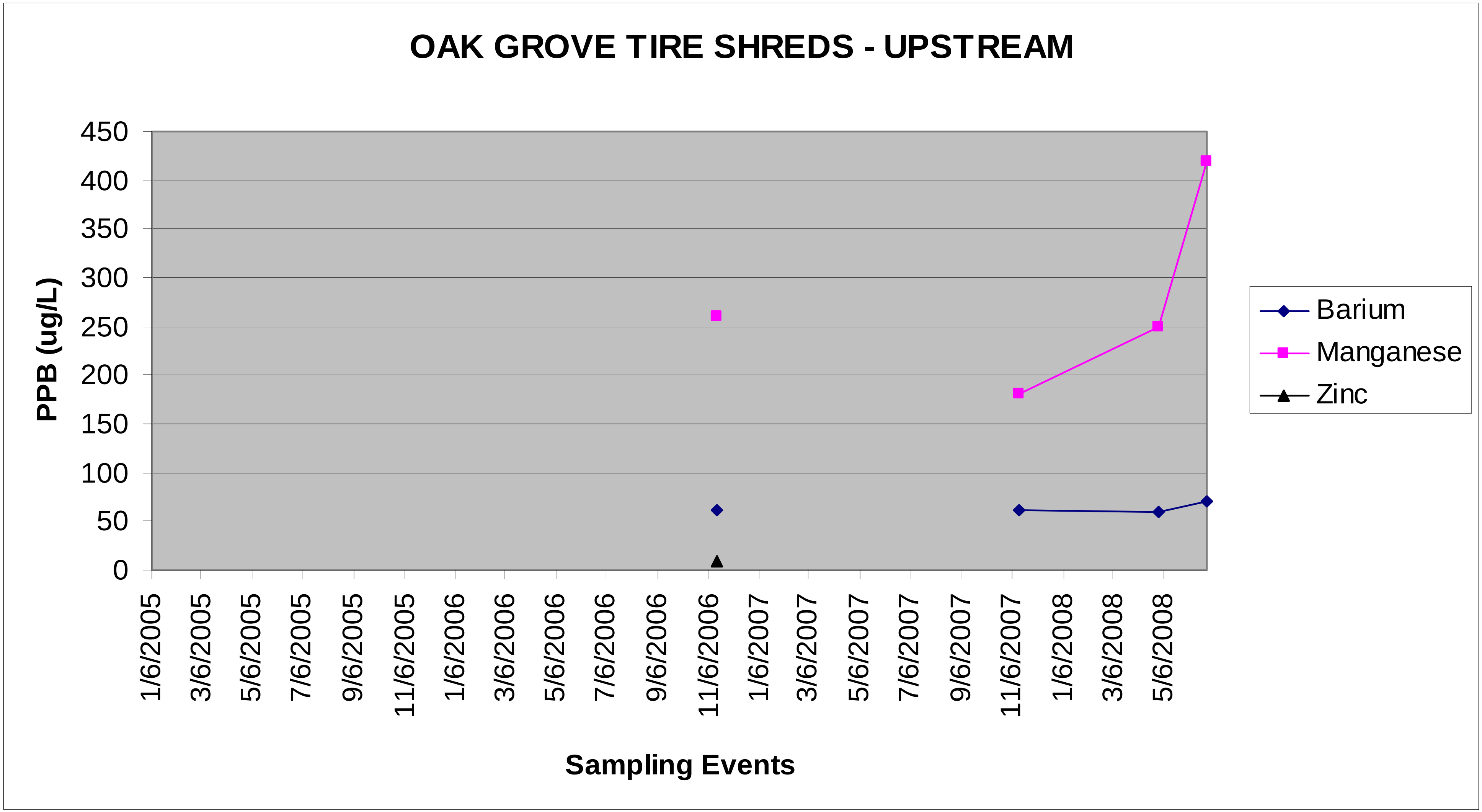

OAK GROVE TIRES SHREDS - OG4
PPB (ug/L)
80000
70000
60000
50000
40000
30000
20000
10000
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Iron

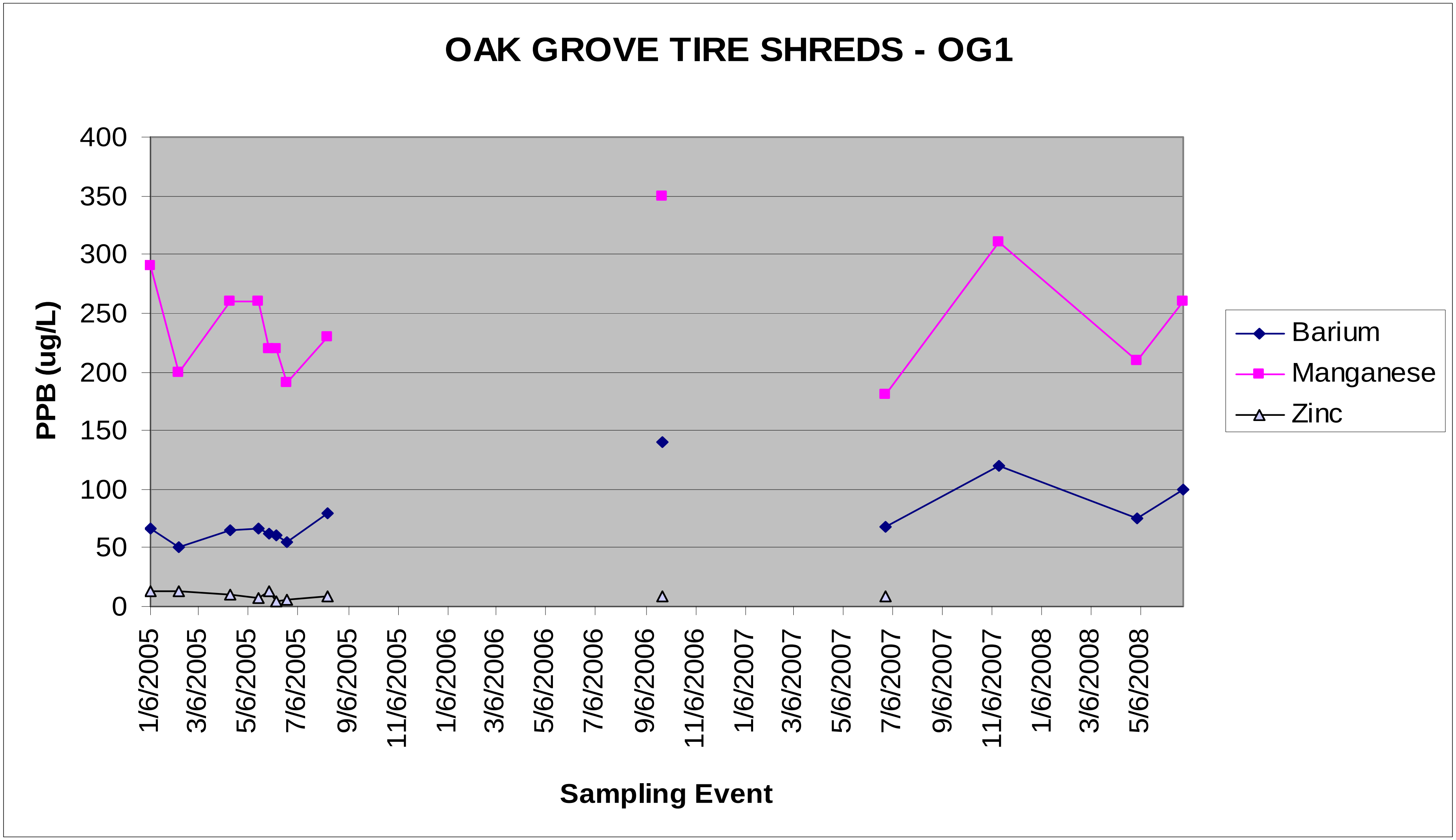

OAK GROVE TIRE SHREDS - OG5
PPB (ug/L)
25000
20000
15000
10000
5000
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Iron

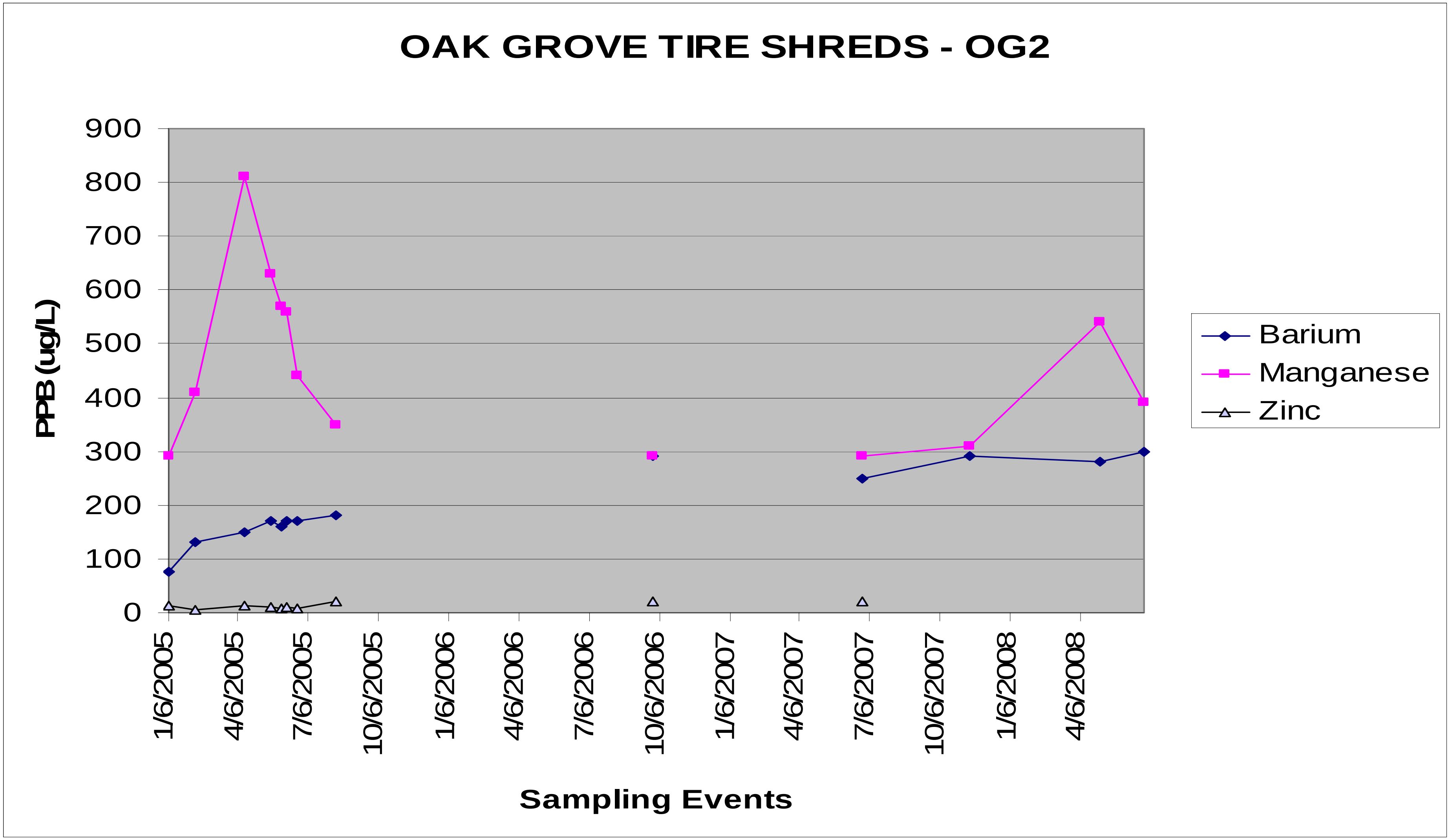

OAK GROVE TIRE SHREDS - OG6
PPB (ug/L)
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Iron

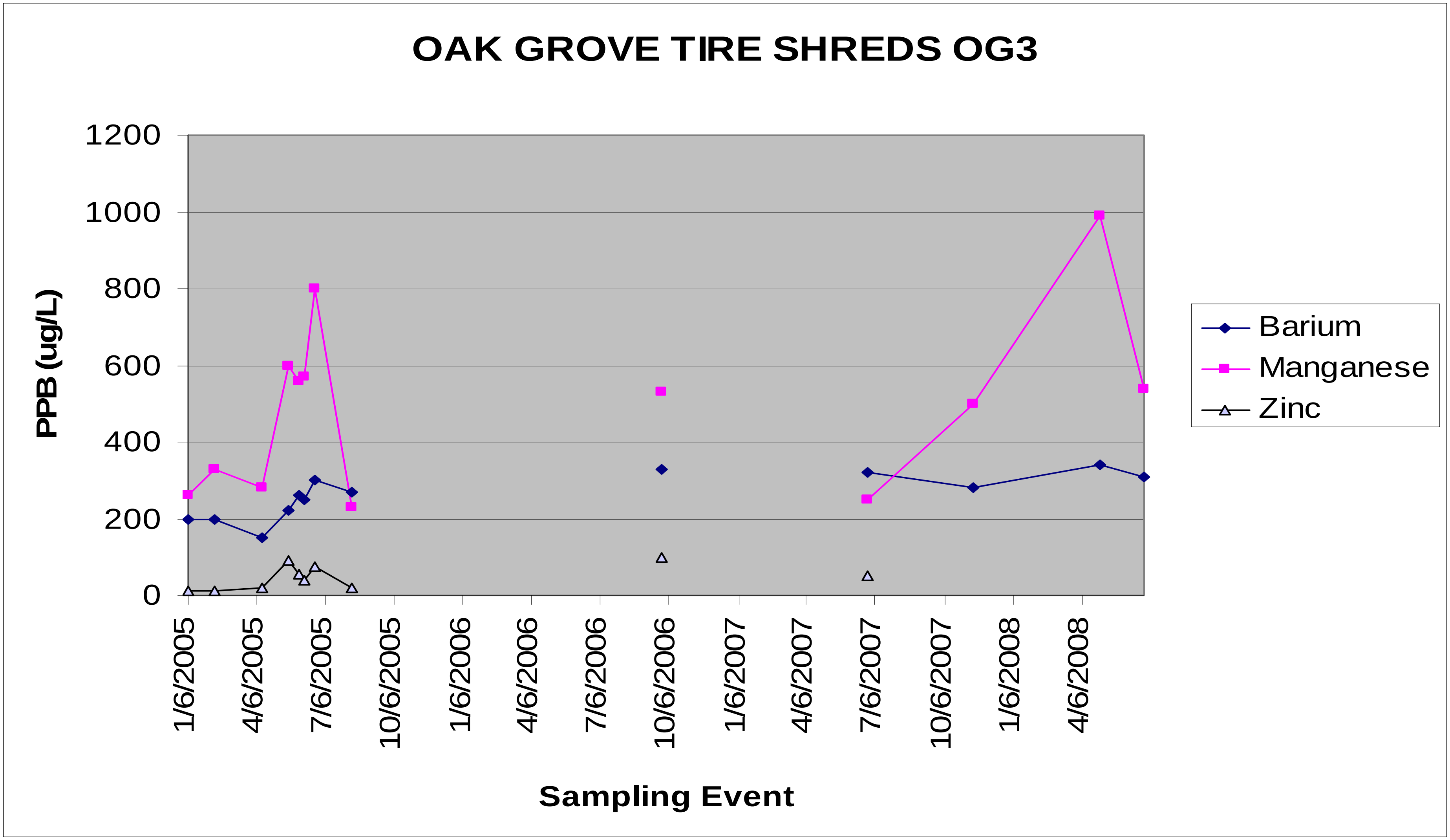

OAK GROVE TIRE SHREDS - CULVERT
PPB (ug/L)
2500
2000
1500
1000
500
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
Sampling Events
Iron

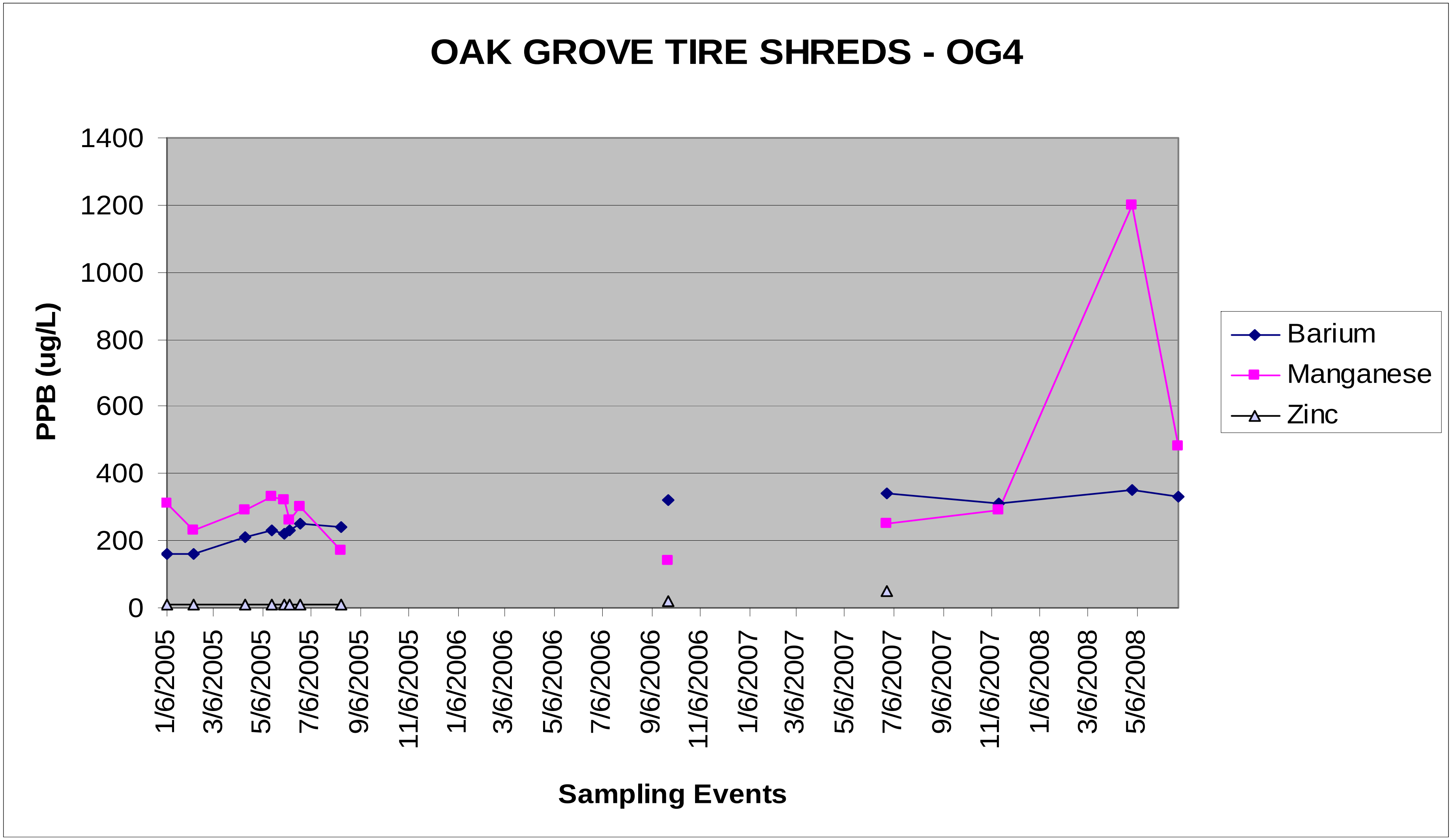

OAK GROVE TIRE SHREDS - DOWNSTREAM
PPB (ug/L)
2500
2000
1500
1000
500
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Iron

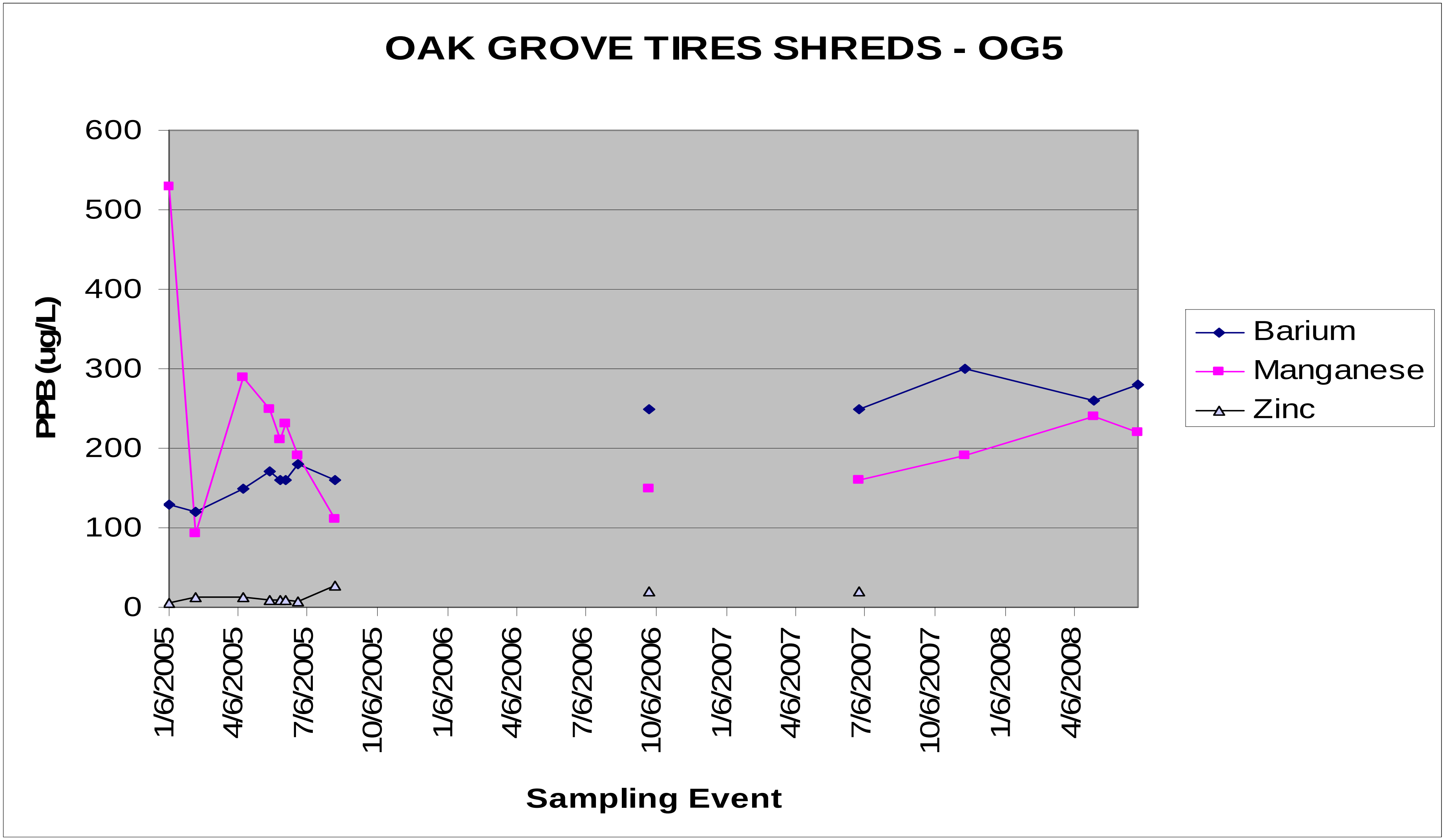

OAK GROVE TIRE SHREDS - UPSTREAM
PPB (ug/L)
450
400
350
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Barium
Manganese
Zinc

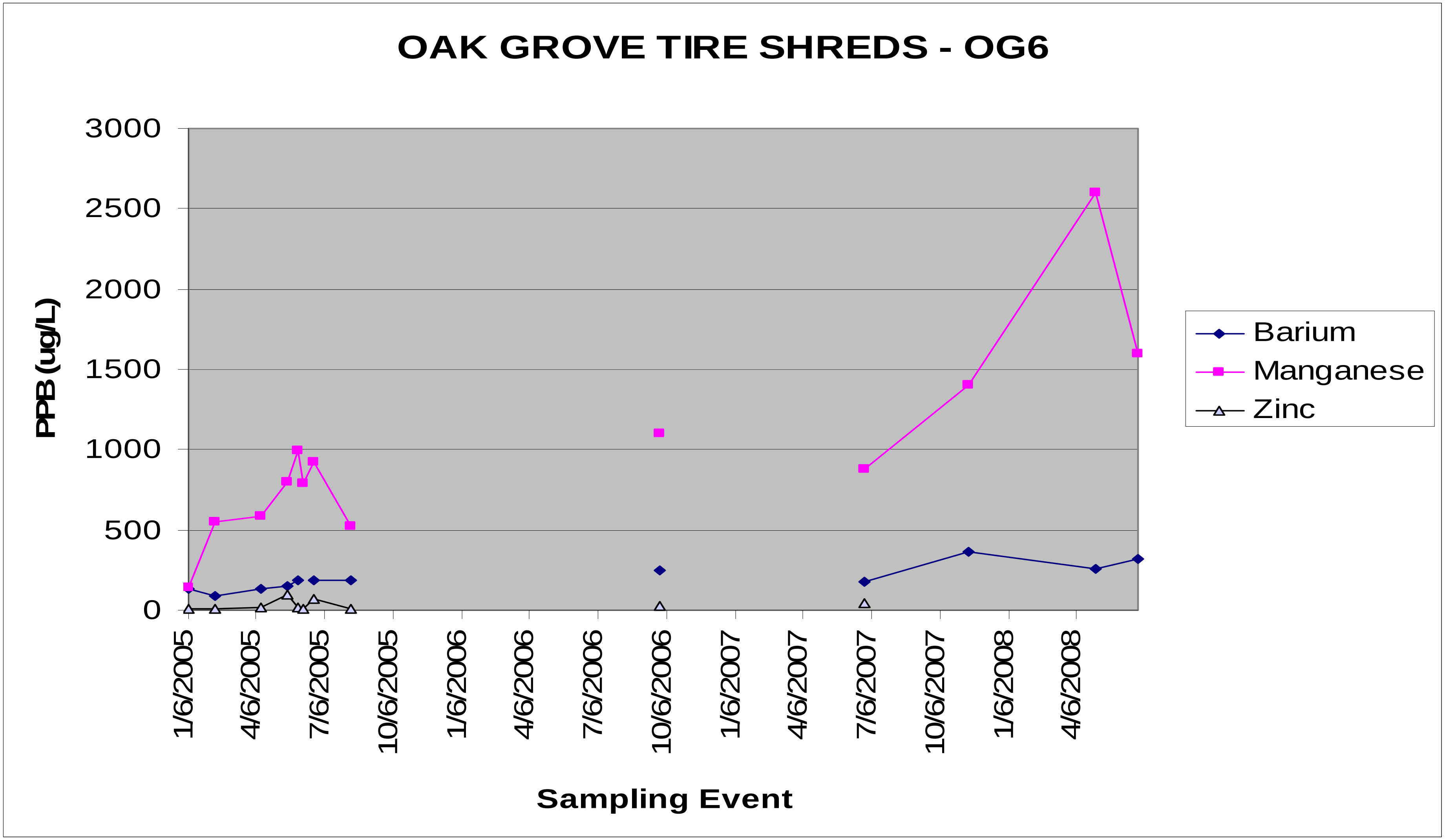

OAK GROVE TIRE SHREDS - OG1
PPB (ug/L)
400
350
300
250
200
150
100
50
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Event
Barium
Manganese
Zinc

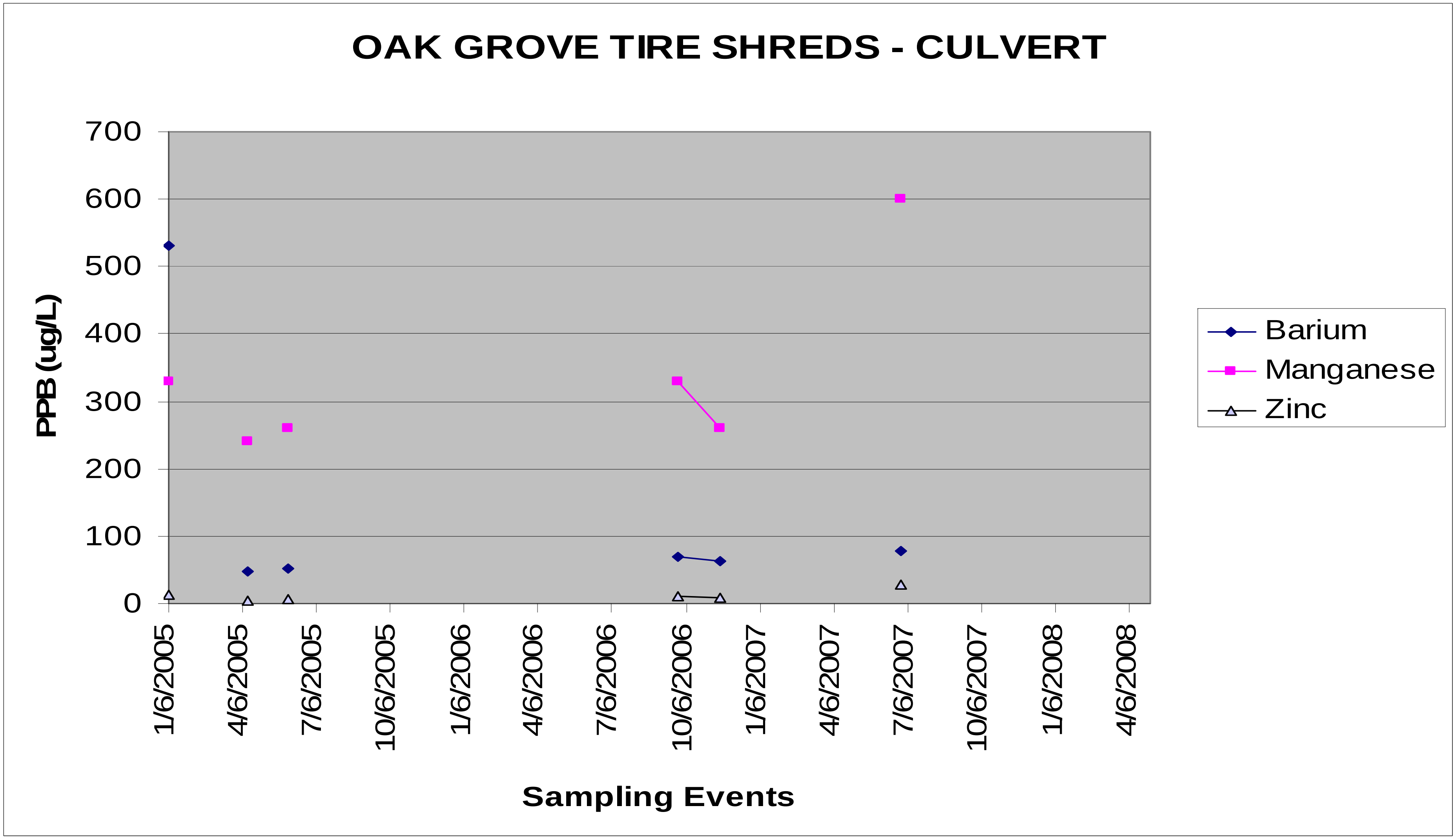

OAK GROVE TIRE SHREDS - OG2
PPB (ug/L)
900
800
700
600
500
400
300
200
100
0
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Events
Barium
Manganese
Zinc

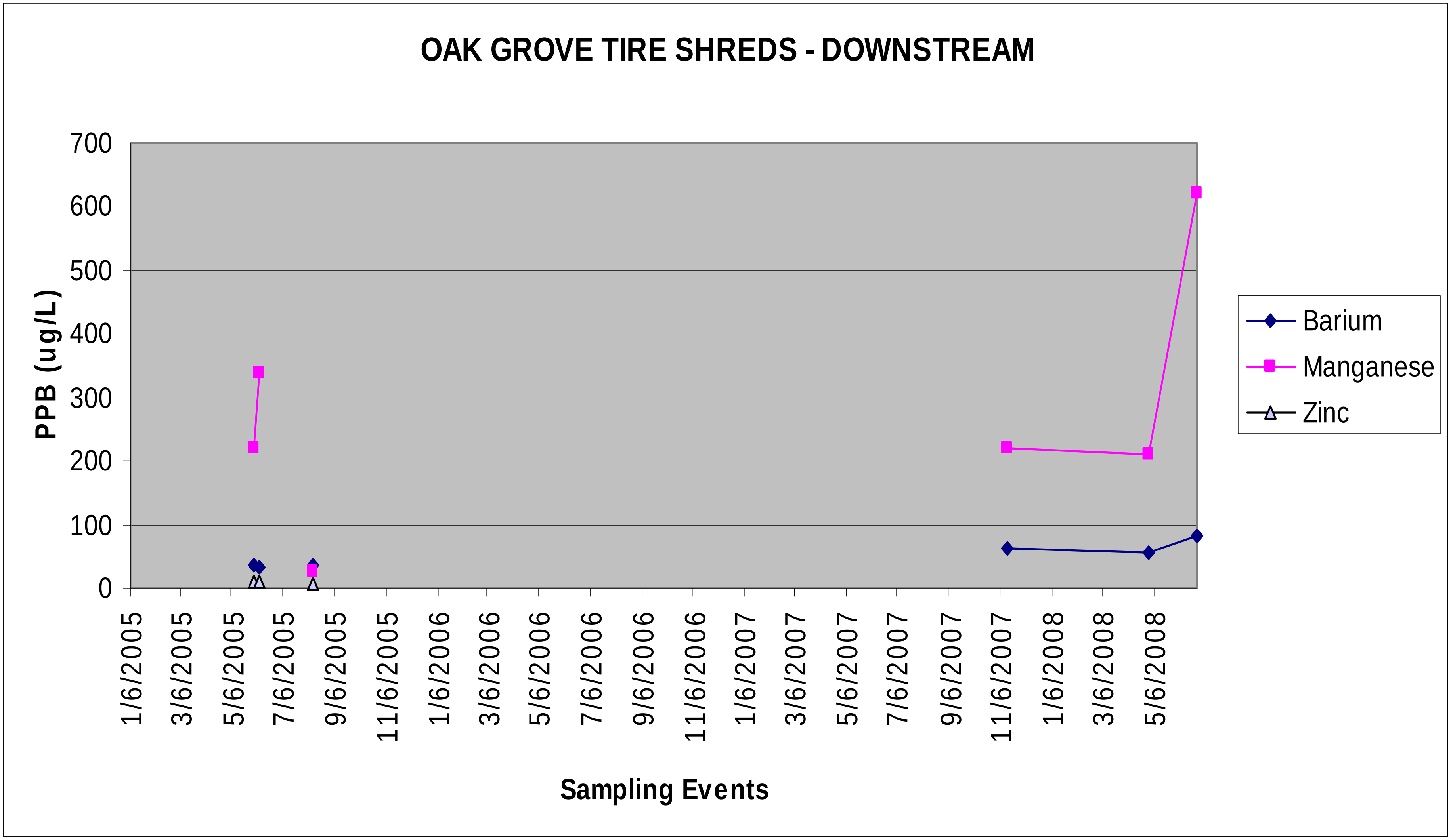

OAK GROVE TIRE SHREDS OG3
PPB (ug/L)
1200
1000
800
600
400
200
0
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Event
Barium
Manganese
Zinc


OAK GROVE TIRE SHREDS - OG4
PPB (ug/L)
1400
1200
1000
800
600
400
200
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Barium
Manganese
Zinc


OAK GROVE TIRES SHREDS - OG5
PPB (ug/L)
600
500
400
300
200
100
0
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Event
Barium
Manganese
Zinc


OAK GROVE TIRE SHREDS - OG6
PPB (ug/L)
3000
2500
2000
1500
1000
500
0
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Event
Barium
Manganese
Zinc


OAK GROVE TIRE SHREDS - CULVERT
PPB (ug/L)
700
600
500
400
300
200
100
0
1/6/2005
4/6/2005
7/6/2005
10/6/2005
1/6/2006
4/6/2006
7/6/2006
10/6/2006
1/6/2007
4/6/2007
7/6/2007
10/6/2007
1/6/2008
4/6/2008
Sampling Events
Barium
Manganese
Zinc


OAK GROVE TIRE SHREDS - DOWNSTREAM
PPB (ug/L)
700
600
500
400
300
200
100
0
1/6/2005
3/6/2005
5/6/2005
7/6/2005
9/6/2005
11/6/2005
1/6/2006
3/6/2006
5/6/2006
7/6/2006
9/6/2006
11/6/2006
1/6/2007
3/6/2007
5/6/2007
7/6/2007
9/6/2007
11/6/2007
1/6/2008
3/6/2008
5/6/2008
Sampling Events
Barium
Manganese
Zinc

APPENDIX O

LETTER FROM MDH ABOUT DRO DATA NON-COMPLIANCE

interpoll

Interpoll Laboratories, Inc.
4500 Ball Road NE
Circle Pines, MN 55014-1819
Tel: 763-786-6020
Fax: 763-786-7854
www.interpoll-labs.com

May 13, 2008

Mr. Harold Bottolfson
MnDOT Modeling & Testing Unit
6000 Minnehaha Av.
St. Paul, MN 55111

Dear Mr. Bottolfson:

The purpose of this letter is to inform you of a finding during a recent routine audit of Interpoll Laboratories, Inc. by the Minnesota Department of Health (MDH), the certifying agency of environmental laboratories.

The MDH has determined that Interpoll Labs was not in compliance with the certification rules regarding the analysis of samples for Diesel Range Organics (DRO). The non-compliance occurred because of the differences between the way in which the raw data of standards and the raw data of samples were processed.

As a result of these differences, the detectable DRO concentrations for the sample(s) reported in the Laboratory Report(s) listed below may be biased high. The actual concentrations of DRO present in the sample(s) may be lower than reported.

> Report Number(s): 21069, 21088, 21174, 21178, 21402, 21526, 21538, 21589, 21592, 21627, 21638, 21673, 21701, 21706, 21901, 21908

Interpoll Labs has taken corrective actions to address the non-compliance. Interpoll Labs apologizes for any inconveniences caused by the non-compliance.

If you have any questions on this matter or need further information, please contact me at 763-786-6020, ext. 40.

Sincerely,

Wayne A. Olson

Wayne A. Olson,
Quality Assurance Officer

WAO/cg

cc: Ms. Denise Schumacher, Certification Officer, MDH