

# WATER QUALITY EVALUATION OF TIRE DERIVED AGGREGATE

By

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## **ABSTRACT**

### **WATER QUALITY EVALUATION OF TIRE-DERIVED AGGREGATE**

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The primary objective of this study is to investigate the rate that potential water quality contaminants leach from tire-derived aggregate (TDA) as a function of time. A laboratory and field experiment is conducted to provide insight into both controlled and field settings. The laboratory portion of this study also provides a basis for evaluating the effect that alternating periods of wet and dry weather have on the potential water quality impacts of the leachate as compared to the worst-case operating condition, when TDA is constantly submerged (i.e., when placed below the permanent groundwater table). The field experiment is used to determine if the leachate constituents identified in the laboratory experiment are observed when TDA is used as a stormwater filtration media. This portion of the study also determines if a TDA fill followed by a soil layer provides removal of urban stormwater runoff constituents.

The laboratory experiment suggests that, of the 83 tested constituents, benzene, methyl isobutyl ketone (MIBK), cadmium, zinc, iron, manganese, total phosphate, and total suspended solids (TSS) are leached from TDA and dissolved oxygen (DO) is altered by TDA. For the eight constituents suspected to leach from TDA, a decrease in release over time was observed, with release rates for the majority of these constituents reaching

values below their respective detection limits by the end of the experiment. Of these constituents with Maximum Contaminant Levels (MCLs), only iron and manganese exceeded their respective Secondary MCLs, and these standards are an aesthetic rather than a human health concern.

The rate at which metals leach from TDA is the highest when continuously submerged. A higher loss in iron, manganese, and zinc was observed for TDA that was always wet compared to TDA that experienced short (1 to 7 days) cycles of wet and dry. At the end of the 15 month experiment, manganese, zinc, and iron cumulative mass losses (per kg of tire) were 1.7, 1.6, and 2.6 times greater under the always wet operating condition compared to the average of the other operating conditions. There was not a difference in the loss rates that could be attributed to the different wet and dry cycles investigated.

The results of the field experiment suggest that a TDA-soil system provides removal of the following constituents from urban stormwater runoff: acetone, cadmium, chemical oxygen demand, iron, lead, manganese, methyl isobutyl ketone (MIBK), oil and grease, phosphate, and zinc. In addition, the constituents suspected to leach from TDA are removed by a TDA-soil system.

The results of this study have demonstrated that the use of TDA as a fill material in civil engineering applications is a responsible method of recycling automotive scrap tires. TDA fills that are seasonally or always saturated are very unlikely to compromise the quality of the receiving water. The number of potentially harmful compounds leaching from the TDA is limited, and the rate of leaching is sufficiently low that the

concentrations of these compounds in the surrounding waters do not pose any environmental degradation. In addition, sufficient dilution and soil adsorption effects further reduce impacts compounds might have on receiving waters. Sufficient dilution and soil adsorption processes further reduce the potential impacts that these compounds might have on any receiving water.

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## **ABBREVIATIONS AND ACRONYMS**

- ASTM: American Society for Testing and Materials
- BOD: biological oxygen demand
- CalRecycle: California Department of Resources Recycling and Recovery
- COD: chemical oxygen demand
- DO: dissolved oxygen
- EPA: United States Environmental Protection Agency
- gpd: gallon per day
- ha: hectare
- MCL: maximum contaminant level
- mg/L: milligram per liter
- MIBK: methyl isobutyl ketone
- ND: nondetect
- PAH: Polyaromatic hydrocarbon
- psi: pounds per square inch
- RMA: Rubber Manufacturers Association
- SVOC: semi-volatile organic compound
- TDA: tire derived aggregate
- TDP: tire derived product
- TOC: total organic carbon
- TSS: total suspended solids
- ug/L: microgram per liter
- umhos/cm: micromhos per centimeter
- VOC: volatile organic compound



## **GLOSSARY OF TERMS**

- **Bead:** the anchoring part of the tire that is shaped to fit the wheel rim and is constructed of bead wire wrapped by the plies (ASTM, 2012).
- **Bead wire:** a high tensile steel wire surrounded by rubber, which forms the bead of a tire that provides a firm contact to the rim (ASTM, 2012).
- **Crumb rubber/ground rubber:** particulate tire rubber (typically non-spherical) with no protruding steel.
- **Groundwater table:** the level at which soil is permanently saturated.
- **Leachate:** liquid that has passed through a porous media.
- **Nondetect (ND):** concentration result of a contaminant for a sample is less than the detection of the laboratory's testing procedure.
- **Scrap tire/waste tire:** a tire that can no longer serve its original purpose due to wear or damage (ASTM, 2012).
- **Steel belt:** rubber-coated steel cords that run diagonally under the tread of steel radial tires and extend across the tire approximately the width of the tread (ASTM, 2012).
- **Tire-derived aggregate:** pieces of scrap tire that adhere to specifications as outlined by ASTM standards (see Specifications section) and are typically intended for use in civil engineering applications.
- **Tire shreds/tire chips:** mechanically-processed pieces of scrap tire that do not necessarily conform to ASTM standard size specifications for TDA; this may include pieces with or without protruding steel wire.
- **Tread:** that portion of the tire which contacts the road (ASTM, 2012).
- **Whole tire:** a scrap tire that has been removed from a rim, but that has not been processed (ASTM, 2012).

## INTRODUCTION

California generated an estimated 42 million scrap tires in 2013 (CalRecycle, 2014). The reuse of scrap automotive tires provides a solution to the current disposal methods of dumping tires at landfills and stockpiles, and improper and illegal disposal. Whole scrap tires are not only impractical in landfills and stockpiles, but have raised public health, environmental, and aesthetic concerns. Whole tires occupy a large amount of space and their large inner void space has the potential to trap gas in landfills, harbor rodents, and provide breeding grounds for mosquitoes. Gas entrapment in a tire may cause the tire to surge to the surface and penetrate the landfill cover, making whole scrap tires problematic for facilities. In addition, rodents and mosquitoes attracted to waste tires are unsightly and may carry diseases. Scrap tires are now banned from landfills in some areas and efforts are increasing to clean up and reduce the number of stockpiles.

In recent decades, there has been increasing interest in the use of waste tires in the form of tire-derived aggregate (TDA) in civil engineering applications. TDA is a light-weight fill material that has desirable engineering properties including compressibility, hydraulic conductivity, and porosity. The media provides an alternative to typical fill material, such as rock aggregate obtained via gravel mining. And unlike other reuse options for scrap tires, the energy-intensive process of removing steel wire from the tires is not included in the manufacturing of TDA and may protrude from the media (Figure 1).



Figure 1. Representative pieces of TDA Type A with protruding wires.

The desirable engineering properties of TDA makes the media an attractive option for a variety of civil engineering applications. These applications include embankment fills, retaining wall and bridge abutment backfills, subsurface insulation layers to limit frost penetration, vibration dampening layers, drainage layers including as a sorptive medium, and septic tank leach fields. The emergence of waste tires used in these applications has motivated numerous studies investigating the potential benefits and detriments associated with this method of reuse. For many of its intended civil engineering applications, TDA comes into contact with water and may leach organic and inorganic compounds, possibly degrading the quality of nearby ground and surface waters.

Existing literature on the environmental suitability of TDA in civil engineering applications has identified the water quality constituents that may be a concern, and corresponding concentrations that would be expected. The preponderance of literature

suggests that the material does not significantly affect surrounding water quality, but a wide variety of experimental conditions and settings has led to an equally wide variety of expected leachate quality. Although the majority of studies suggest constituents that leach from TDA generally decrease over time, the leaching rate and extent of leaching have not been identified. The primary objective of this study is to investigate the potential for leaching of TDA constituents as a function of time. A laboratory and field experiment is conducted to provide insight in both controlled and field settings. The laboratory portion of this study also provides a basis for evaluating the operating condition that the literature suggests is the worst-case scenario, when TDA is constantly submerged (i.e., when placed below the permanent groundwater table).

## **LITERATURE REVIEW**

Existing literature related to the focus of this study was reviewed. The composition of tires, properties of TDA, field and laboratory studies on water quality effects of tire-derived products, and relevant soil properties were investigated. A summary of this information is provided here.

### **Chemical Composition of a Tire**

An automotive tire must contain compressed air subject to heavy loads, high speeds, a wide range of temperatures and harsh conditions. It is a complex product composed of a variety of materials combined via several processes. A typical tire is made of vulcanized rubber (usually a styrene-butadiene copolymer), a rubberized fabric containing circumferential reinforcing textile cords, steel, or fabric belts, and steel-wire-reinforced rubber beads (Dodds et al., 1983). The composition of typical tire rubber and each constituent's function is provided (Table 1).

Table 1. Typical composition of tire rubber (adapted from Dodds et al., 1983).

<b>Component</b>	<b>Percent Mass</b>	<b>Function</b>
Styrene-butadiene copolymer	62.1	body
Carbon black	31.0	strengthen and impart abrasion resistance
Extender oil (typically mixture of aromatic hydrocarbons)	1.9	softening agent to increase workability
Zinc oxide	1.9	enhance physical properties of rubber and provide control in the vulcanization process
Stearic acid	1.2	enhance physical properties of rubber and provide control in the vulcanization process
Sulfur	1.1	harden the rubber and prevent excessive deformation
Accelerator	0.7	act as a catalyst for vulcanization

To enhance the tire-manufacturing process and produce desirable properties (i.e., structural integrity, wear resistance and traction), other ingredients such as reinforcing chemicals, anti-degradants, adhesion promoters, curatives, and processing aids are introduced into the tire. Manufacturers can vary several of the parameters to achieve optimal tire properties, making it difficult to know the exact (often proprietary) composition of a particular tire (Dodds et al., 1983). Goodyear (2011) reports that their tire (weighing approximately 10 kg) is composed of five different types of synthetic rubber, eight types of natural rubber, eight types of carbon black, and 40 different types of chemicals, waxes, oils, pigments, etc. The ingredients of a tire by percent mass from several different sources are provided (Table 2).

Table 2. Composition of a typical new tire by percent mass as reported by indicated sources.

<b>Component</b>	<b>Asplund (not dated)</b>	<b>Basel (1999)</b>	<b>Goodyear (2011)</b>	<b>RMA (not dated)</b>
Synthetic Rubber	24	47	27	27
Natural Rubber	23	*	20	14
Carbon Black	25	21.5	23	28
Steel Cord	14	16.5	7	14-15
Steel Bead Wire	*	*	5	*
Polyester and nylon	4	5.5	5	16-17
Chemicals, waxes, oils, pigments, etc.	10	9.5	14	*

\*Values in the row directly above reflect the sum of both components

As seen in Table 2, the amount of reinforcing wire (which includes the steel cord and steel bead wire) in a typical tire ranges from 12-16.5 percent. Other studies have reported lower values. Pehlken and Essadiqi (2005) report the value to be in the range of 10-15 percent. Deese et al. (1981), as cited by Miller and Chadik (1993), determined that scrap tires contain 44 pounds of steel per ton, or approximately 2.2% steel by weight. This value, however, is contradictory to the expected increase in steel content by mass due to the reduced weight from wear during its use (estimated as approximately 20% (RMA, not dated)).

The manufacturing of TDA produces relatively small pieces of material from the whole tire. Most of the components of the original tire are exposed in the final product, including the steel cord and wire. A typical composition of the steel belts and bead wire, less the iron content, is provided (Table 3).

Table 3. Typical composition of steel cord, less the iron content, by percent mass (RMA, not dated).

<b>Constituent</b>	<b>Steel Belts</b>	<b>Bead Wire</b>
Carbon	0.67-0.73	0.60 min.
Manganese	0.40-0.70	0.40-0.70 min.
Silicon	0.15-0.30	0.15-0.30
Phosphorus	0.03 max.	0.04 max.
Sulfur	0.03 max.	0.04 max.
Copper	Trace	Trace
Chromium	Trace	Trace
Nickel	Trace	Trace

The elemental content of tire chips has been further investigated via high temperature combustion (Selbes, 2009) and via the EPA's Toxicity Characteristic Leaching Procedure (Ealding, 1992) (Table 4). Several of the compounds are substantially different across the two studies (e.g., iron and zinc), which is likely due to variation in the both tire chip product and method of evaluation. Selbes (2009) reports cutting the steel wire of the chips such that no more than 0.5 inches protruded from any tire chip. Ealding (1992) does not provide specifications for the tire chips used. The results reported by Ealding (1992) reflect concentrations when tire chips are subject to an acidic solution for approximately 20 hours. A large portion of the tire chips were likely still intact at the end of the procedure, unlike in the combustion procedure performed by Selbes (2009). Based on the presented numbers, it appears the concentration in the extract was multiplied by a factor assuming a density for the tire material. Because the experimental procedures implemented in these studies do not simulate conditions of typical TDA applications, these results provide only a relative ratio of the various



elements in a tire rather than the total expected mass of each element that would be leached in actual field conditions.

Table 4. Content of scrap tire chips reported in milligram of element per gram of tire pieces by indicated sources.

Element	Ealding (1992)	Selbes (2009)
Aluminum	0.42	0.52±0.22
Arsenic	-	ND
Cadmium	2.84	0.54±0.11
Calcium	0.0044	0.002±0.000
Chromium	0.0079	0.04±0.02
Copper	0.235	0.31±0.14
Iron	341	110.4±56.1
Lead	-	0.59±0.38
Magnesium	0.307	0.15±0.02
Manganese	-	0.66±0.14
Molybdenum	-	ND
Nickel	-	0.31±0.15
Phosphorus	0.113	0.05±0.03
Potassium	-	0.17±0.01
Selenium	0.0556	0.04±0.01
Silver	-	1.16±0.06
Tin	-	ND
Zinc	30	11.54±0.24

(-) = not included in analysis, ND = nondetect

## Tire-Derived Aggregate Properties

### Specifications

In accordance with ASTM standards, TDA is defined as "pieces of scrap tires that have a basic geometrical shape that are generally between 12 and 305 mm in size and are intended for use in civil engineering applications" (ASTM, 2012). A maximum of 1% (by

weight) of TDA can be metal fragments that are not at least partially encased in rubber (ASTM, 2012). A maximum of one inch (25 mm) of protruding metal from the cut edge is allowable for metal fragments partially encased in rubber for 75% of the pieces (by weight) and a maximum of two inches (50 mm) for 90% of the pieces (by weight) (ASTM, 2012). These specifications are consistent with the conditional waiver of waste discharge requirements for tire shreds reuse in road construction projects developed by the California Regional Water Quality Control Board, San Francisco Bay Region (CRWQCB, 2011).

TDA can be classified as Type A or Type B. The maximum dimension, measured in any direction, for Type A and Type B is 8 inches and 18 inches, respectively (ASTM, 2012). In addition, for Type B TDA, a minimum of 90% (by weight) of the pieces must have a maximum dimension, measured in any direction, of 12 inches. Finally, a minimum of one side wall must be severed from the tread of each tire based on a physical examination of a representative sample (ASTM, 2012). Further size specifications for square mesh sieve analysis are provided (Table 5).

Table 5. Minimum percent passing (by weight) for Type A and Type B TDA (adapted from ASTM, 2012).

<b>Sieve Opening (in)</b>	<b>Type A</b>	<b>Type B</b>
8	N/A	75
4	100	N/A
3	95	50
1.5	50	25
0.187	5	1

### Engineering Properties

The engineering properties (e.g., hydraulic conductivity and porosity) of TDA can vary greatly depending on the size and manufacturing of the tire chips. A brief summary of select properties is provided for chip sizes similar to that of those used in this study. To achieve the desired values within the ranges provided here, specifications (e.g., tire chip size, length of protruding steel wire, amount of debris) should be included in contract documents with the supplier (Finney et al., 2013).

The hydraulic conductivity of TDA is predicated on the size distribution of the tire chips and the applied load. Finney et al. (2013) stated that, above approximately 2 psi, Type A and Type B had similar hydraulic conductivities. An investigation of literature conducted by Finney et al. (2013) indicated that hydraulic conductivities can range from 0.003-0.869 ft/s when subject to various pressure loads.

Finney et al. (2013) compacted Type A TDA by a static load (2.95 psi) and observed that a compressional limit was reached when the thickness of the TDA was 25% less than its original thickness. Several dynamic loads were tested (Table 6). Because of the larger pieces of TDA in the Type B batch, the initial void ratio for the Type B batch was greater than that of Type A or the Type A/B mixture. Although the Type B batch initially deformed more than the other batches under compaction, the stress/strain curves for the three different batches had nearly identical slopes when the load exceeded 2.0 psi. Therefore, Finney et al. (2013) concluded that all three batches exhibit similar compressive behavior after the initial compaction.

Table 6. Compaction testing parameters of TDA Type A, B, and A/B (adapted from Finney et al., 2013).

<b>TDA Type</b>	<b>Dry Density (slug/ft<sup>3</sup>)</b>	<b>Loaded Weight (lbf)</b>	<b>Pressure (psi)</b>	<b>Porosity at Seating Load (%)</b>	<b>Void Ratio under Seating Load</b>	<b>Porosity under Load (%)</b>	<b>Void Ratio under Load</b>	<b>Specific Gravity</b>	<b>Specific Weight (lbf/ft<sup>3</sup>)</b>	<b>Maximum Size (in.)</b>	<b>Met Type A or B TDA Specification</b>
A	2.47	2,057	2.95	62.9	1.69	53.1	1.13	1.28	79.6	7.56	Yes
A	2.72	68,967	100	63.5	1.74	15.7	0.19	1.40	87.6	7.56	Yes
A	2.54	73,077	105	62.4	1.66	10.6	0.12	1.31	81.9	7.88	Yes
B	2.60	69,511	101	68.2	2.14	12.3	0.14	1.34	83.8	24.19	No
B	2.67	66,573	96	67.2	2.05	15.5	0.18	1.38	86.0	41	No
A and B	3.60	78,437	114	62.9	1.7	8.9	0.10	1.34	83.8	17.25	No

## Regulations

Based on the chemical composition of tires and a search of the available, applicable literature, the potential problematic constituents have been identified. A large number of regulatory frameworks that include standards for these constituents were examined (Table 7). Other frameworks that were investigated but that do not provide additional perspectives for this project include Detection Limits for the Purposes of Reporting (DLRs), Reference Dose (RfD), Drinking Water Equivalent Level (DWEL), and the Maximum Concentration of Contaminants for the Toxicity Characteristic. Although TDA is not considered a toxic waste, the Maximum Concentration of Contaminants for the Toxicity Characteristic regulatory levels are provided in a subsequent section as a point of reference.

Many of the presented regulatory frameworks in Table 8 (e.g., drinking water standards) would not be applicable to a typical TDA application permit, but serve as useful reference values. Public health goals (PHGs) define a level at which a contaminant in drinking water does not pose a known risk to health (OEHHA, 2015a). Public health goals are non-enforceable, but provide values of potential trajectories for regulatory standards. Regulatory standards must be set as close to the respective PHGs as feasibly possible considering available technology and the cost of treatment. Environmental standards developed in the United Kingdom by the Environment Agency (2011) are also provided (Table 9). This framework serves as a guide for installations and waste operations that discharge ‘simple’ effluent to a receiving water body. Effluent is

considered ‘simple’ once the components and their respective toxicity levels and any other potential effects have been identified. Values reflect mean annual concentrations.

Table 7. Descriptions of regulatory frameworks investigated.

<b>Regulatory Framework</b>	<b>Agency</b>	<b>Application</b>	<b>Source</b>
California Maximum Contaminant Level (CA MCL)	California Department of Public Health	Drinking water	CA EPA (2015)
Public Health Goal (PHG)	California Office of Environmental Health Hazard Assessment	Drinking water	OEHHA (2015b)
Maximum Contaminant Level (MCL)	US EPA	Drinking water; health-based	US EPA (2015)
Maximum Contaminant Level Goal (MCLG)	US EPA	Drinking water; health-based, but non-enforceable	US EPA (2015)
Secondary Maximum Contaminant Level (Secondary MCL)	US EPA	Drinking water; aesthetics-based	US EPA (2013b)
Removal Action Level (RAL)	US EPA - Office of Solid Waste and Emergency Response	Contaminated drinking water sites	US EPA (1997)
Average Monthly Effluent Limitation (AMEL)	North Coast Regional Water Quality Control Board	Wastewater effluent discharged to Pacific Ocean in Fort Bragg, CA	NCRWQCB (2015)
Most Stringent Water Quality Objectives (WQO)	North Coast Regional Water Quality Control Board	Wastewater effluent discharged to Pacific Ocean in Fort Bragg, CA	NCRWQCB (2015)
Multi-Sector General Permit Benchmark (MSGP Benchmark)	US EPA	Stormwater discharges associated with industrial activity	US EPA (2013)

Table 8. Regulatory limits and goals for constituents of interest<sup>1</sup>. Blank cells indicate a standard is not available.

Parameter	CA MCL	PHG	MSGP Benchmark	MCLG	MCL	Secondary MCL	AMEL	WQO	RAL
1,2-Dichloroethane (ug/L)	0.5	0.4	5	0					
Acetone (ug/L)									3500
Aluminum (mg/L)		0.6	(T) 0.75 (pH 6.5-9)			0.05 to 0.2			
Ammonia (mg/L)								0.6	34
Benzene (ug/L)	1	0.15		0	5				100
Cadmium (mg/L)	0.005	0.00004	0.0021	0.005	0.005				0.005
Chemical Oxygen Demand (mg/L)			120						
Copper (mg/L)	N/A	0.3	(T) .014	1.3	1.3*	1	53	0.003	1.3
Iron (mg/L)			1			0.3			
Lead (mg/L)	0.015	0.0002	(T) 0.082	0	0.015*				0.003
Manganese (mg/L)						0.05			
Magnesium (mg/L)			(T) 0.064						
Nitrate (as N) (mg/L)	45	10		10	10				10
Oil and Grease (mg/L)							25		
pH						6.5-8.5			
Total Phosphorus (mg/L)			2						
TSS (mg/L)			100			500	30		
Sulfate (mg/L)						250			250
Zinc (mg/L)			(T) 0.12			5	620	0.02	3

<sup>1</sup>Information related to the frameworks presented here is described in Table 7

(T)=total recoverable

(\*)= treatment technique action level

Table 9. Environmental quality standards (mean annual) for Priority Substances, Non-Statutory substances, and other pollutants (adapted from Environment Agency (UK), 2011).

Compound	Rivers and Freshwater Lakes	Transitional and Coastal Waters
Benzene (ug/L)	10	8
Cadmium (dissolved ug/L)	<0.08 (CaCO <sub>3</sub> <40 mg/L)	0.2
Cadmium (dissolved ug/L)	0.08 (40 mg/L < CaCO <sub>3</sub> < 50 mg/L)	0.2
Cadmium (dissolved ug/L)	0.09 (50 mg/L < CaCO <sub>3</sub> < 100 mg/L)	0.2
Cadmium (dissolved ug/L)	0.15 (100 mg/L < CaCO <sub>3</sub> < 200 mg/L)	0.2
Cadmium (dissolved ug/L)	0.25 (CaCO <sub>3</sub> > 200 mg/L)	0.2
Lead and its compounds (total ug/L)	7.2	7.2
Napthalene (total ug/L)	2.4	1.3
Polyaromatic Hydrocarbons (ug/L)	N/A	N/A
Sulfate (mg/L)	400	N/A
Unionized ammonia as nitrogen (ug/L)	N/A	21
Iron (dissolved mg/L)	1	1
Toluene (ug/L)	50	40
Zinc (ug/L)*	8 (CaCO <sub>3</sub> <50 mg/L)	40
Zinc (ug/L)*	50 (50 mg/L < CaCO <sub>3</sub> <100 mg/L)	40
Zinc (ug/L)*	75 (100 mg/L < CaCO <sub>3</sub> < 250 mg/L)	40
Zinc (ug/L)*	125 (CaCO <sub>3</sub> > 250 mg/L)	40

(\*)= concentrations for rivers and freshwater lakes are total concentrations and concentrations for transitional and coastal waters reflect dissolved concentrations.



## **Experimental Methods and Tests for Potential Water Quality Impacts**

Various test methods can be used to evaluate the potential adverse effects TDA may have on surrounding water quality. An overview of the typical methods and relevant studies used to investigate TDA leachate is presented here. The results of these studies are discussed in the subsequent sections.

Portions of studies that investigated water quality effects of TDA and soil mixtures are not included as these conditions are not representative of typical civil engineering applications of the material. The focus of this literature review is the leaching of TDA constituents in a liquid or TDA leachate after it passes through soil.

For the remainder of this literature review, the term 'TDA' is used in reference to tire pieces that essentially meet the aforementioned ASTM standards. For studies that have not specified that the tire product of interest is TDA, the terms 'tire shreds' and 'tire pieces' are used interchangeably. Where available, the dimensions of these tire products are included.

### **Batch Tests**

Laboratory batch tests are a common method to determine potential constituents that may leach from TDA. This method typically consists of submerging a known mass of TDA in a known volume of stagnant water. There is not a standard protocol for the masses of TDA and water for this type of test and it is therefore common to express this information using a solid to liquid ratio (i.e., mass of TDA to volume of liquid). These experiments help characterize the behavior of TDA in water, but conditions are often not

representative of what would occur in the field. Results from laboratory batch tests typically provide an overestimation of the concentration of contaminants since actual applications of TDA would typically have flow-through conditions with the presence of dispersive and adsorptive effects. A summary of representative batch experiments that are relevant to this study is provided (Table 10).

#### The Toxicity Characteristic Leaching Procedure

To address water quality concerns associated with the material's usage, TDA has been subjected to the EPA's Toxicity Characterization Leaching Procedure (TCLP) (Downs et al., 1996; Ealding, 1992; Radian, 1989; Selbes, 2009). The TCLP (EPA Method 1311) is used to determine whether or not a solid waste should be considered hazardous or toxic by determining the concentrations of the analytes it leaches during the testing procedure. If the concentration of any of the listed analytes (Table 11) in the TCLP extract is equal to or greater than the corresponding regulatory level, the waste is considered a hazardous waste.

#### The Extraction Procedure Toxicity Characteristic Test

Tire-derived aggregate has also been the subject of the Extraction Procedure Toxicity Characteristic (EP) (Edil et al., 1990; Radian, 1989; TCTC, 1990). The EP Toxicity test was also developed to determine if a waste should be considered hazardous, but has since been replaced by the TCLP. Comparison studies of the two toxicity tests (Bricka et al., 1989; Radian, 1989) suggest that the two procedures are comparable.

Table 10. Summary of relevant, representative batch experiments performed by indicated sources.

Source	Solid to Liquid Ratio (kg of TDA to L of liquid)	Tire Product	Sampling Schedule	Leachate Analysis
Downs et al. (1996)	1:2	tire chips: maximum size of 7.5 cm x 7.5 cm	end of 10 months	total and dissolved metal, and volatile and semivolatile organic compounds
Ealding (1992)	2:1	shredded tires (exact size not specified)	periodically over 14.5 months	17 metals
Gunter (1999)	1:1	tire chips: approximately 2-10 cm (longest dimension of each chip)	five times over one year	VOCs, inorganics, TOC
Miller and Chadik (1993)	6:20	tire chips: maximum of 4" x 4"	sampled at days: 7, 14, 28 or 30, 63, and 91	organics, seven metal ions, and conventional parameters
O'Shaughnessy and Garga (2000)	1:1	tire chips: typically 50 mm x 50 mm	three times over 400 days	metals and select organics
Selbes (2009)	1:20	tire chips: 1"x1", 2"x2", 4"x2", 6"x2" (protruding wire cut to protrude no more than 0.5")	15 times over 28 days	dissolved organic carbon and selected inorganics
TCTC (1990)	6:25	2" cross sections of whole tires cut into four pieces	end of 24 hours	14 different metals, PAHs

Table 11. Contaminants and regulatory levels for the Toxicity Characteristic (US EPA, 2006).

<b>Analyte</b>	<b>Regulatory Level (mg/L)</b>	<b>Analyte</b>	<b>Regulatory Level (mg/L)</b>
Arsenic	5	Hexachlorobenzene	0.13
Barium	100	Hexachlorobutadiene	0.5
Benzene	0.5	Hexachloroethane	3
Cadmium	1	Lead	5
Carbon tetrachloride	0.5	Lindane	0.4
Chlordane	0.03	Mercury	0.2
Chlorobenzene	100	Methoxychlor	10
Chloroform	6	Methyl ethyl ketone	200
Chromium	5	Nitrobenzene	2
o-Cresol	200	Pentachlorophenol	100
m-Cresol	200	Pyridine	5
p-Cresol	200	Selenium	1
Cresol	200	Silver	5
2,4-D	10	Tetrachloroethylene	0.7
1,4-Dichlorobenzene	7.5	Toxphene	0.5
1,2-Dichloroethane	0.5	Trichloroethylene	0.5
1,1-Dichloroethylene	0.7	2,4,5-Trichlorophenol	400
2,4-Dinitrotoluene	0.13	2,4,6-Trichlorophenol	2
Endrin	0.02	2,4,5-TP (Silvex)	1
Heptachlor (and its epoxide)	0.008	Vinyl chloride	0.2

### Aquatic Toxicity Tests

Several studies (Table 12) have been conducted to evaluate the potential effects TDA leachate may have on surface waters and the organisms that inhabit these waters. The studies investigated for this literature review performed aquatic toxicity tests using leachate from previously-constructed field experiments. Similar to other laboratory experiments, aquatic toxicity tests do not necessarily reflect conditions that would occur

in a field application. Leachate migration through soil and dilution are not accounted for in all of the studies. Thus, some results may reflect concentrations higher than would be seen in nearby surface waters, where these mechanisms would be a factor.

Table 12. Summary of aquatic toxicity experiments.

Source	Leachate Characteristics	Tire Product Description	Research	Species
Sheehan et al. (2006)	Collected from two previously-constructed field sites: one above the groundwater table (Humphrey and Katz, 2000) and one below the groundwater table (Humphrey and Katz, 2001)	Maximum dimension of approximately 7.6 cm; mixture of steel- and glass-belted scrap tires	Short-term toxicity tests	<i>Ceriodaphnia dubia</i> and larval fathead minnows ( <i>Pimephales promelas</i> )
TenEyck and Markee (2006a)	Collected from previously-constructed field site (three years prior) (Edstrom et al., 2008)	Tire shreds (size not specified)	Static-renewal water-only toxicity tests measuring survival and reproduction rates	Fathead minnows ( <i>Pimephales promelas</i> ), insect larvae ( <i>Chironomus dilutu</i> ), and cladoceran ( <i>Ceriodaphnia dubia</i> )
TenEyck and Markee (2006b)	Collected from previously-constructed field site (three years prior) (Edstrom et al., 2008)	Tire shreds (size not specified)	Toxicity Reduction Evaluation	Fathead minnows ( <i>Pimephales promelas</i> ), insect larvae ( <i>Chironomus dilutu</i> ), and cladoceran ( <i>Ceriodaphnia dubia</i> )

*Field Tests*

A variety of experimental field tests have been conducted that utilize TDA in a setting similar to an actual field application (Table 13). The results from some of these studies are not readily available for review, however several previous literature reviews (Edil, 2007; Humphrey and Swett, 2006; Tatlısoz, 1996) on potential water quality effects of TDA reference these field studies. A note is made in instances in which information obtained from existing literature reviews was not verifiable via the original source.

Table 13. Summary of select field studies.

Source	Site Description	Tire Product Size	Sampling Schedule	Analytes
Aydilek et al. (2006)	two 2.4-ha cells constructed in landfill. Cell 1 (control): 0.6-m-thick layer of gravel. Cell 2: tire chips on geocomposite drainage layer	ranged from 25-100 mm in length	every three to four months for four years	13 metals, nitrite/nitrate, sulfate, and 37 VOCs
Burnell and McOmber (1997)	three experimental subsurface drain fields 30 ft long, 20 ft wide and 1 ft deep: one with half tires, one with tire chips, and one with gravel	0.5" - 2.5" tire chips and half tires	once after four weeks	organics, metals
Dickson et al. (2001)*; Brophy (2004)	TDA layer up to 10 ft thick covered by 4.9 to 6.6 ft of embankment fill	nominal size of 12"	three times over approximately 1.5 years	metals and water quality indices
Edstrom et al. (2008)	over 7 million pounds of tire shreds wrapped in geotextile fabric below road base and below seasonal groundwater table	tire chips; exact size not specified	periodically over five years	TSS, COD, alkalinity, ammonia, TOC and selected metals
Finney et al. (2013)	wastewater leach field	TDA Type A	16 times over 17 months	84 different water quality constituents
Humphrey (1999)	TDA and mixture of TDA and aggregate base placed below paved road	tire chips: maximum size of 3"	one time	twelve metals, two anions, and organic compounds

(\*) = as cited in Humphrey and Swett (2006)

Table 13. Summary of select field studies.(Continued).

Source	Site Description	Tire Product Size	Sampling Schedule	Analytes
Humphrey and Katz (1995)*	950-ft long TDA fill with granular soil cover	tire chips: maximum size of 2"	three times over one year	metals and common water quality index parameters
Humphrey and Katz (2000); Exponent, (2003)*; Sheehan et al. (2006)	Five 100 ft long sections: one control section, four sections with 2-ft thick TDA layer topped with 2.5-4.5 ft of granular soil and 0.42 ft of pavement	tire chips: maximum size of 3"	periodically between 1994-2002	organic substances, inorganic substances with primary and secondary drinking water standards, pH, and other water quality index parameters; aquatic toxicity
Humphrey and Katz (2001)	three sites with 1.4 metric tons of tire shreds buried in a trench below the water table	tire chips: maximum size of approximately 75 mm	periodically over four years	range of metals, VOCs, and semivolatile organics
Kaliakin et al. (2012)	roadway embankment	not specified	eight times over two years	metals

(\*) = as cited in Humphrey and Swett (2006)



## **Potential Environmental Concerns**

Although the preponderance of literature suggests that the constituents that leach from tire products do not pose a significant threat to the environment (e.g., Edil and Bosscher, 1992; Humphrey and Swett, 2006; O'Shaughnessey and Garga, 2000), some water quality concerns still exist with placement of a TDA fill. While multiple studies have suggested that a TDA fill below the groundwater table has negligible off-site effects on water quality (Edstrom et al., 2008; Humphrey and Katz, 2001), others postulate the material may pose a threat to groundwater quality if it is placed below the groundwater table (Aydilek et al., 2006). A comprehensive review of relevant and available literature has been conducted and summarized in this section. The literature presented herein reflects studies conducted that are representative of conditions that occur in typical civil engineering TDA applications. Extreme environmental settings such as extreme pH conditions are not included in this review.

### Toxicity/Hazardous

As previously mentioned, studies conducted to evaluate the toxicity of tire pieces via the EP Toxicity test (Edil, et al., 1990; Radian, 1989; TCTC, 1990) and the TCLP test (Downs et al., 1996; Ealding, 1992; Radian, 1989; Selbes, 2009) indicate that TDA is not a hazardous waste. The experimental procedure for the TCLP does not simulate expected field conditions of a typical TDA application and the inorganic concentration results (Table 14) are therefore substantially higher than would likely occur in the field, where the effects of dilution and dispersion would occur. The provided results of the TCLP tests

(Table 14) are considered representative of the tests performed in other studies. The only TCLP-regulated organic compound detected in a TCLP analysis was 1,2-dichloroethane (Downs et al., 1996). The concentration in the extract was 7 ug/L, significantly lower than the TCLP regulatory standard of 500 ug/L.

#### Inorganics – Metals

Past studies indicate that TDA leachate contains metals, likely from any exposed steel wires. The surrounding environment and the properties of TDA itself are two of the primary factors that govern the amount and rate at which metals may leach from the material. Differences in these (and other) parameters have led to a wide range in results and conclusions. Some studies suggest that the resulting concentration of metals in the leachate do not exceed primary drinking water standards (Downs et al., 1996; Ealding, 1992; TCTC, 1990) and are not likely to pose a risk to the surrounding environment (Gunter, 1999; O'Shaughnessy and Garga, 2000), while other studies conclude further investigation of the water quality effects of TDA is needed (Miller and Chadik, 1993). With the exception of asbestos, cyanide and nitrite (which are not suspected of leaching from TDA), all inorganic chemicals with primary drinking water standards were directly monitored in at least one of the seven field studies reviewed by Humphrey and Swett (2006). They concluded that TDA is not likely to cause metals with primary drinking water standards to increase above naturally occurring background levels in the surrounding area.

Table 14. Concentration (mg/L) of element in TCLP extract from select representative studies.

<b>Element</b>	<b>Ealding (1992)</b>	<b>Selbes (2009)</b>
Aluminum	0.148	$0.039 \pm 0.003$
Arsenic	-	ND
Cadmium	0.00155	$0.002 \pm 0.001$
Calcium	1	$4.549 \pm 1.506$
Chromium	0.0028	$0.007 \pm 0.005$
Copper	0.083	$0.017 \pm 0.009$
Iron	120	$21.427 \pm 10.212$
Lead	0.0196	$0.018 \pm 0.012$
Magnesium	0.108	$0.113 \pm 0.050$
Manganese	-	$0.152 \pm 0.038$
Molybdenum	-	ND
Nickel	0.0397	$0.008 \pm 0.004$
Phosphorus	-	$0.021 \pm 0.008$
Potassium	-	$0.920 \pm 0.035$
Selenium	-	ND
Silver	<0.001	-
Tin	<0.025	-
Zinc	10.6	$0.814 \pm 0.306$

(-) = not included in analysis, ND = nondetect

Of the metals that have been analyzed, iron is typically detected at higher concentrations in both laboratory and field studies (Table 15 and Table 16, respectively) relative to the other tested metals (Downs et al., 1996; Ealding, 1992; Edil et al., 1990; Edstrom et al., 2008; Finney et al., 2013; Humphrey and Katz, 2001; Kaliakin et al., 2012; Sheehan et al., 2006; TCTC, 1990). Iron concentrations exceeded the secondary drinking water standard (0.3 mg/L) in some studies (Downs et al., 1996; Edil et al., 1990; Humphrey and Swett, 2006), but not in others (O'Shaughnessy and Garga, 2000). Although one study has suggested that iron levels increase over time (Edil et al., 1990), longer studies report that iron concentrations decrease over time (e.g., Brophy and

Graney, 2004; Miller and Chadik, 1993). A field study with approximately 250,000 shredded tires conducted by Brophy and Graney (2004) serves as an illustrative example of the reduction in concentration over time (Figure 2). This trend was also noticed in a 34,000 gpd aerated lagoon wastewater treatment plant where a decrease in iron concentration over an eight-year period was observed in a tire-shred-filled constructed wetland. After construction of the wetland, iron was detected in the effluent at 8.56 mg/L (Mackinnon, 2015). The effluent iron concentration had decreased to 0.51 mg/L in a sample collected in July, 2015. In other studies, a consistent increasing or decreasing trend in iron concentration over time (Aydilek et al., 2006; Edstrom et al., 2008). The absence of a consistent trend is illustrated by Edstrom et al. (2008) who observed increases, decreases, and steady iron concentrations in several wells near a tire shred fill (Figure 3).

The variation in iron results across the investigated studies is expected and is partially attributed to the difference in the type of tire products used in these studies. In a study (Selbes, 2009) that evaluated both crumb rubber and tire chips, all detected constituents were higher for crumb rubber except for iron, suggesting that the steel wire is likely the source.

Table 15. Metal concentrations (mg/L) for select laboratory batch studies.

<b>Constituent</b>	<b>Downs et al. (1996)</b>	<b>Gunter et al. (1999)*</b>	<b>Selbes (2009)</b>	<b>TCTC (1990)</b>
Aluminum	0.091	-	0-0.009	0.036
Arsenic	<0.015	-	-	-
Barium	0.11	0.078-0.205	<0.00003	0.174
Cadmium	<0.005	-	<0.0002	<0.005
Calcium	262	42	0.074-13.5	1.82
Chromium	<0.002	-	<0.0004	-
Copper	<0.004	<0.008	<0.0003	-
Lead	<0.015	0.001-0.02	<0.0013	<0.038
Iron**	366	150-698	<0.0003 - 0.48	0.531
Potassium	-	-	<0.001-0.54	-
Magnesium**	2.270	37	0.001-0.35	0.295
Manganese**	0.437	0.764-3.09	<0.00003-0.061	-
Mercury	<0.0000001	-	-	-
Silver	<0.005	-	-	-
Sodium	7.5	110	-	-
Sulfur	-	-	0.028-1.28	1.99
Zinc**	0.006	0.731	0.02-5.03	3.38

\*As reported by Edil (2007), \*\*One or more results exceeds one or more regulatory limits or goals presented in Table 8, (-) Numeric results not reported or constituent was not included in the study

Table 16. Metal concentrations (mg/L) of leachate for select field experiments.

Source	Aydilek (2006)*	Aydilek (2006)*	Burnell and McOmber (1997)	Burnell and McOmber (1997)	Edstrom et al. (2008)	Edstrom et al. (2008)	Finney et al. (2013)*	Finney et al. (2013)*	Humphrey and Katz (2001)	Humphrey and Katz (2001)
Setting	Leachate collection system	Leachate collection system	Subsurface sewage disposal system	Subsurface sewage disposal system	Below road base, below seasonal groundwater table	Below road base, below seasonal groundwater table	Leach Field	Leach Field	Trench, below groundwater table	Trench, below groundwater table
Length of Study	Four years	Four years	Four weeks	Four weeks	Four years	Four years	17 Months	17 Months	Four years	Four years
Metal	Control (gravel)	Through Tire Chips	Dosing Chamber	Through Tire Chips	Back-ground	Through or Adjacent to Tire Chips	Max. Rock Effluent	Max TDA Effluent	Background	Through Tire Chips
Arsenic	0.008-0.027	ND-0.02	-	-	-	-	-	-	<0.015	<0.015
Barium	0.16-0.24	0.12-0.2	-	-	0.068-0.14	0.18-0.36	-	-	<0.006-0.033	0.0017-0.057
Cadmium	ND	ND	<0.005	<0.005	-	-	ND	ND	<0.005	<0.005
Chromium	0.03-0.13	ND-0.09	<0.05	<0.05	-	-	-	-	0.003-0.128	<0.006-0.114
Copper	ND-0.007	0.004-0.02	0.02	0.03	<0.05	<0.05	-	-	<0.003-0.011	<0.003-0.004
Iron**	20-230	4.1-156	0.49	1.42	0.66-2.7	14-180	1.3	12	0.0184-3.16	<0.015-86.9

ND = not detected, \*detection limit not specified, \*\*metal is typically lower prior to tire chip contact, (-) = Numeric results not reported or constituent was not included in study

Table 16. Metal concentrations (mg/L) of leachate for select field experiments.(Continued).

Source	Aydilek (2006)*	Aydilek (2006)*	Burnell and McOmber (1997)	Burnell and McOmber (1997)	Edstrom et al. (2008)	Edstrom et al. (2008)	Finney et al. (2013)*	Finney et al. (2013)*	Humphrey and Katz (2001)	Humphrey and Katz (2001)
Setting	Leachate collection system	Leachate collection system	Subsurface sewage disposal system	Subsurface sewage disposal system	Below road base, below seasonal groundwater table	Below road base, below seasonal groundwater table	Leach Field	Leach Field	Trench, below groundwater table	Trench, below groundwater table
Length of Study	Four years	Four years	Four weeks	Four weeks	Four years	Four years	17 Months	17 Months	Four years	Four years
Metal	Control (gravel)	Through Tire Chips	Dosing Chamber	Through Tire Chips	Back-ground	Through or Adjacent to Tire Chips	Max. Rock Effluent	Max TDA Effluent	Background	Through Tire Chips
Lead	ND -0.007	ND -0.007	<0.05	<0.05	-	-	0	0	<0.015	<0.015
Manganese**	1.1-22.4	1.2-6.8	-	-	0.18-0.35	0.14-1.6	0.2	0.25	0.027-0.67	0.376-3.34
Nickel	0.16-0.2	ND-0.007	-	-	-	-	-	-	-	-
Zinc**	0.11-17	0.017-1.5	0.087	0.618	0.008-0.009	0.02-0.1	0.046	0.25	<0.002-0.009	<0.0057-0.12

ND = not detected, \*detection limit not specified, \*\*metal is typically lower prior to tire chip contact, (-) = Numeric results not reported or constituent was not included in study

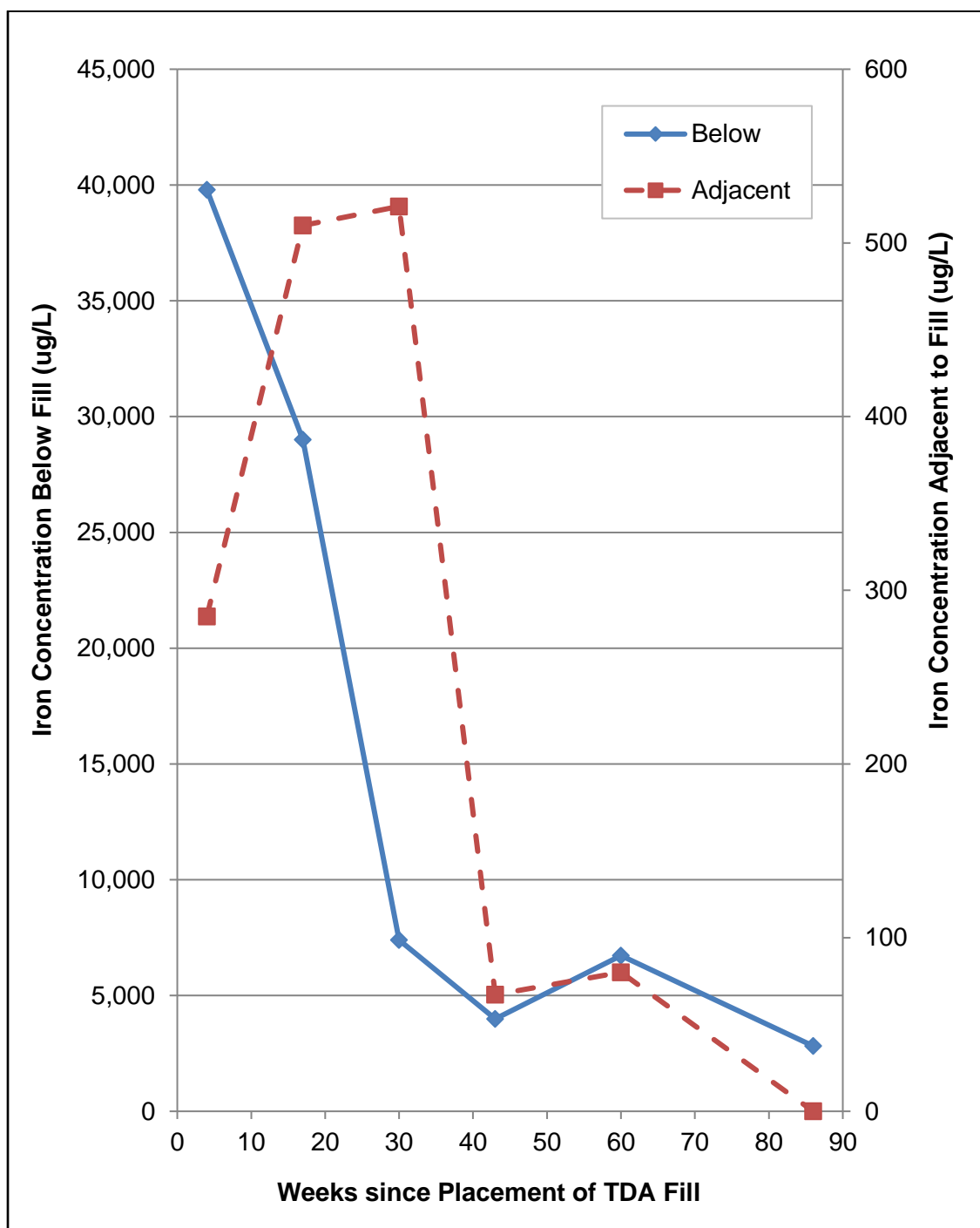


Figure 2. Iron concentration for 10-ft thick TDA layer below embankment fill (adapted from Brophy and Graney, 2004). (Note: secondary vertical axis for concentration adjacent to fill).



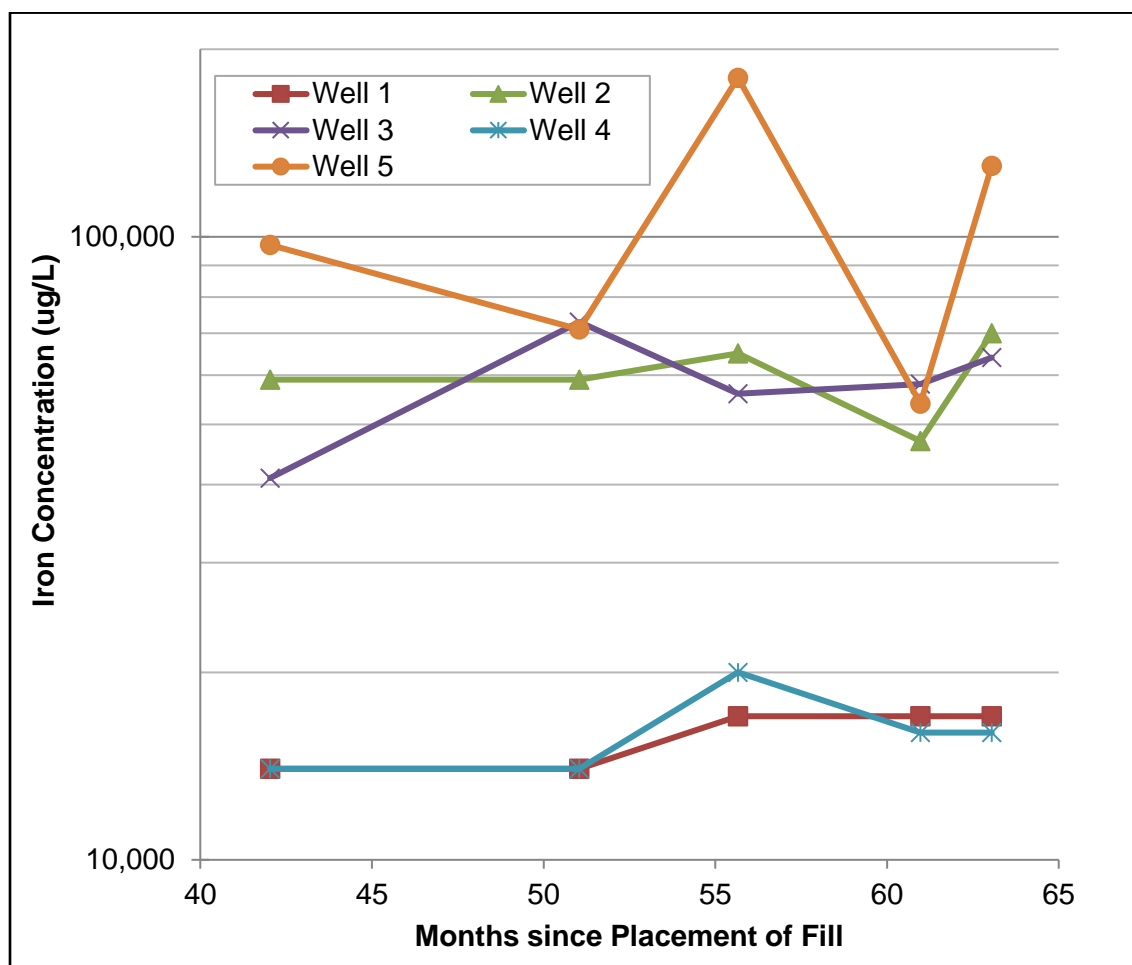


Figure 3. Iron concentrations observed in five wells for a fill placed below the groundwater table where Well 1 is located before the tire chip fill and Wells 2-5 are located in a 12,735-cubic yard tire shred fill (adapted from Edstrom et al., 2008). (Note: logarithmic vertical scale).

Zinc has also been detected at elevated levels (Table 15) (Downs et al., 1996; Ealding, 1992; Edil and Bosscher, 1992; Edil et al., 1990; Edstrom et al., 2008; Humphrey and Katz, 2001; Kaliakin et al., 2012; Miller and Chadik, 1993; TCTC, 1990;), although typically at levels that do not exceed regulatory standards (Downs et al., 1996; Edil et al., 1990; Finney et al., 2013; O'Shaughnessy and Garga, 2000). It has been suggested that zinc concentrations decrease over time (Brophy and Graney, 2004;

Humphrey and Katz, 2001; Miller and Chadik, 1993; Selbes, 2009). This behavior over time was observed by Brophy and Graney (2004) in a demonstration project in which tire shreds were used to construct a highway exit ramp (Figure 4). A study performed on crumb rubber reported an initial pulse of elevated levels of zinc followed by steady, decreased levels (Rhodes et al., 2012). Other studies report no detectable trend (Aydilek et al., 2006).

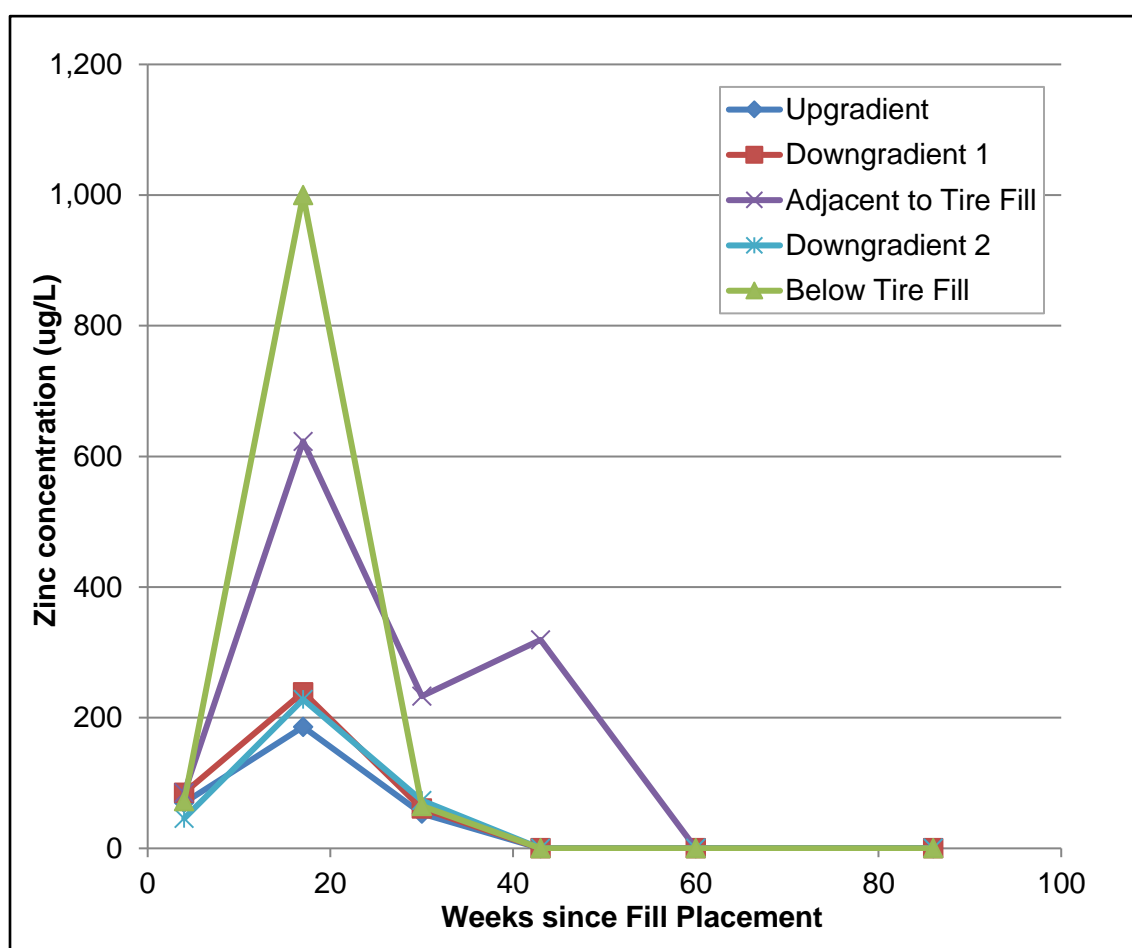


Figure 4. Zinc concentration for 10-ft thick TDA layer below embankment fill (adapted from Brophy and Graney, 2004). Note: the Secondary MCL for zinc is 5 mg/L.

Several studies have suggested that manganese is released from TDA (Downs et al., 1996; Edil et al., 1990; Edil and Bosscher, 1992; Edstrom, 2008; Kaliakin et al., 2012; Humphrey and Katz, 2001; Humphrey and Swett, 2006; Sheehan et al., 2006) and concentrations may exceed its current secondary drinking water standard of 0.05 mg/L (Downs et al., 1996). However, the concentration of manganese in a four-year field study (Humphrey and Katz, 2001) appeared to decrease over time and approached background concentrations in the last sampling event.

Although multiple studies suggested that TDA may cause elevated levels of barium (Edstrom et al., 2008; Humphrey and Katz, 2001), a four-year field study in which TDA was placed below the groundwater table showed that the constituent was below its primary drinking water standard (2000 ug/L) even in the sampling well located in the tire shred trench (Humphrey and Katz, 2001). This finding supports the conclusions drawn in other studies (Edil and Bosscher, 1992; O'Shaughnessy and Garga, 2000) that suggest that TDA does not increase barium concentrations to a concerning level.

Most results indicate that the following metals are not likely to pose a threat to groundwater quality: lead (Downs et al., 1996; Edil and Bosscher, 1992; Finney et al., 2013; Gunter, 1999; O'Shaughnessy and Garga, 2000), copper (Humphrey and Katz, 2001; O'Shaughnessy and Garga, 2000;), chromium (O'Shaughnessy and Garga, 2000), mercury (Downs et al., 1996), and cadmium (Downs et al., 1996; Finney et al., 2013).

The concentration of metals in solution measured during laboratory experiments (Table 15) provide insight into the relative differences in concentrations between metals.

Varying amounts of tire products and leachate solution, however, make comparison across studies difficult. One method of standardizing leachate concentrations is converting concentrations from mass of element per volume of water to mass of element per mass of tire product (Table 17). Although this accounts for differences in tire product mass and solution volume, factors such as time exposure to liquid and the length of the total study are neglected.

Laboratory results have provided insight into the contaminants that may leach into water and the relative difference between the various constituents, but lack accurate representations of field application settings, which often result in lower concentrations. Despite efforts to standardize laboratory results, the large variation in experimental conditions across studies (i.e., difference in tire product size, time of exposure to liquid, characteristics of the liquid, and amount of tire product and liquid used) cannot easily be captured. In field experiments, the rate at which potential contaminants are leached from TDA is predicated on its environment. The conditions of the surrounding soil and the rate at which groundwater flows through the fill are two possible explanations for differing results observed in the field studies.

Table 17. Standardized (mg of element/kg of tire) results from select laboratory studies. Blank cells indicate element was not included in analysis.

<b>Element</b>	<b>Downs et al. (1996)</b>	<b>Ealding (1992)<sup>1</sup></b>	<b>Grefe (1989)<sup>2</sup></b>	<b>Gunter (1999)</b>	<b>Kim (1995)<sup>2</sup></b>	<b>Miller and Chadik (1993)<sup>2</sup></b>	<b>RMA (1990)<sup>2</sup></b>	<b>TCTC (1990)<sup>1</sup></b>
Aluminum	0.18	ND - 0.27						0.14
Arsenic	0.07	ND - <0.015				0.02		ND
Barium	0.11	ND - 0.78	0.55	0.023 - 0.2	0.37		0.1	0.7
Cadmium		ND - 0.02						ND
Calcium	522	1.4 - 11		44				7.28
Chromium	<0.004	ND - 0.02		0.0004 - 0.001	0.019		0.008	ND
Copper		ND - 0.15		0.041				
Lead		ND - 0.02	0.075	0.001 - 0.021	0.14		0.003	ND
Iron	149	11.4 - 103	1.15	7.47 - 67				2.12
Magnesium	4.52	0.2 - 1.8		38.7				1.18
Manganese	0.87		1.5	0.4 - 3				
Mercury		ND - <0.007					7.20E-05	ND
Selenium		ND - <0.019			0.05			ND
Silver		ND						ND
Sodium	149			12				
Zinc	0.012	0.2 - 15	3.15	0.013 - 0.302	1.13	5.02		13.52

ND= nondetect, <sup>1</sup>Detection limit not specified, <sup>2</sup>As reported in Tatlisoz (1996)

## Organics

Most studies that investigated the leaching of organics from TDA in typical civil engineering application settings suggest the material has negligible effects on surrounding groundwater quality (Aydilek et al., 2006; Burnell and McOmber, 1997; Edil, 1992; Edstrom et al., 2008; Gunter et al., 1999; Humphrey and Katz, 2001; Humphrey, 1999). In contrast to the available literature on inorganic compounds, the literature that covers organic compounds spans a wider range of constituents. Repeated studies of organic compounds are more scarce than that of inorganic compounds. In some instances, an investigation of available literature provided only a single study for a given compound. This literature review addresses compounds that have been targeted as a concern or have been detected in multiple studies.

A four-year field study conducted by Edstrom et al. (2008) in which TDA was placed below the seasonal groundwater table indicates that aniline, benzothiazole, and naphthalene may leach from tire chips (Table 18). The study monitored several wells that provided upstream and downstream concentrations, as well as five wells with well screens to monitor water quality within the tire shred fill. The thickness (i.e., depth of tire chips submerged) of the tire shred fill for the five wells varied from 0.4-6.8 feet. The variation in the tire shred thickness was used to correlate detected compounds with the thickness of the tire chip fill, indicating that these compounds come from the TDA (

Table 19). 2-Hydroxybenzothiazole and 4-Acetylmorpholine were detected at higher concentrations within the tire shred road base (Edstrom et al., 2008). However, the decrease over time of 2-Hydroxybenzothiazole and the lack of available information on the compound, and the relatively low concentration and non-threatening nature of 4-

Acetylmorpholine (Edstrom et al., 2008) have negated the need for further discussion of these compounds.

Table 18. Range of concentrations (ug/L) detected in a four-year field study for tire chips placed below the seasonal groundwater table (Edstrom et al., 2008).

<b>Compound</b>	<b>Background</b>	<b>Within Tire Chip Fill</b>
Aniline	<3.2 - <10	<9.3 - 380
Benzothiazole	<5 - <10	<5 - 45
2-Hydroxybenzothiazole	<5 - <10	<5 - 1500
4-Acetylmorpholine	<5 - <10	<5 - 24
Benzoic Acid	<2.8 - <11	<9.3 - <10
Carbazole	<1.2 - <11	<9.3 - <22
4(1-Methyl-1-phenylethyl)phenol	<5	<5
4(2-Benzothiazolythio)-morpholine	<5	<5
Naphthalene	<0.045	<0.045-0.45

Table 19. Linear correlation coefficients of select organic compounds and thickness of submerged tires at end of four-year study (Edstrom et al., 2008).

<b>Parameter</b>	<b>Correlation Coefficient (<math>r^2</math>)</b>
Aniline	0.96
Benzothiazole	0.92
2-Hydroxybenzothiazole	0.92
4-Acetylmorpholine	0.96

Aydilek et al. (2006) investigated the use of TDA for leachate collection by performing a four-year comparison between two collection cells: one with tire chips and one with gravel. Ranges of concentrations detected in the cells (Table 20) only reflect three of the sampling events and are not necessarily representative of the entire study. One such example is cis,1-2-dichloroethene. Although the range of concentrations detected in the three sampling events for the tire chip cell appears to be lower than that of

the gravel cell, a comparison of average concentration over the entire study indicates that cis,1-2-dichloroethene may leach from TDA (Figure 5). A ratio of concentration in the tire chip cell to the concentration in the gravel cell greater than one for a given compound is indicative that the compound may leach from TDA.

In a four year field study of TDA placed below the groundwater table, Humphrey and Katz (2001) detected cis-1,2-dichloroethene in most samples. The highest concentration of cis-1,2-dichloroethene 0.6 meters downstream of the TDA trench was 9.8 ug/L, slightly above the current California MCL of 6 ug/L.



Table 20. Range of concentrations detected in experimental leachate collection system (Aydilek et al., 2006).

<b>Contaminant</b>	<b>Control (gravel) (ug/L)</b>	<b>Through Tire Chips (ug/L)</b>
Acetone	560 - 3,790	230 - 5,040
Benzene	ND - 4.6	ND - 1.6
2-Butanone	3,580 - 5,910	420 - 7,060
Chloroethane	ND - 10	ND - 1.5
1,2-Dichlorobenzene	ND - 5.4	ND
1,4-Dichlorobenzene	ND - 1.4	ND
1,1-Dichloroethene	ND - 6.5	ND - 6.8
cis-1,2-Dichloroethene	ND - 2.2	ND - 1
Dichloromethane	ND - 67	ND - 2.5
Ethylbenzene	ND - 18	ND - 1.1
4-methyl-2-pentanone	ND - 61	ND - 137
Methyl-tert-butyl-ether	ND - 21	ND - 11
Naphthalene	ND - 3.7	ND
Styrene	ND - 4.6	ND
Toluene	14 - 186	8.5 - 35
Vinylchloride	ND - 2	ND - 1.9
Xylenes	ND - 61	ND - 4.3

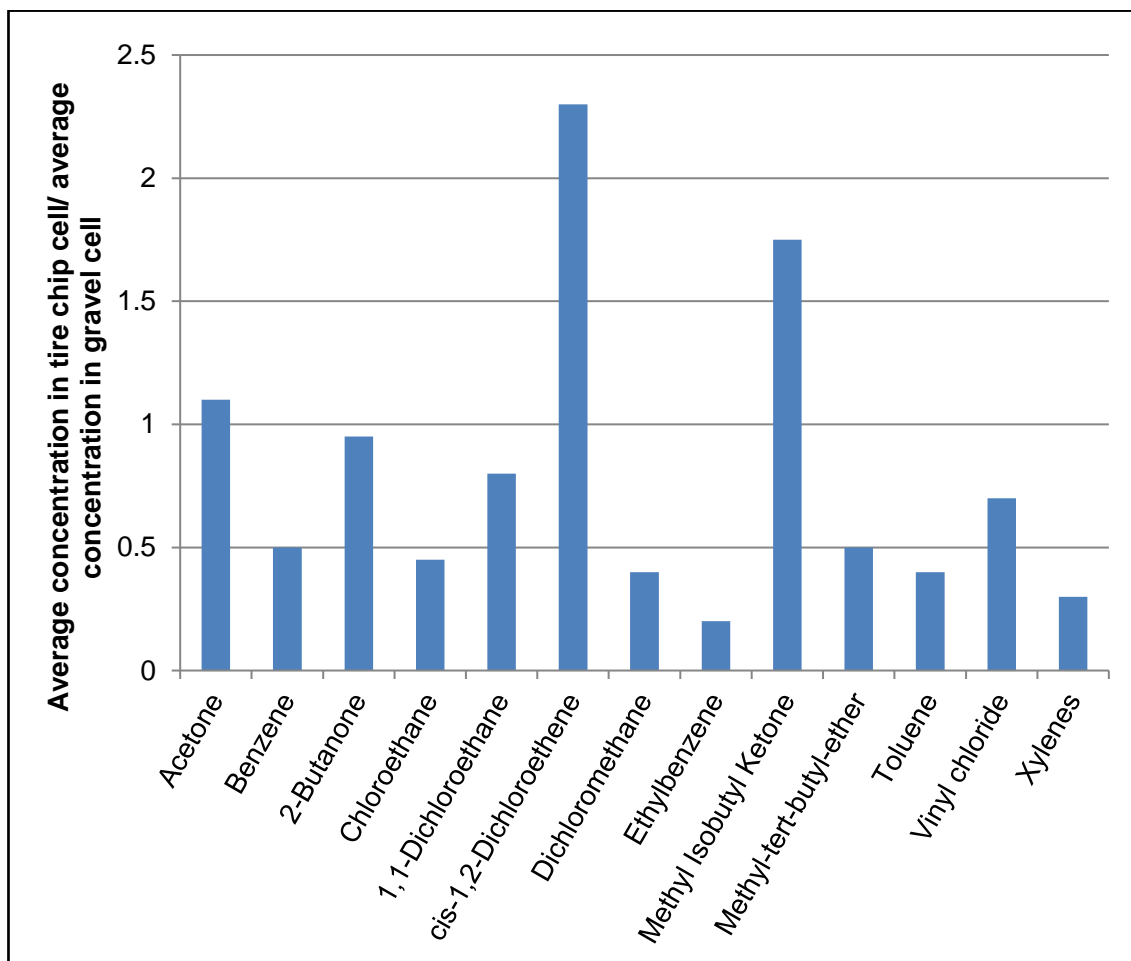


Figure 5. Average ratio of compound concentration in tire chip cell to concentration in gravel cell for experimental leachate collection system (adapted from Aydilek et al., 2006).

### *Volatile Organic Compounds*

VOCs are introduced in the tire manufacturing process for purposes such as enhancing the mixing of rubbers and promoting elasticity (Miller and Chadik, 1993). According to the US EPA (1981) as cited in Miller and Chadik (1993), approximately eight percent of these compounds are sorbed into the rubber.

Humphrey and Katz (2001) detected low concentrations of 1,1-dichloroethane (nondetect to 19 ug/L) in a tire shred trench placed below the groundwater table, but downgradient concentrations were below the detection limit by the end of the study (four years after construction). In a comparison study of gravel and tire shreds for a municipal solid waste leachate collection system, 1,1-dichloroethene was not detected in the cell containing tire chips (Aydilek et al., 2006).

Although acetone has been detected in tire shred studies (Aydilek et al., 2006; Gunter et al., 1999; Humphrey and Katz, 2001), its low levels and behavior over time suggest the compound is unlikely to significantly compromise groundwater quality. Humphrey and Katz (2001) detected acetone (nondetect to 54 ug/L) in a tire shred trench, but the compound was only detected once (10 ug/L) over a four-year period at the downgradient wells. In their leachate collection system study, Aydilek et al. (2006) reported acetone concentrations ranging from 230-5,040 ug/L in the tire shred system, but comparable concentrations were observed in the gravel control system (560-3,790 ug/L). In a laboratory study that investigated tire shred behavior in various water types (groundwater, marsh water, and deionized water), acetone was not detected in the groundwater sample (Gunter et al., 1999). Acetone was, however, detected in the marsh and deionized water initially (0.1149 mg/kg tire and 0.0014 mg/kg tire, respectively), but was not detected seven months later (Gunter et al., 1999).

Several studies have detected benzene in TDA or TDP leachate (Gunter et al., 1999; Humphrey and Katz, 2001; Miller and Chadik, 1993). Gunter et al. (1999) found that benzene concentrations were reduced to insignificant after a seven-month study. This

behavior over time was also observed in a 90-day laboratory experiment by Miller and Chadik (1993) who reported benzene concentrations were highest initially, but decreased rapidly and exponentially. Because benzene was suspected to accumulate from gasoline contamination onto the tire chips, it is expected to leach from the media when first exposed to an aquatic environment (Miller and Chadik, 1993). A comparison of results from a laboratory study showed a decrease in benzene of washed chips compared to unwashed chips (Downs et al., 1996). Although detected in the laboratory portion of the study conducted by Miller and Chadik (1993), it was never detected in the field phase. Results from a field experiment in which TDA was placed below the groundwater table suggest that benzene is released from tire shreds at trace levels (Humphrey and Katz, 2001).

It has been suggested that methyl isobutyl ketone (MIBK) may be released from tire shreds (Aydilek et al., 2006; Gunter et al., 1999; Humphrey and Katz, 2001). Aydilek et al. (2006) detected higher concentrations of MIBK in a tire shred landfill leachate collection system than in that of gravel, as illustrated in Figure 5. Due to the overall variation in the concentration of VOCs across the two systems, Aydilek et al. (2006) hypothesized that the municipal refuse is the source of MIBK. The compound has, however, been detected in other studies. Humphrey and Katz (2001) reported concentrations that range from nondetect to 140 ug/L within the tire shred trench, but the highest concentration 0.6 meters downstream of the tire shreds was 31 ug/L. Gunter et al. (1999) detected MIBK in their laboratory experiment, but reported that concentrations decreased to insignificant levels after seven months.

In their laboratory study, Miller and Chadik (1993) found that toluene was initially not detected or detected at low concentrations and increased exponentially over the course of the three-month study. In the field portion of their study, however, toluene was detected at low concentrations or not at all. Gunter et al. (1999) also reported nondetects or low concentrations (0.0012 mg/kg of tire) at the onset of their laboratory experiment, but the compound was not detected in any of the three containers seven months later. In a four-year study in which tire shreds were placed below the permanent groundwater table, Humphrey and Katz (2001) reported that toluene was well below its drinking water standard of 100 ug/L. In a fifteen-month leach field study, Finney et al. (2013) did not detect toluene in the TDA effluent.

#### *Semi-Volatile Organic Compounds*

Aniline has been detected in studies in which tire shreds were placed below the groundwater table (Edstrom et al., 2008; Humphrey and Katz, 2001). Aniline is reported to be used as an antidegradant in the rubber manufacturing process (Fishbein (1991) as cited by Downs et al. (1996)). In a four-year study, concentrations ranged from <10 ug/L to 380 ug/L (Edstrom et al., 2008). Edstrom et al. (2008) postulated that these levels would be lower if dissolved oxygen were above 2 mg/L. Downstream of the tire shred placement, aniline was not detected. Similar results were noticed by Humphrey and Katz (2001). Aniline was detected during the first three years of the study, but was never detected downstream of the tire shred trenches (Humphrey and Katz, 2001). Furthermore, the compound was not detected at any of the sampling locations in the last samples of the four-year study (Humphrey and Katz, 2001). Although Edstrom et al. (2008) suggest aniline is released from the tires, as indicated by its linear relationship with the thickness of the tire shred fill (

Table 19), results suggest that the compound remains contained within the tire shred placement (Edstrom et al., 2008; Humphrey and Katz, 2001). Edstrom et al. (2008) stated that should aniline migrate, it will not bioaccumulate in aquatic biota and, volatilization and biodegradation would significantly contribute to the reduction of the compound in surface waters.

Although benzoic acid has been detected in studies, its low concentrations and apparent immobility when placed below the groundwater table suggest that it does not pose a threat to groundwater quality (Humphrey and Katz, 2001). A laboratory study detected concentrations as high as 400 ug/L (Downs et al., 1996). However, concentrations of the compound in a field setting have not reached such levels. In a four-

year study in which tire shreds were placed below the seasonal groundwater table, benzoic acid was not detected once (MDL = 10 ug/L) (Edstrom et al., 2008). In their four-year field study in which tire shreds were placed below the groundwater table, Humphrey and Katz (2001) found that benzoic acid was released at trace levels. Approximately one quarter of their samples taken from within the tire shred trench had detectable levels of the compound, which ranged from <10 to 100 ug/L. However, benzoic acid was not detected in the sampling wells located downgradient of the tire trench.

Fishbein (1991) as cited by Downs et al. (1996) reports that benzothiazoles are used as accelerators in the rubber manufacturing process. Humphrey and Katz (2001) tentatively detected the compound in a few samples and concluded that it may be released from the tire shreds intermittently at low concentrations. Edstrom et al. (2008) also detected the compound (<50 ug/L), but report that it appears to remain within the tire shred fill. Benzothiazole is expected to have a low potential to bioaccumulate in aquatic biota (Edstrom et al., 2008).

Phenol was detected during the first three years of a study in which tire shred trenches were placed below the groundwater table, but the compound was not detected downstream of the trenches nor was it detected during the last samples of the four-year study (Humphrey and Katz, 2001). In a sewage disposal drain field study, Burnell and McOmber (1997) reported that phenol concentrations were below the detection limit (9 ug/L) for all samples.

### *Polynuclear Aromatic Hydrocarbons (PAHs)*

Studies that have investigated TDA leachate behavior under basic conditions have detected Total Petroleum Hydrocarbons and Polynuclear Aromatic Hydrocarbons (PAHs) (Miller and Chadik, 1993; TCTC, 1990). Although Miller and Chadik (1993) suggested further research needs to be conducted regarding the leaching of PAHs, Kellough (1991) found that only Anthracene-d<sub>10</sub> and Chrysene-d<sub>12</sub> were detected of the PAHs tested. However, these two substances were also detected in the control containers of the experiment and were therefore not considered to originate from the tire products (Kellough, 1991). One field experiment in which tire shreds were placed below the seasonal groundwater table detected low levels (less than <1 ug/L) of total PAHs within the tire shred fill (Edstrom et al., 2008). No PAHs were detected downstream and no carcinogenic PAHs were detected in any of the samples.

### *Polychlorinated biphenyls (PCBs) and Organochlorines (OCs)*

With the exception of dichlorodiphenyldichloroethylene (DDE), Kellough (1991) reported no detection of any PCBs/OCs tested when cut and whole tires were placed in an aquarium for 60 days. Kellough (1991) concluded the DDE was likely introduced from the gold fish since the compound was also found in the control sample.

### *Oil and Grease*

Because oil and grease is not targeted as a compound of concern that may leach from TDA, it is not typically included in water quality analyses. However, foreign material that may be attached to waste tires could introduce oil and grease to a TDA



batch. In addition, the increased attention for TDA stormwater applications may result in future interest in the potential leaching of oil and grease. Gunter et al. (1999) observed that oil and grease increased in their one-year laboratory experiment in all tanks, including the control tanks. However, oil and grease was higher in the tanks containing tire chips. Gunter et al. (1999) postulated that the source of its presence was due to foreign material on the tire chips, or the tank themselves, which may not have been cleaned to ASTM standards.

#### Common Water Quality Index Parameters

Typical parameters that commonly serve as indicators of water quality include pH, total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia, sulfate, phosphate, specific conductance (EC), and dissolved oxygen (DO).

Previous studies indicate that the TDA itself will not typically cause the pH to deviate from neutral conditions (Humphrey and Swett, 2006; O'Shaughnessy and Garga, 2000). While Miller and Chadik (1993) found that tire chips may decrease pH, Humphrey and Swett (2006) reported that the pH of five project sites varied from 6.79 to 7.51, which falls within secondary drinking water standards (US EPA, 2013). Neutral pH in tire shred leachate was also reported by Aydilek et al. (2006) in a leachate collection system field study. Miller and Chadik (1993) postulate that a decrease in pH observed in their laboratory study may be due to microbial enzymatic activity during the biodegradation of organic compounds, however, this hypothesis was not confirmed. A

slight decrease in pH was also noticed in a four-year field study conducted by Edstrom et al. (2008).

Edstrom et al. (2008) suggest that a tire shred fill may increase the COD, but levels appeared to decrease over the course of the four-year field study. Hypothesis testing conducted by Humphrey and Swett (2006) showed that the COD in the control section of one of the investigated field studies was statistically equal to the TDA section with a 90% level of confidence, suggesting that the TDA fill did not affect the COD. Similar results were noted by Finney et al. (2013).

Hypothesis testing conducted by Humphrey and Swett (2006) showed that the total dissolved solids, total solids, and BOD in the control section of one of the investigated studies was statistically equal to the TDA sections with a 90% level of confidence, suggesting that the TDA fill did not affect these parameters. Edstrom et al. (2008), however, found that TSS levels increased over the four-year field study in which TDA was placed below the seasonal groundwater table.

Edstrom et al. (2008) observed an increase in specific conductance during the study, sometimes exceeding 1000 umhos/cm. They hypothesized the increase was likely due to an increase in dissolved inorganic and organic compounds.

Ammonia, not typically analyzed in TDA water quality experiments, was detected in a four-year field study in which TDA was placed below the seasonal groundwater table (Edstrom et al., 2008). Concentrations ranged from 6-12 mg/L over the course of the study; however, the nearby surface water contained less than 1 mg/L ammonia. The source of the ammonia was not identified in the study, but Edstrom et al. (2008) stated

ammonia may be leaching from the tire shreds or may have migrated to the study site from a nearby sod farm. A comparison of rock and TDA in a leach field study showed no significant difference of ammonia between the two materials (Finney et al., 2013).

#### Toxicity to Aquatic Ecosystems

For some potential applications, TDA may come into contact with water that flows to surface waters. Several studies (Sheehan et al., 2006; TenEyck and Markee, 2006a; TenEyck and Markee, 2006b) have suggested that leachate from a TDA fill placed below the groundwater table may have toxic effects on certain organisms (Table 21). These studies, however, generally simulate applications in which the leachate would not pass through soil or experience dilution prior to mixing with surface water, a situation that would likely occur in typical TDA applications. An illustrative example of potential dilution rates was reported by Sheehan et al. (2006), who observed an iron concentration of 80 mg/L in the tire shred fill and a concentration of 6.1 mg/L after passing through 0.61 meters of soil.

Table 21. Summary of select aquatic toxicity tests.

Source	Results
Sheehan et al. (2006)	Significant reductions in survival and reproduction in <i>C. dubia</i> for leachate collected from below the groundwater table tire shred fill. No adverse effects on <i>P. promelas</i> survival or growth for leachate collected from above the groundwater table tire shred fill.
TenEyck and Markee (2006a)	Survival significantly reduced for <i>P. promelas</i> for leachate collected below the groundwater table. Survival significantly reduced for <i>C. diluts</i> for two of the five well samples, but not for remaining three. Survival significantly reduced and reproduction partially reduced for <i>C. dubia</i> .

Water samples consisting of runoff that passed through a TDA fill placed above the groundwater table did not have adverse effects on the survival of *Pimephales promelas* and *Ceriodaphnia dubia* (Sheehan et al., 2006) while leachate collected from sites with a fill below the groundwater table reported significantly reduced survival rates of the same two species (Sheehan et al., 2006; TenEyck and Markee, 2006a). TenEyck and Markee (2006a) suggested that the decline in survival may be due to increased levels of ammonia, which ranged from 1.7 to 15.1 mg/L in the TDA wells compared to the 0.067 mg/L in the reference well. The source of the elevated levels of ammonia are not known and may be originating from a nearby sod farm (Edstrom et al., 2008). It has been suggested that iron precipitates are the causative agent of toxicity to *C. dubia* (Sheehan et al., 2006; TenEyck and Markee, 2006a). However, the results of a Toxicity Reduction Evaluation conducted by TenEyck and Markee (2006b) suggested that reducing iron concentrations to as low as 0.04 mg/L did not result in a significant increase in survival of *Pimephales promelas* or *Ceriodaphnia dubia*.

Results of an investigation of representative aquatic toxicity studies suggest that the toxicity of TDA leachate depends on several factors including distance from fill placement, the species of interest, and whether the fill is placed above or below the groundwater table. Using a groundwater model (discussed in a subsequent section), Sheehan et al. (2006) estimated that a 3.0 meter buffer between a tire shred fill and the nearest surface water would provide sufficient distance for aquatic life protection.

### **Factors that may Affect Leaching**

As indicated by the large variation in aforementioned laboratory and field studies results, the leaching behavior of TDA is predicated on its aquatic environment and the size of the tire product. Further discussion of these factors is given below.

### pH

Several studies (Ealding, 1992; O'Shaughnessy and Garga, 2000; Selbes, 2009; TCTC, 1990) have evaluated the effects pH has on the contaminants that may leach from tire products. The available literature indicates that metals are detected at the highest concentrations in acidic conditions (Ealding, 1992; O'Shaughnessy and Garga, 2000; Selbes, 2009; TCTC, 1990). Although it has been suggested that pH has little or no effect on the leaching of organic compounds (Miller and Chadik, 1993), the majority of studies that have evaluated pH show that alkaline conditions result in higher concentrations of organics (e.g., O'Shaughnessy and Garga, 2000). Ealding (1992) reported bulging of plastic containers with tire shreds in a low pH solution (pH of 4). This study, however, created an environment conducive to biological activity. Substituting benzoic acid for acetic acid combated this problem, which verified that the TDA was not the cause of the gas generation. The results from this study, and the majority of other studies, suggest that neutral pH conditions are optimal for TDA applications (Ealding, 1992; Selbes, 2009).

### Size

Several studies have investigated the effects the size of TDA or tire shred has on the leaching behavior of its constituents (Miller and Chadik, 1993; Selbes, 2009). In general, these studies have shown that smaller pieces (e.g., 1'' x 1'') tend to more readily

leach organics. Miller and Chadik (1993) found that, in general, tire shred size was the primary factor that governed the leaching of organics; however, they found that the specific effect varied with the compound of interest. Results indicated that benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds were most affected by shred size. Medium (between 2''x 2'' and 4''x 4'' in size) and large (between 1''x 1'' and 2''x 2'' in size) pieces leached more benzene than small pieces (between 0.5''x 0.5'' and 1''x 1''), and small pieces leached more toluene and 1,2,3-Trimethylbenzene (Miller and Chadik, 1993). The benzene behavior does not follow the more commonly observed trend (i.e., smaller pieces tend to result in greater rates of leaching) and no explanation was provided. Ethylbenzene, both xylenes, 2-ethyltoluene, and 1,2,4-Trimethylbenzene appeared to behave similarly, regardless of the shred size (Miller and Chadik, 1993).

Selbes (2009) conducted a 28-day study investigating the behavior of dissolved organic carbon and inorganic compounds that may leach from various tire derived products (TDPs). Results indicated that the compounds of interest leached most readily from the smallest chip size (1''x 1''), while leaching behavior was similar for the remaining sizes (2''x 2'', 4''x 2'' and 6''x 2''). Further analysis of the results suggested that the increased side surfaces of the smaller tire pieces likely contributed to increased levels of dissolved organic carbon (Selbes, 2009). Data normalized for side-surface area suggested that the organic leaching is more dependent on the side surface area rather than the total size of the TDA. Selbes (2009) postulated that this is likely due to the freshly-cut and exposed side material, rather than the more weathered top and bottom surfaces. In a comparison of tire chips and crumb rubber, all detected constituents were significantly

higher for crumb rubber except for iron, suggesting that the steel wire is likely the source (Selbes, 2009). Similar to iron, this behavior is expected for the other components of steel. The behavior of the inorganics found in steel are expected to be less dependent on the actual size of the TDA and more dependent on the amount of protruding steel wire, which is governed by the specifications and the manufacturing of the material.

### **Fate of Compounds that may Leach into Soil**

In typical civil engineering applications, TDA is surrounded by soil. The behavior of the potential contaminants that may leach from the material as it interacts with the surrounding soil is therefore an integral component of evaluating potential environmental concerns. Processes that govern contaminant migration are complex interactions and highly-dependent on soil characteristics. An in-depth analysis of such behavior is beyond the scope of this study, but the literature presented here provides a basic framework for understanding the fate of compounds that may leach from TDA. Based on the contaminants of concern in the available literature, the migration of selected metals is the focus of this evaluation. A brief overview of general soil characteristics that affect the transport of metals is presented followed by a summary of TDA studies that evaluated leachate behavior through soils.

#### **Summary of Relevant Soil Properties**

Although metals may leach from TDA, they are also known to naturally occur in soil at trace levels (Table 22). Because of the complex nature of physical and chemical

soil processes, the potential effect of metals in soils continues to be a topic of investigation (Smolders et al., 2009). Typically, soil retains metals until the soil retention capacity is exceeded (McLean and Bledsoe, 1992). The soil retention capacity is predicated on various processes, including oxidation-reduction reactions, precipitation and dissolution reactions, complexation, and adsorption and desorption reactions (McLean and Bledsoe, 1992). The factors that govern the rate of these reactions include soil composition, characteristics of surrounding environmental conditions (e.g., pH), and the amount and inherent behavior of the metal of interest. As discussed in the following section, previous studies suggest that the metal concentration in the leachate plume is greatly reduced by the soil immediately surrounding the TDA fill.

Table 22. Ranges of select metals found in soil (Lindsay, 1979 as cited in McLean, 1992).

<b>Metal</b>	<b>Common Range for Soils (mg/kg)</b>
Aluminum	10,000 - 300,000
Iron	7,000 - 55,000
Manganese	20 - 3,000
Copper	2 - 100
Zinc	10 - 300
Lead	2 - 200

#### Tire Product Studies on Soil

Migration of contaminants through soil has not been the focus of most TDA studies. Several studies (e.g., Downs et al., 1996; O'Shaughnessey and Garga, 2000) have evaluated the effects of soils on TDA leaching behavior by mixing the two media. This setting, however, is not typical of common TDA applications and will not be discussed.



The studies that have investigated the behavior of tire product leachate through soils suggest that constituents that leach from TDA in the field do not migrate far (Downs et al., 1996; Edstrom et al., 2008; Horner, 1996; Humphrey and Katz, 2001; Sheehan et al., 2006). Humphrey and Katz (2001) and Edstrom et al. (2008) report that tire shreds have negligible off-site water quality effects when placed below the water table. This conclusion was supported by Sheehan et al. (2006), who continued water quality analyses for the site Humphrey and Katz (2001) studied. Iron concentrations through the TDA fill were 80 mg/L and decreased to 6.1 mg/L less than one meter (0.61 m) downgradient (Sheehan et al., 2006). One year later, iron concentrations through the fill were 51 mg/L, and 2.4 mg/L at the downgradient location (Sheehan et al., 2006). Similar recovery behavior was observed for dissolved oxygen, which increased from 0.8 to 3.1 mg/L for the first sample and from 1.6 to 3.7 mg/L one year later (Sheehan et al., 2006).

Sheehan et al. (2006) further investigated subsurface transport of tire shred leachate fate using a three-dimensional dispersion and infiltration model. The objective of the modeling study was to determine the groundwater travel distance required to reduce leachate concentrations to 12.5% of the total groundwater volume (Sheehan et al., 2006). This target percent leachate was selected based on an evaluation of toxicity criteria. Sheehan et al. (2006) reported that the most sensitive toxicity criteria was the reproduction of *C. dubia* and this criterion would therefore provide the most conservative estimate to reduce leachate levels to nontoxic. Model constants, parameters, and results are provided (Table 23 and

Table 24). Sheehan et al. (2006) concluded that a buffer of approximately 3.0 meters between the tire shred fill and the nearest surface water is sufficient to provide protection for aquatic life in nearby surface waters. This distance was determined assuming dissolved oxygen levels of at least 2.0 mg/L and a pH greater than 5.8. For

applications in which the environment has a lower pH and less dissolved oxygen, model results indicate a buffer distance of approximately 11 meters (Sheehan et al., 2006).

Table 23. User-specified constant model parameters (Sheehan et al., 2006).

<b>Parameter</b>	<b>Value</b>
Initial source concentration	1,000 mg/L
Porosity	0.4
Bulk soil density	1.7 g/cm <sup>3</sup>
First-order decay constant	0 d <sup>-1</sup>
Width of source area	30 m
Depth of source area	0.61 m
Duration of groundwater flow	3,650 d

Table 24. Model scenario descriptions and results (adapted from Sheehan et al., 2006).

<b>Aquifer Material</b>	<b>Hydraulic Conductivity (m/d)</b>	<b>Hydraulic Gradient (m/m)</b>	<b>Distance (m)</b>	<b>Leachate Concentration (% Leachate)</b>
Coarse sand	85	0.1	1.5	0.76
Coarse sand	85	0.01	1.5	6.59
Coarse sand	85	0.001	7.6	11.51
Fine Sand	0.85	0.1	7.6	11.51
Fine Sand	0.85	0.01	50	12.38
Fine Sand	0.85	0.001	12	9.25
Silt	0.0085	0.1	12	9.25
Silt	0.0085	0.01	1.5	1.84
Silt	0.0085	0.001	1.5	0

In a study assessing the migration of heavy metals from a ten-year old tire dump, Horner (1996) demonstrated a tendency for metal concentrations to decrease

exponentially (Figure 6) with increasing distance from the tires. Values reflect concentrations from the provided equation and reported distances at which soil samples were collected. The results of the study indicate a log-linear relationship of distance from the dump location with concentration of cadmium, lead, and zinc (respective correlation coefficients of -0.962, -0.982, and -0.986 with a p-value  $<0.001$ ) (Horner, 1996). Based on these log-linear relationships, the distance at which concentrations were reduced to half of the concentration detected at the base of the tire fill was determined. Results suggested a distance of 10.79 meters (cadmium), 16.10 meters (lead), and 21.50 meters (zinc) would provide a sufficient distance to reduce concentrations by 50 percent.

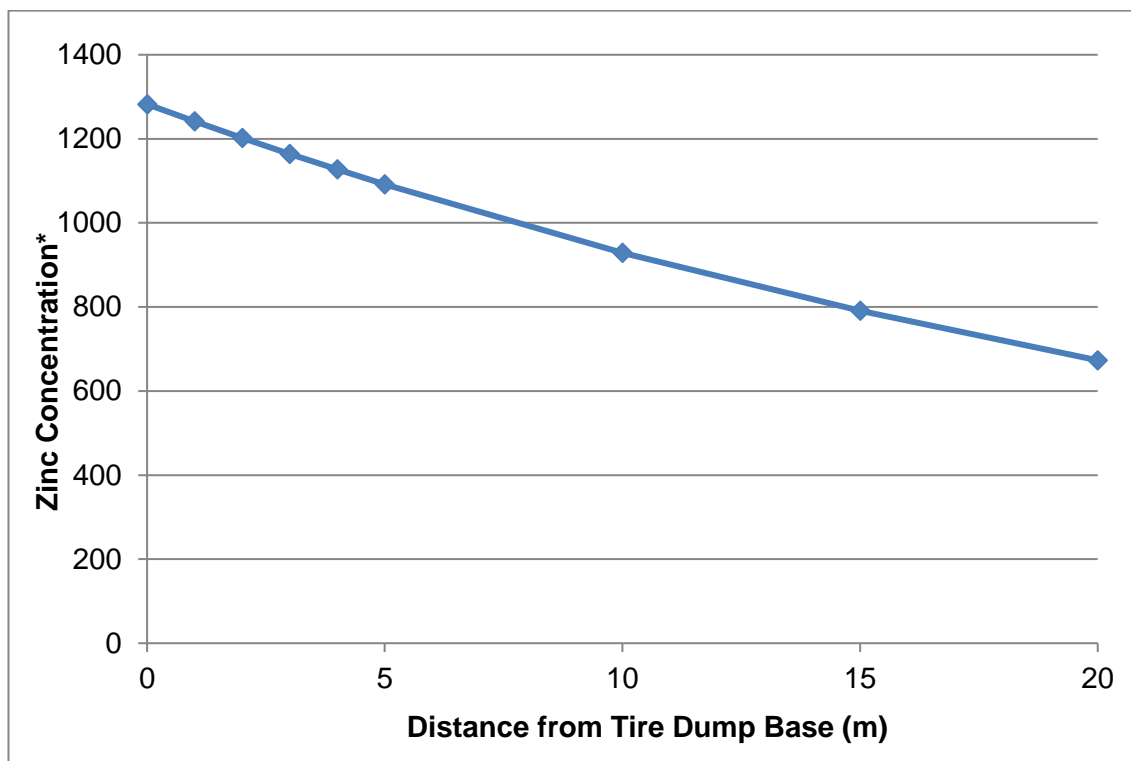


Figure 6. Behavior of zinc at tire dump (\*units not specified) (adapted from Horner, 1996).

### Potential Treatment Capabilities of TDA

An investigation of available literature has revealed the potential of tire products to remove contaminants from water. The focus of relevant literature has included sorption of organic compounds in settings that experience elevated concentrations. Kim et al. (1997) suggest that sorption occurs primarily onto polymeric materials as well as diffusion through the tire rubber matrix.

Several studies (Edil et al., 2004; Finney et al., 2013; Kim et al., 1997; Park et al., 1996; Park et al., 2003) have investigated the sorption capacity of TDA. Kim et al. (1997) reported that the organic compound sorption capacity of ground tires ranges from 1.1 to

4.4% of granular activated carbon (GAC). Park et al. (1996) performed a series of batch sorption-desorption tests and analyzed sorption capacity by testing for methylene chloride, trichloroethylene, toluene, and *m*-xylene. Results suggested that the tire chips, which ranged from 0.6 to 2.5 cm, have 1.4 to 5.6% of the sorption capacity of GAC (by volume) and reach sorption equilibrium within two days. Park et al. (1996) expect that significant levels of organic compounds could be sorbed to a 30-cm thick tire chip layer if used as a primary leachate collection system. In a leach field study, Finney et al. (2013) noticed a higher COD removal rate in a TDA leach field than that of a rock leach field. The COD of the TDA leach field effluent was 10-30 percent lower than in the influent, which was attributed to the attached biological growth facilitated by the TDA (Finney et al., 2013). Similar results were noticed for sulfate and total phosphate (Finney et al., 2013).

In an 800-day laboratory batch experiment, Park et al. (2003) simulated landfill leachate in contact with tire chips and reported a 43% reduction in mercury concentration as compared to landfill leachate in a control tank without tire chips. The results of this study also indicated adsorption of sulfur, arsenic, and selenium from the synthetic landfill leachate to tire chips. A second experiment conducted by Park et al. (2003) that used test cells to simulate a landfill leachate collection system suggested that oil and grease, arsenic, cobalt, lead and nickel are sorbed to tire chips more readily than to gravel. The results of these cell tests also showed that BTEX (benzene, toluene, ethylbenzene, and xylenes) compound concentrations were higher in the gravel-lined cell than in the tire chip cell, which lead to the conclusion that three (toluene, ethylbenzene, and xylenes) of

the four compounds are removed with tire chips. Park et al., (2003) conclude that tire chips can be used as a sorbent for environmental cleanup at sites with high contamination levels.

Edil et al. (2004) further explored tire chips as a drainage medium in landfills. A large-scale tank test and field test indicated that the tire chips significantly reduce VOCs present in the leachate. This not only reduces the migration of these compounds from a landfill site, but may also aid in preserving the (low) hydraulic conductivity of the clay liner of a landfill (Edil et al., 2004). Sorption of toluene in a landfill experiment was also postulated by Aydilek et al. (2006).

### **Summary of Available Literature**

Numerous research efforts have demonstrated that TDA does not have a significant impact on surrounding groundwater, even when placed below the groundwater table. The inorganic compounds that have been consistently detected at elevated levels include iron and zinc, and to a lesser extent, manganese. These compounds are regulated by the EPA's Secondary Drinking Water Standards, which indicates they are an aesthetic, and not a human health, concern. Organic compounds that may leach from TDA include 1,1-dichloroethane, acetone, benzene, cis-1,2-dichloroethane, MIBK, toluene, aniline, and benzothiazole. In contrast to the detected inorganic compounds, the presence of these compounds is not consistent across the available literature. However, the levels at which these compounds are detected do not typically exceed applicable standards. The literature suggests that the compounds that may leach from TDA typically remain within the TDA

fill area and do not pose a threat to surrounding groundwater or surface water quality. Research on these compounds' leaching behavior as a function of time is inconclusive. Although most studies suggest the concentration of the compounds detected decreases over time, the maximum concentration and rate of decrease is not agreed upon.

The literature shows that TDA not only provides desirable engineering properties, but may also provide treatment capabilities. The media supports the growth of bacteria that can degrade and sorb several contaminants. Research has shown that TDA can be used in a wide range of civil engineering applications as a substitute for commonly-used materials such as stone aggregate and soil. The aim of this research is to investigate the rate at which compounds may leach from TDA and evaluate its use as a filtration media in a stormwater application.

## METHODS

An overview of the experimental methods used in this study is provided in this section. Some specific details are also included in the results section where actual numeric values help to illustrate implementation procedures.

### Materials

The TDA used in this project was manufactured by Tri-C Manufacturing in Sacramento, CA. An 80-pound sample of the TDA batch was sent to the TDA Technology Center at California State University, Chico to perform a gradation analysis. The TDA Technology Center determined the type of TDA using a gradation standard that corresponds with ASTM D6270-08 "Use of Scrap Tires in Civil Engineering Applications" (Fraser et al., 2014). TDA is classified as Type A based on the amount (by mass) of free steel, the length of protruding metal on any given shred, and the dimensions of each shred. The sample met all Type A specification requirements except the maximum dimension requirement, which specifies a maximum length of eight inches in any direction of each piece. Approximately 1.8% of the total mass of the TDA sample exceeded the maximum dimension requirement. To provide a reference point for the amount of steel, and therefore iron, in the sample, 0.003 percent (by mass) of the pieces had exposed wire longer than two inches, 0.018 percent had exposed wire longer than one inch, and free steel (steel not attached to rubber) amounted to 0.0007 percent (by mass) of



the entire sample. Representative pieces of TDA from the same batch analyzed by the TDA Technology Center are shown (Figure 7).



Figure 7. Representative pieces of TDA used in this project.

### **Laboratory Experimental Design**

TDA was placed in a nested set of plastic storage containers. The innermost 14 gallon perforated container (the "basket") contained eight kilograms of TDA and rested inside of an 18 gallon container (Figure 8). A small aquarium pump rests in the 18 gallon container to move water to a second 18 gallon container (the "reservoir") that holds the water during the dry operational condition. Total water volume in the container was planned to be approximately 40 liters. The resulting TDA mass to liquid ratio of 1:5 is in the range of the batch experiments reported in Table 10. The basket rests on the aquarium pump to minimize TDA contact with water when in its dry phase. When the TDA is

submerged, a second pump that rests on top of the TDA circulates the water through the material to mimic the conditions of a flow through TDA media filter. Two of these configurations were set up without TDA to act as "blanks" to account for any potential contaminant contribution from the containers, pumps, and the tubing connected to the pumps.

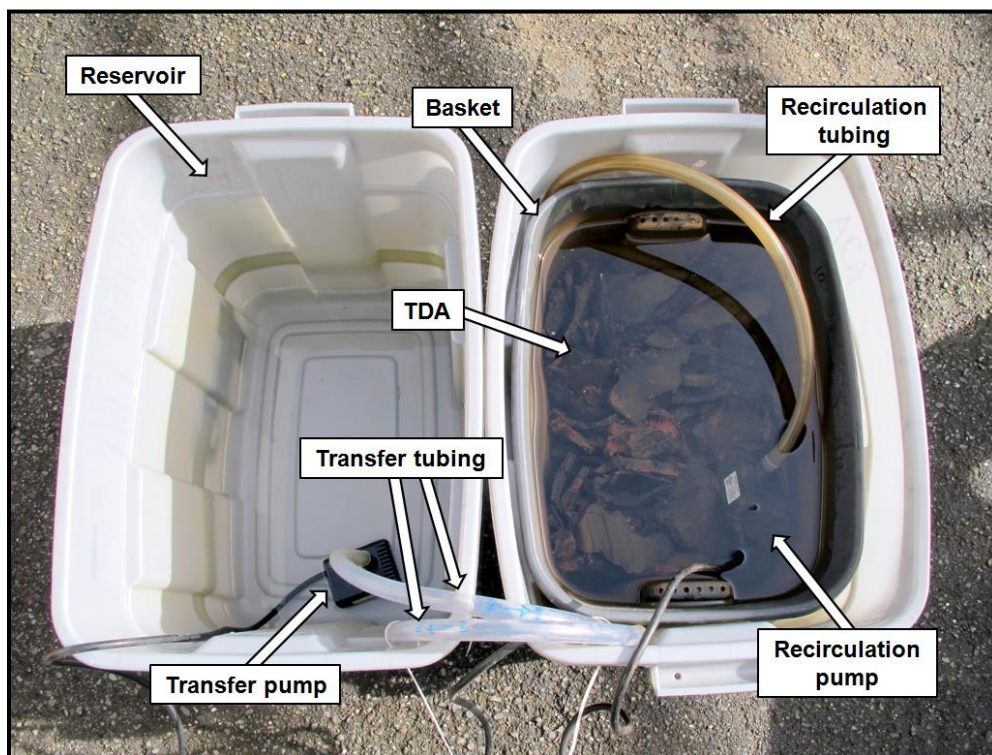


Figure 8. Configuration for paired TDA containers. Note that a second transfer pump rests beneath the perforated basket.

#### Laboratory Sampling Program

A series of the plastic storage containers were assembled to explore the leaching behavior of TDA constituents (Figure 9). The literature indicates that TDA constituents may leach more readily when the material is placed below the groundwater table, which

suggests the 'worst-case' scenario is subjecting TDA to an environment in which it is constantly submerged. This setting was explored in the laboratory experiment of this study. To investigate the behavior of leaching in additional settings (i.e., intervals of dry periods), several other operating conditions were simulated (Table 25). Two identical setups were used as replicates for each operating condition to account for random variability. The variation of exposure time patterns investigated in this study not only simulates conditions with the maximum expected concentrations (constantly submerged), but also simulates conditions that are representative of a range of the length of dry periods between water exposure.



Figure 9. Experimental setup for the laboratory portion of the study.

Table 25. Operating description for each pair of containers.

Containers	Operating Description
1 and 2	Always wet
3 and 4	Alternating 1 day wet, 1 day dry for 6 days followed by 1/2 day wet, 1/2 day dry for 7th day
5 and 6	Alternating 3.5 days wet, 3.5 days dry
7 and 8	Alternating 1 week wet, 1 week dry
9 and 10	Alternating 1 day wet, 1 day dry for 6 days followed by 1/2 day wet, 1/2 day dry for 7th day for 6 months followed by 6 months of dry, followed by initial cycle for 3 months

Because literature suggests that the most material will leach from the TDA at the onset of its exposure to water, containers were sampled every two weeks for the first two months. Budgetary constraints dictated the total number of samples that could be analyzed and containers were therefore sampled every three weeks for the following two collections, and once per month for the remainder of the fifteen month study. The sampling procedure consisted of draining and weighing the water from each of the paired containers so that the water volume could be determined. The containers and pumps were scrubbed with the washings added to the drained water. After thorough mixing, a representative water sample was collected to be analyzed for cadmium, iron, lead, manganese and zinc concentrations. Wash water accounted for 1% (by mass) of the total water volume and did not appreciably change the concentration or mass of the constituents tested. Two of the operating conditions (always wet and alternating one week wet, one week dry) were also analyzed for select organic compounds. After the

samples were taken, the containers were filled with fresh source water and put back into operation. The source water, City of Arcata chlorinated potable water, was analyzed for the aforementioned metals and select organic constituents. The temperature and the dissolved oxygen concentration of each of the operating containers was measured every week.

Initially, the inside surface area of the tubing was assumed to be insignificant for accumulation of leached TDA constituents. However, after 30 weeks, visual inspection of the tubing indicated the mass accumulation in the tubing may be appreciable. The inside of the circulation pump tubing was therefore scrubbed to remove the visible contaminant accumulation. Independent setups were used to determine the rate of metal accumulation in the tubing which was then used to adjust the results for samples collected during the first 30 weeks.

#### TDA Metals Content Analysis

An additional portion of the laboratory experiment investigated the amount of metals that may leach from the wire that protrudes from TDA. TDA can contribute metals to the receiving environment from oxidation of exposed steel wire and the leaching of metals from the rubber compound. The unit mass of the primary metals in TDA, iron, manganese, zinc, and cadmium, was determined for pieces of exposed wire and shavings of rubber. The mass of exposed, and therefore oxidizable steel wire, was estimated by soaking two batches (approximately 4.5 kilograms of TDA) in a 31.45% hydrochloric acid (non-laboratory grade) solution. The batches were soaked until no

visible steel wire remained (approximately two weeks). To account for the change in mass of the rubber alone, pieces with no exposed wire were also soaked in an acid bath. Prior to each experiment, TDA was rinsed with water, dried in a 105 °C oven, desiccated and weighed. After the acid baths, the TDA was soaked in water for several days, dried in the oven, desiccated and weighed. In addition to the acid bath, representative pieces of TDA were sent to the laboratory for determine the elemental content of both the steel wire and rubber.

### **Field Experiment**

To compliment the laboratory experiment, a field experiment investigating the use of TDA in a stormwater treatment setting was performed. The experiment took place in Arcata, California (Figure 10), which is characterized by moderate temperature, frequent periods of rain in the late fall and winter, and dry conditions from May to October. The site is a street rain garden located in the downtown area (Figure 11). The rain garden receives stormwater runoff from half of the crowned street and has an approximate drainage area of 4,300 square feet.





Figure 10. Location of field experiment (image adapted from ESRI, Inc.)

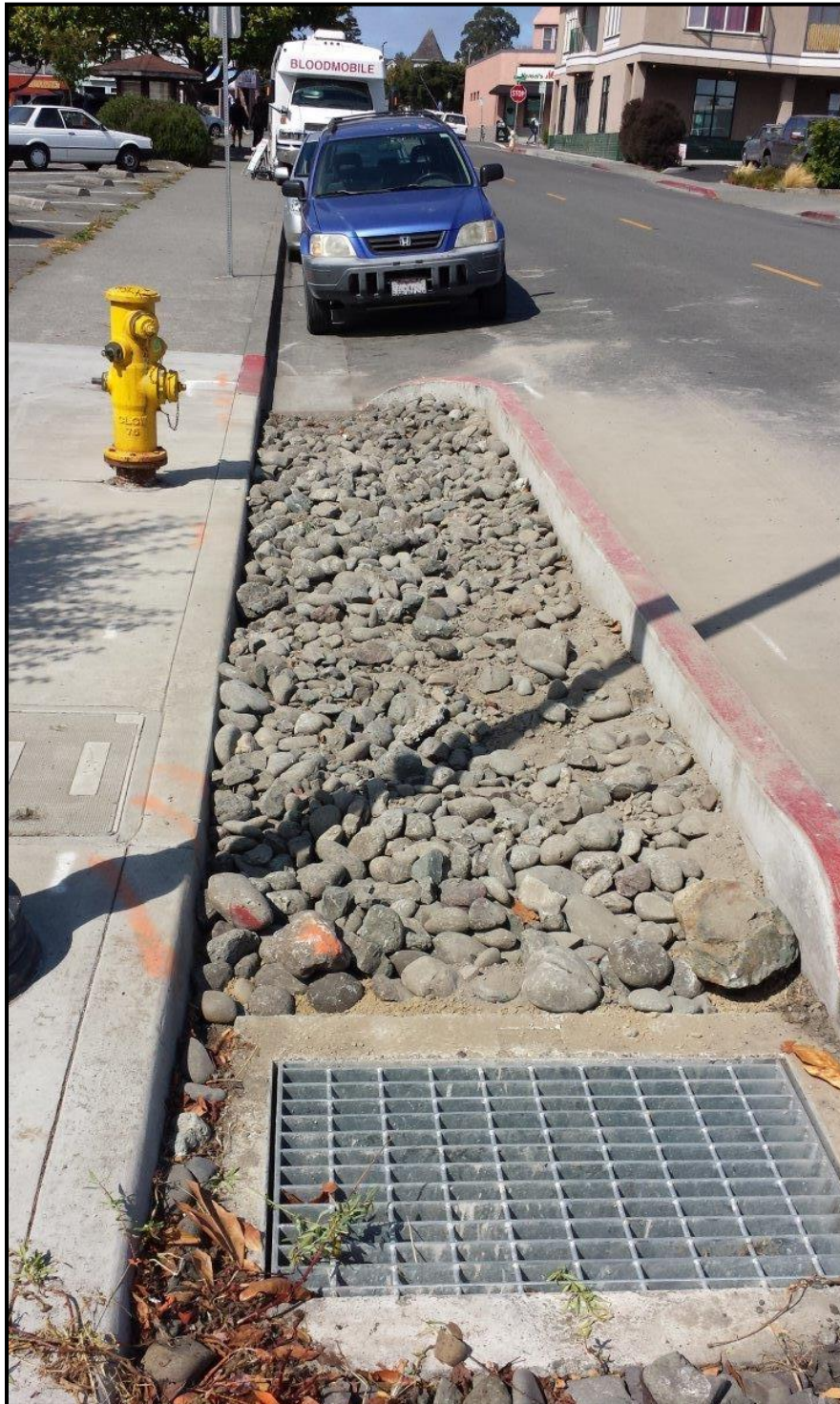


Figure 11. Street rain garden in which TDA was placed.



Stormwater runoff flows from the street gutter, underneath cobble placed on an impermeable liner, and then infiltrates the TDA fill (Figure 12 and Figure 13). Runoff is first collected in the gutter at the opening of the rain garden ('gutter'), after which it flows through the rock-covered surface and collects in a half round piece of four-inch PVC pipe ('pre-TDA') that spans the width of the street rain garden. The runoff then spills over the lip of the horizontal PVC pipe section and into the TDA fill. The post TDA water samples are collected using two different collection devices. A lysimeter and pan are located approximately two feet below the TDA fill. The lysimeter is a soil moisture extraction system that consists of four porous polyethylene nylon membrane covered ceramic caps with tubing connected to sampling bottles, located near the ground surface (Figure 14). The pan, is a five-gallon bucket with a permeable mesh lid and two tubes, one supplying vent air and one for extracting the water sample, that extend from the bucket to the ground surface (Figure 14). Two collection systems below the TDA fill were installed to provide redundancy in case of a failure of one of the systems and to minimize the chance of collecting an insufficient volume of water during a storm event. Although the lysimeter is more likely to provide representative samples of stormwater, there were concerns that the system would not collect enough water to test for all of the constituents. A monitoring port upstream of the TDA fill is used to retrieve undisturbed groundwater samples that are not under the influence of the stormwater passing through the TDA.

Prior to each rain event, the lysimeter collection bottles and the pan were emptied (i.e., pumped) to minimize potential groundwater dilution. To facilitate the extraction of

water from the pore spaces of the soil, a vacuum ranging from 40 – 50 kPa was applied to the lysimeter system. During a rain event, gutter and pre-TDA samples were collected using a hand pump. Pan and lysimeter samples were typically collected at the same time as the gutter and pre-TDA samples, but because of the time required for the runoff to collect in the sampling points below the TDA, these samples were occasionally collected up to 12 hours later than the surface samples. The up-gradient groundwater monitoring port was sampled for the last three storm events. Two pressure transducers were used onsite in perforated PVC pipes to determine the water levels in the TDA fill (Figure 14).

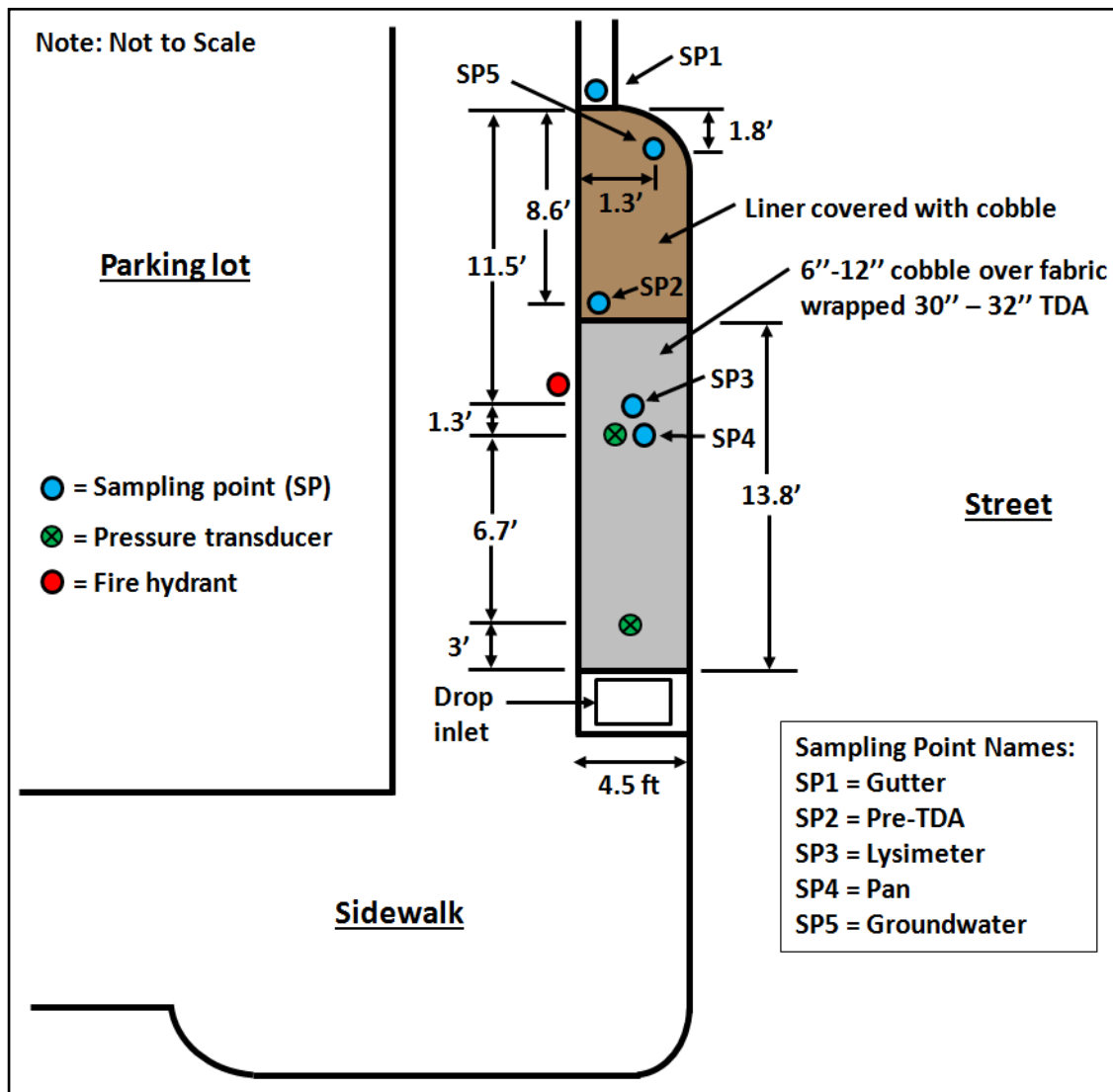


Figure 12. Schematic of field experiment (not to scale).

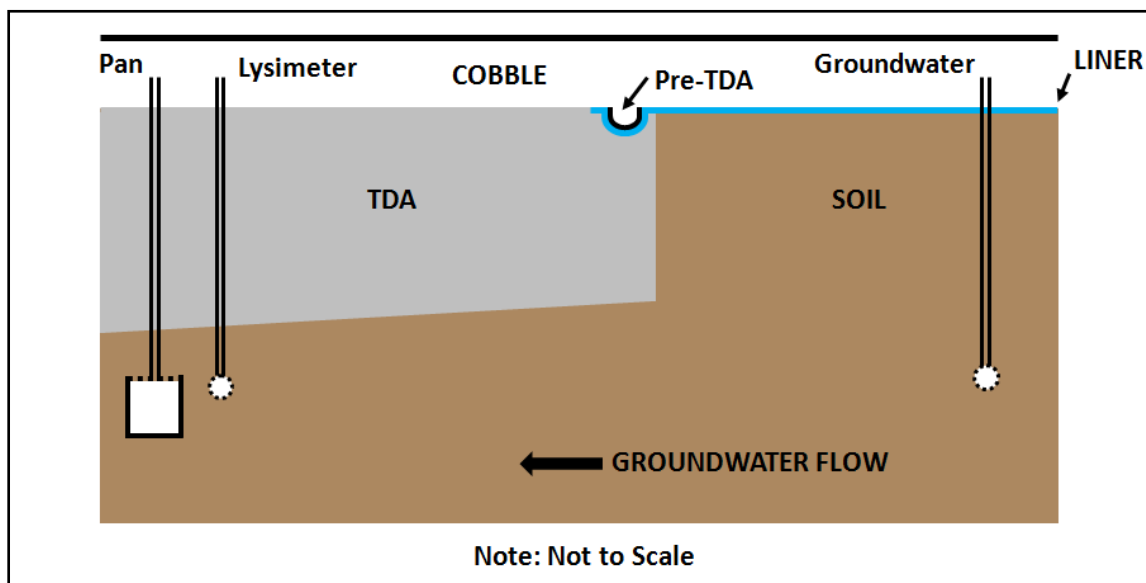


Figure 13. Cross-section schematic of field experiment. Liner is impermeable.

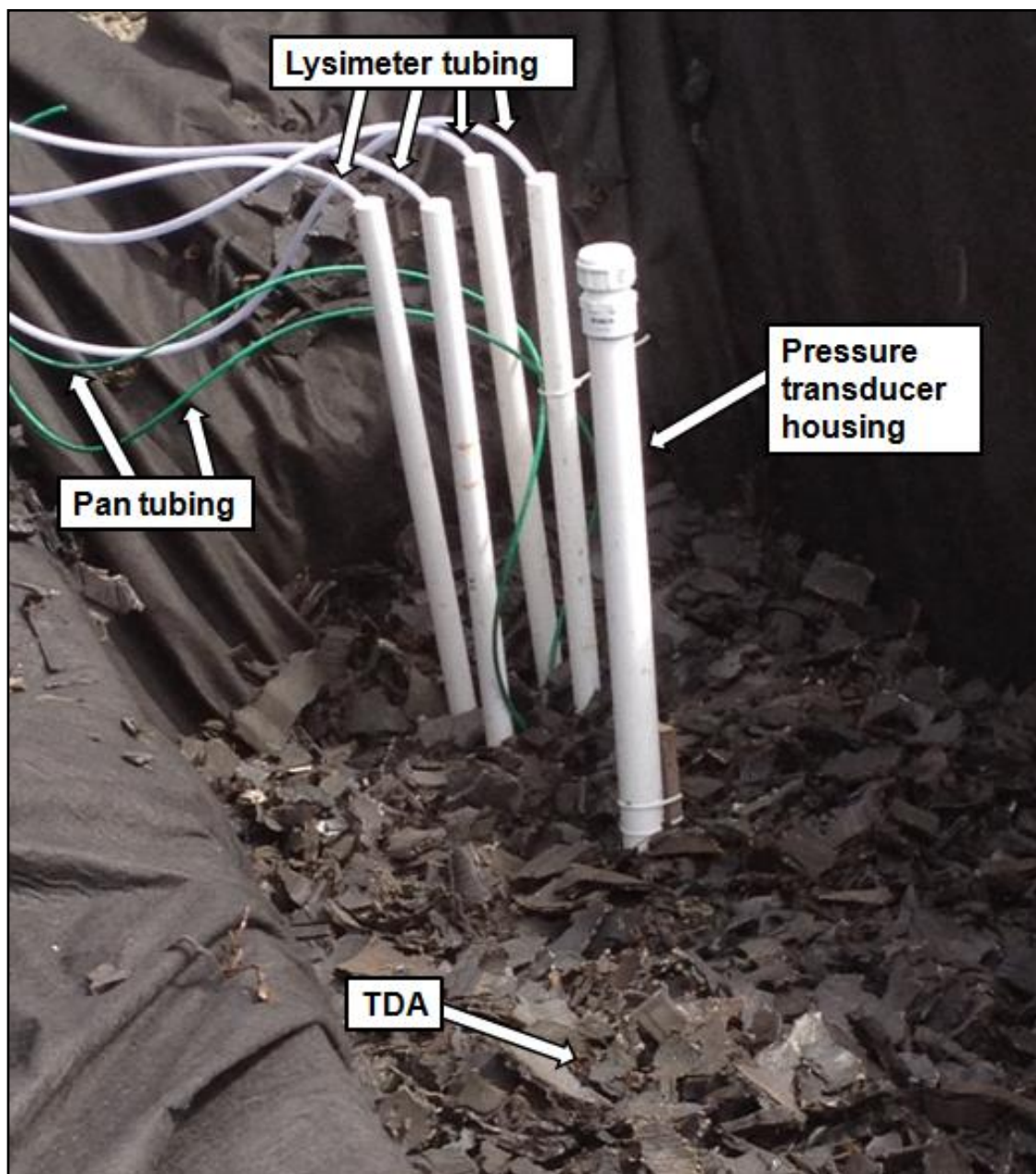


Figure 14. Sample collection tubing for the lysimeter and pan.

## RESULTS

The results of this study are divided into those of the laboratory experiment and those of the field experiment. Information and considerations pertaining to both portions of the study are addressed here. Details specific to each experiment are outlined in the following sections.

All samples were analyzed by Alpha Laboratories in Ukiah, California. The laboratory provides detection and reporting limits for each test procedure (Appendix A). For the purposes of this report, all sample concentrations above the detection limit, which are reported at the 99% confidence limit, will be used. Detection limits change with laboratory sample dilutions, therefore the detection limits shown in the results for some constituents vary over the course of the experiment. Concentrations below the detection limit will be shown on figures as a zero. Considerations for both the laboratory and field portions of this study:

- Figures may have one or more data points with a value of zero during a sampling event and they might not all be visible. If a data point is not visible, then the value is likely zero. All instances in which a data point is missing will be mentioned in text.
- Several graphs include a logarithmically-scaled vertical axis. Nondetects, depicted as zeroes, do not appear on a logarithmic scale. Instances in which nondetects do not appear on graphs will be mentioned in text.

- Detection limits are indicated on graphs only when some results were below the limit. The detection limit is not included in the graph in instances in which the concentration in all collected samples was greater than the limit.
- Hold times were exceeded periodically for nitrate and consistently for pH. However, results showed no indication of significant effects.

### **Laboratory Results**

One of the objectives of the laboratory portion of the project was to determine the rate that potential water contaminants leach from TDA; therefore, the results are generally shown as mass of constituent leached into the surrounding water during the sample period per mass of TDA in the container. However, the concentrations of the constituents in the water may also be of some interest as it might be considered a “worst case” scenario of a setting where the water saturating a TDA fill is suddenly released into a receiving environment. The volume of water used in the containers varied somewhat from container to container and from one sample period to the next. Typical water volumes used in the containers varied between 36 and 42 liters but ranged from as low as 30 up to 60 liters (Appendix B). This resulted in a solid to liquid ratio (kg of TDA per liter of water) of approximately 1:5, within the range of the investigated batch studies (Table 10). Because water volumes across containers are often slightly different, comparison of concentrations across containers and operating conditions must be done with caution. However, it is useful to compare the concentrations of the constituents observed under these “worst-case” conditions compared to the various regulatory

standards. In addition, the magnitude of the concentration compared to detection limits and regulatory standards provides a way to characterize the potential for a constituent leaching from TDA to be a water quality concern.

Other considerations for interpreting results:

- Several graphs include lines between data points. These lines are not included to imply a change in concentration or mass over time, but serve as an aid to ease the identification of a common series of values.
- When data is presented to evaluate differences in operating conditions, the shown naming convention (Table 26) will be used.
- Mass results are reported as either the “specific loss rate”, defined here as the constituent mass divided by the mass of the TDA in the container and length of the leaching (sample) period (mg/kg/day or ug/kg/day), or the “cumulative specific loss”, defined as the accumulated mass leached over the entire experimental period per mass of TDA in the container (mg/kg or ug/kg).
- The reported mass of a constituent is the mass found in the water at the end of the sample period, and is corrected to account for the mass introduced by the source water.
- Concentration results do not account for the variation in time between sampling events.
- All averages are computed as arithmetic means.



- Source water concentrations are included on plots only when a constituent is suspected to originate from the source water.
- The regulatory standards used for comparison to concentrations of TDA leachate serve only as a point of reference for these worst-case scenarios. The selected standards apply to drinking water and are not necessarily representative of appropriate regulatory frameworks for typical TDA applications.
- Bar graphs are used for several constituents to aid in identifying that a constituent originates in the source water.

Table 26. Naming convention based on operating condition.

Operating Condition Description	Name	Containers
Always wet	Always	C1, C2
Alternating 1 day wet, 1 day dry for 6 days followed by 1/2 day wet, 1/2 day dry for 7th day	1 day	C3, C4
Alternating 3.5 days wet, 3.5 days dry	3.5 days	C5, C6
Alternating 1 week wet, 1 week dry	7 days	C7, C8
Alternating 1 day wet, 1 day dry for 6 days followed by 1/2 day wet, 1/2 day dry for 7th day for 6 months followed by 6 months of dry, followed by initial cycle for 3 more months	1 day*	C9, C10

(\*) = these results will only be included in the '1 day' results for the first 6 months. These containers will be evaluated separately when the effects of seasonality (i.e., an extended dry period) are being analyzed.

### TDA Metals Content Analysis

Results from the metal analysis of the TDA steel wire verified that the primary metal is iron (Table 27). Note that the laboratory reported a unit mass 1.1 kg of iron/kg of wire, which is impossible, but indicates that the wire is essentially all iron, with just trace amounts of other elements. There is nearly 200 times more iron than manganese, and

nearly 2,000 times more iron than zinc in the wire. The primary metal in the rubber is zinc, followed by iron. The cadmium content of both the wire and the rubber is negligible compared to the other metals examined.

Results from the TDA acid bath experiment suggest that approximately 2.1% (by weight) of a Type A TDA batch is exposed (oxidizable) steel. Documentation of the TDA mass before and after the steel was oxidized can be found in Appendix C. Assuming that 2.1% of the TDA mass is exposed wire, based on the results in Table 27, there is approximately 21,000 mg of exposed iron per kg of TDA used in this experiment. While there is a substantial amount of zinc in the rubber component of the TDA, the reported value of 14,000 mg/kg was found after acid digestion of slivers of rubber. Most of the zinc will likely not leach out in a water environment, and it is likely that the leachable zinc is a very small fraction of the reported composition value.

Table 27. Component metal content of TDA wire and rubber after acid digestion.

<b>Metal</b>	<b>Steel Wire (mg/kg)</b>	<b>Rubber (mg/kg)</b>
Cadmium	0.490	0.0710
Iron	1,100,000	290
Manganese	5,400	3.7
Zinc	510	14,000

#### Variation within Containers

Two setups for each operating condition were assembled to account for variation introduced by factors such as random error, measurement error during sampling or laboratory analysis, and differences in TDA pieces. Variation was observed in setups that operated under the same operating condition, as illustrated by the iron mass loss rate of

four containers that alternated one day wet and one day dry for the first 26 weeks of the experiment (Figure 15).

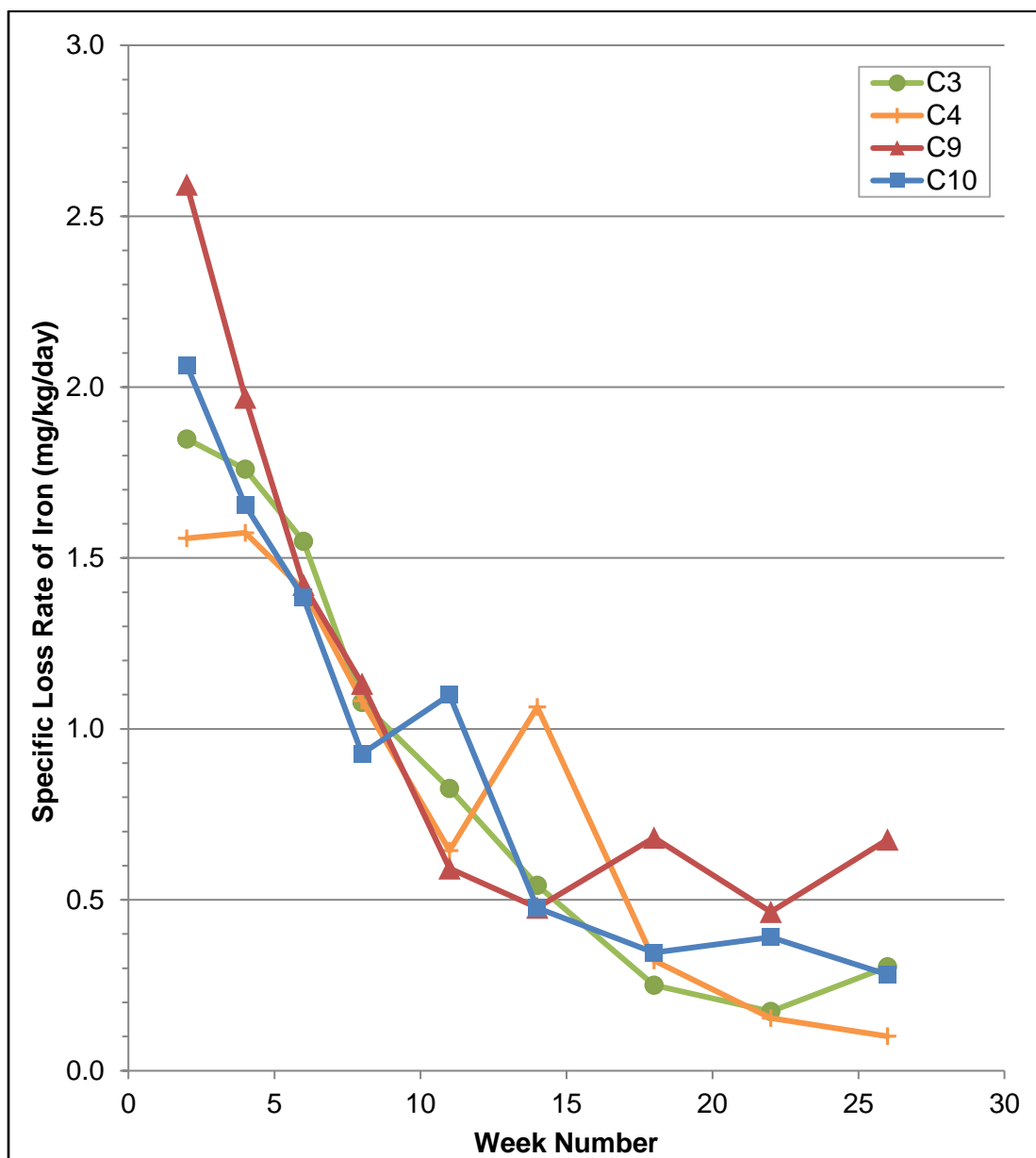


Figure 15. Variation in specific loss rate of iron for containers operating under the same condition.

### Tubing

The inside wall surface area of the recirculation tubing available for accumulation of leached constituents was initially assumed to be insignificant. However, as the experiment progressed, the accumulation of mass in the tubing appeared to be appreciable and was included in the analysis. Starting with the Week 34 sample, the inside of the tubing was scrubbed and the accumulated material mixed with the other leachate. To account for the mass accumulation in the tubing during the previous sample periods, independent containers were assembled to mimic the always wet condition. All original sampling procedures (e.g., water replacement schedule) were applied to the containers and a minimum of one container was sampled at a week corresponding with the original sampling intervals. The interior of the tubing was 'scrubbed' with a brush to remove the matter attached inside. For Week 34, each container was sampled twice, 'pre-scrub' and 'post-scrub', to determine the accumulation in the tubing.

These samples were initially analyzed for all constituents. After several sample periods, results indicated that the only detectable constituents that were accumulating in the tubing were iron, manganese, and zinc, so adjustments to the samples collected prior to Week 34 were only required for those constituents. The mass accumulation in the tubing for each week corresponding with the original sampling collection schedule was plotted. In instances where the pre-scrub concentration was greater than the post-scrub concentration due to sampling variation and analytical laboratory errors, data are included as zeroes. Trend lines were fit to the iron and manganese plots (Figure 16 and Figure 17, respectively) and the equations were used to adjust the mass observed in the original

always wet containers. Unlike the trend observed for iron and manganese, there did not appear to be evidence of an increasing accumulation of zinc in the tubing over time (Figure 18). A conservative assumption of a total of 4.0 milligrams of zinc accumulation inside the tubing was made. This mass was added only to the first sampling collection since the data does not suggest an increase in mass over time.

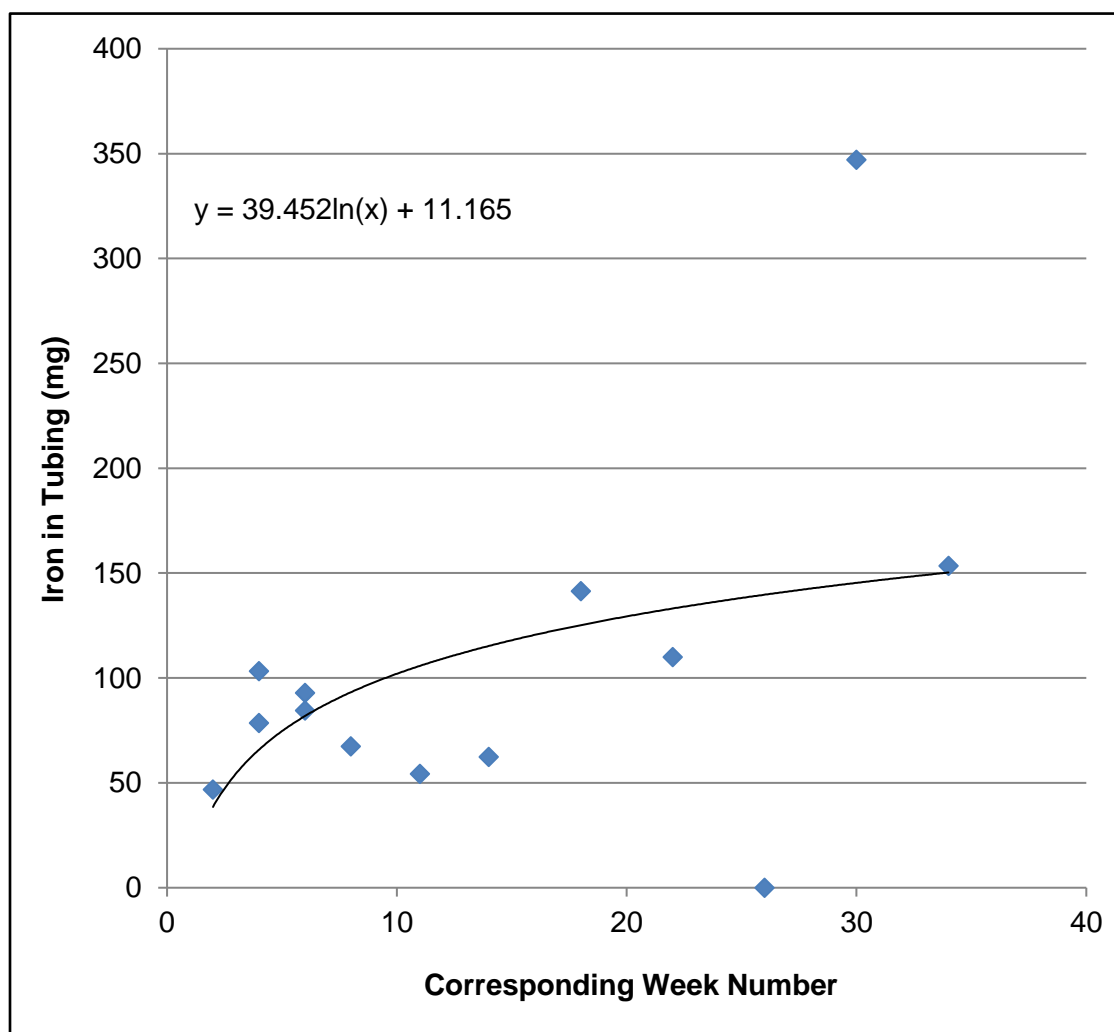


Figure 16. Iron mass accumulation in the tubing over time with a logarithmic trend line fit to data.

Adjustments to the mass of iron, manganese, and zinc for samples collected prior to Week 34 were also made to the other operating condition containers. These adjustments were made by scaling the adjustment made to the always wet containers based on the ratio of the uncorrected constituent concentration and that of the always wet containers. Once the mass values were adjusted, concentrations were back-calculated using each container's water volume. All iron, manganese, and zinc results presented from herein reflect these adjusted values, but the original, uncorrected data can be found in Appendix D.

The operating conditions of the tubing accumulation analysis are the same as that of the always wet operating condition and therefore can provide additional data for this condition. The 'post-scrub' results ('CT') during the 30-week tubing analysis show similar behavior to that of one of the always wet containers, as indicated by the iron specific loss rate results (Figure 19). These 'post-scrub' results will be included as an additional data point for the first 30 weeks of the experiment for iron, manganese, and zinc in the 'Always' results.

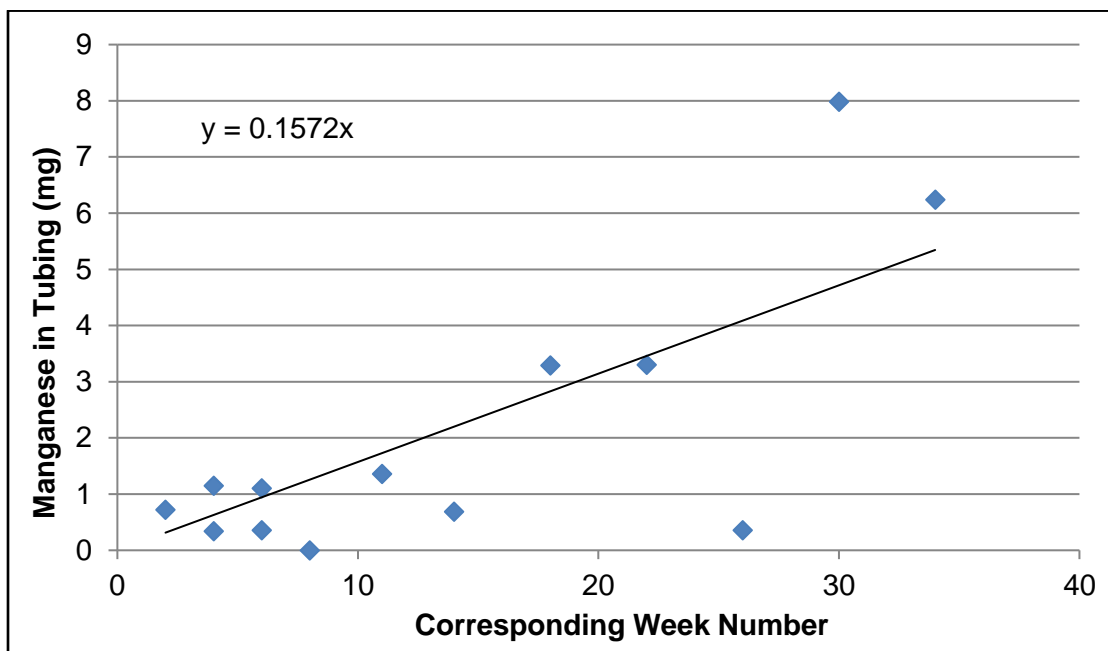


Figure 17. Manganese mass accumulation in the tubing over time with a linear trend line fit to data.

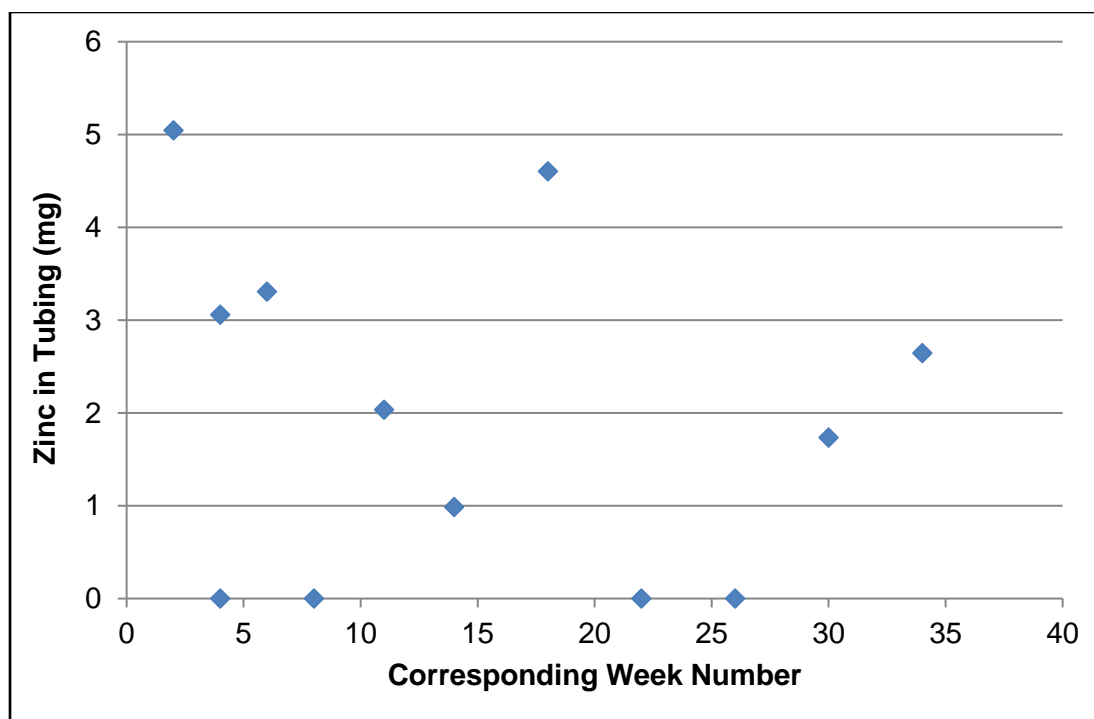


Figure 18. Zinc mass accumulation over time.

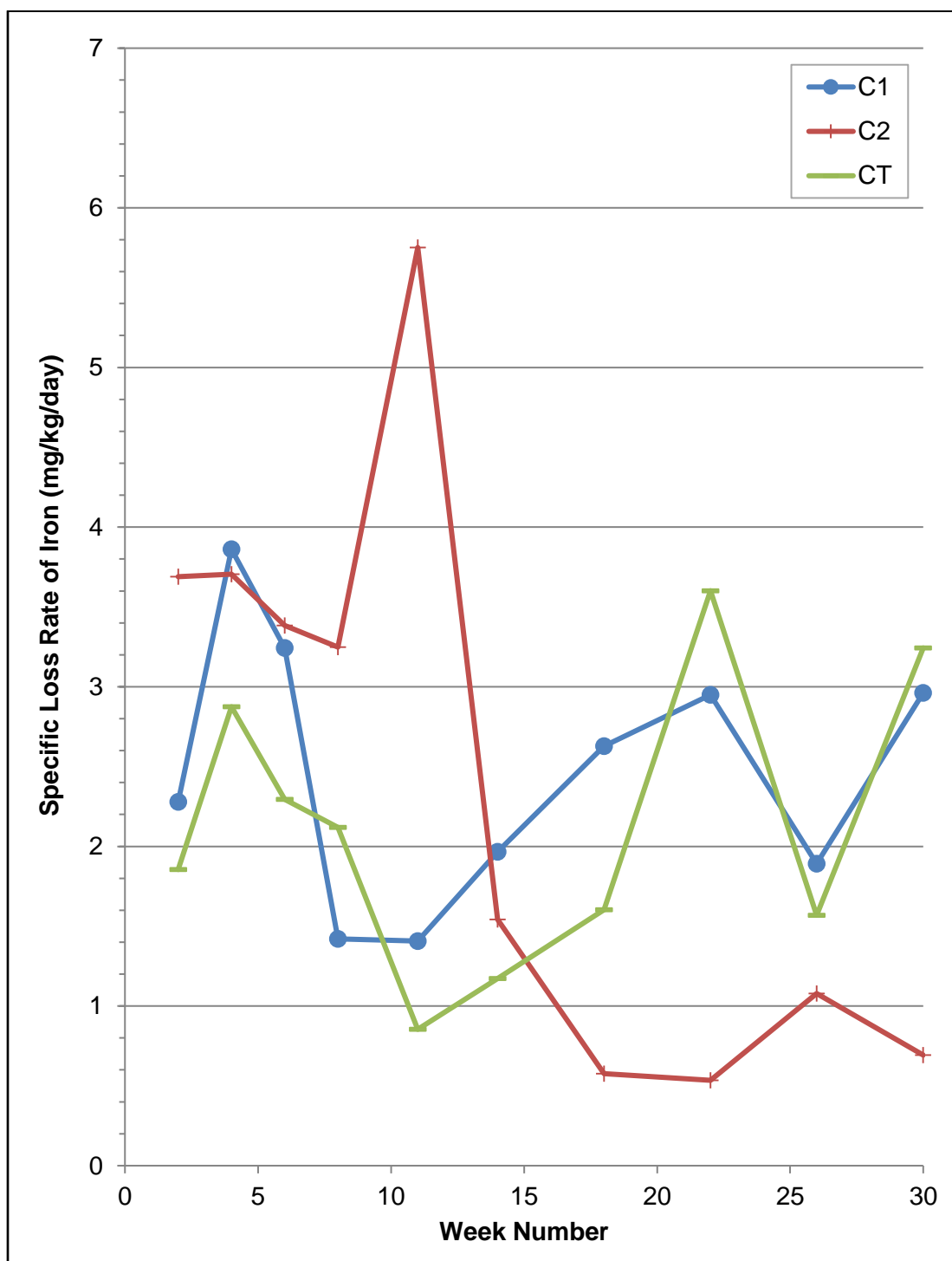


Figure 19. Iron comparison of always wet and post-scrub tubing results for the first 30 weeks.



## Metals

The source water collected for the Week 14 samples inadvertently was not analyzed for metals. For the purposes of this report, Week 14 source water metals concentrations were assumed to be the average concentration found in the source water over the entire study.

Of the five metals analyzed, lead and cadmium were detected at low concentrations relative to selected regulatory standards. Neither constituent exceeded their respective California Maximum Contaminant Level (CA MCL) for any sample. Although lead was detected in the containers, it was also detected in the source water at similar concentrations (Figure 20). All samples were above the laboratory's detection limit, which varied from 0.00002 mg/L to 0.00008 mg/L. There was little evidence that the observed concentrations of lead were related to the operating conditions, so points reported in Figure 20 are not distinguishable by condition. Each data point is an average of the two containers of the same operating condition. The TDA may have contributed slightly to lead concentrations, but less than a third of all samples had concentrations higher than that of the source water, with the majority of these instances occurring in the first half of the 15-month experiment. These results suggest that water quality impairment by lead from TDA leachate is unlikely.

Results for cadmium suggest that the compound is released at low levels (Figure 21). The concentration in individual containers is shown rather than averaging over a pair of identically operated containers to allow results that were below the detection limit to appear. With the exception of a single anomalous result (0.0018 mg/L in C8, Week 34),

the maximum concentration was detected during Week 2 in C2 (an always wet container) at 0.00016 mg/L, well below the CA MCL of 0.005 mg/L. Cadmium was not detected in the source water during the 15-month experiment.

The detection limit of cadmium increased fourfold for most containers during Week 4 and for all weeks after Week 14, due to dilutions performed in the analysis by the laboratory. For Week 4, Week 18 and Week 26, C1 was not diluted and therefore had a lower detection limit than the rest of the containers. These instances are the three points shown below the detection limit in Figure 21. Because the detection limit increased to a level above the concentrations of previous samples, a decrease in cadmium concentration after Week 14 cannot be verified. However, the increased detection limit is more than an order of magnitude less than the CA MCL. These results suggest that cadmium leaching from the use of TDA below the groundwater table does not pose a threat to groundwater quality. This finding is supported by previous literature in which cadmium was below the detection limit in both field (Aydilek et al., 2006; Burnell and McOmber, 1997; Edstrom et al., 2008; Humphrey and Katz, 2001) and laboratory (Downs et al., 1996; Selbes, 2009; TCTC, 1990) studies.

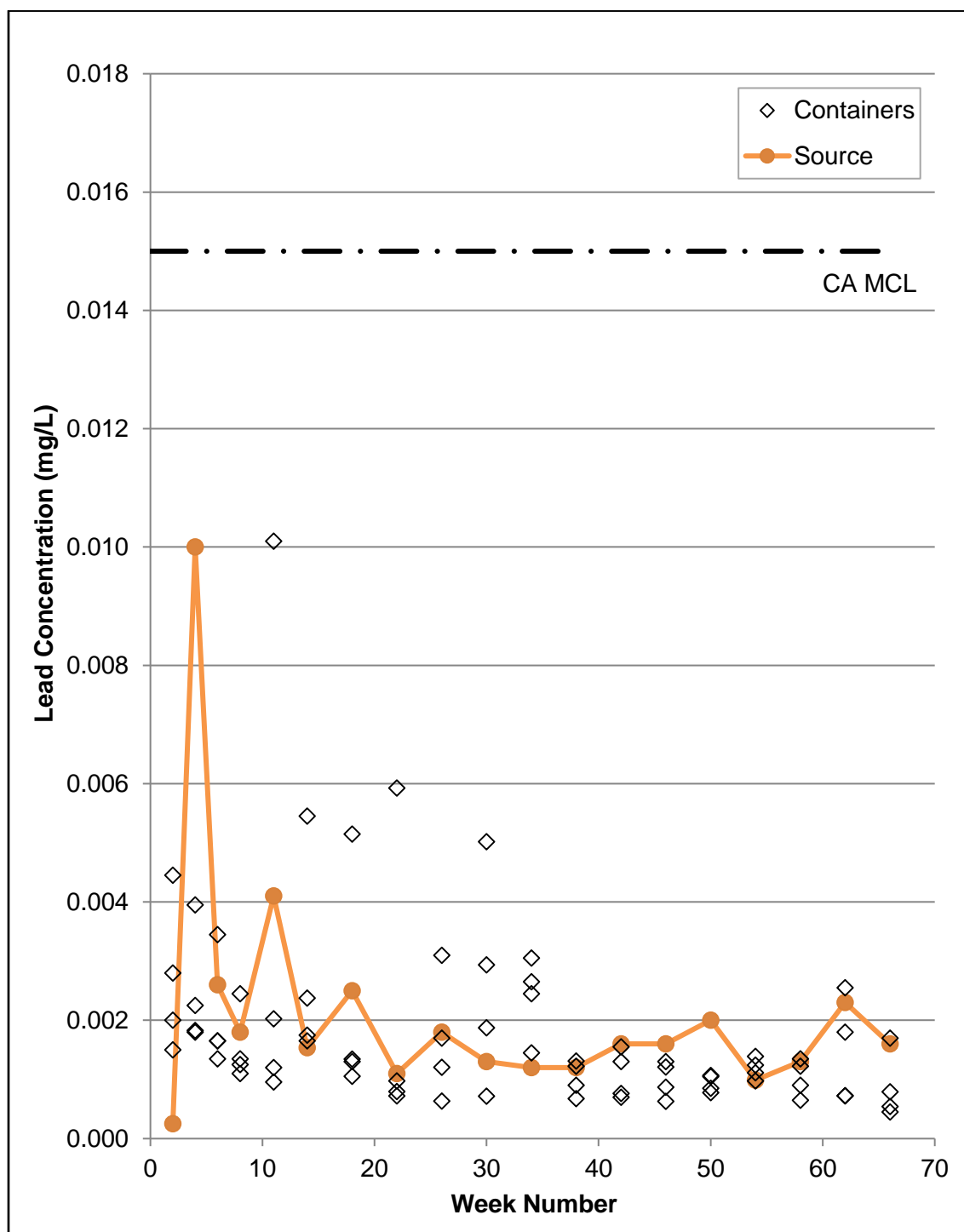


Figure 20. Average lead concentration of paired containers compared to the source water and CA MCL.

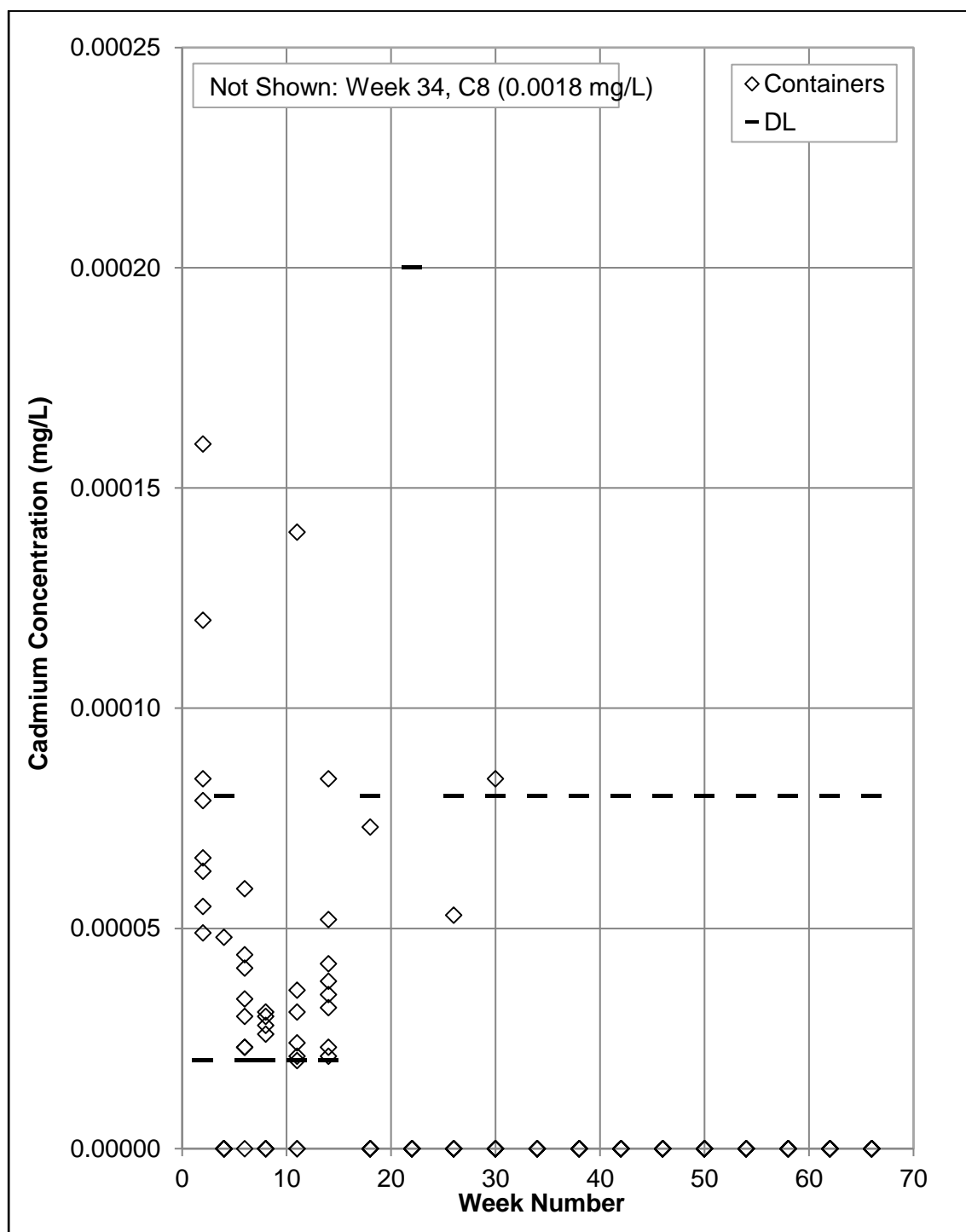


Figure 21. Cadmium concentration in each container with indicated detection limit for each week (varied between 0.00002 mg/L and 0.00008 mg/L). California MCL (not shown) is 0.005 mg/L.

The concentration of zinc was above the detection limit of 0.0005 mg/L in all but a single sample, but typically at least an order of magnitude less than the Secondary MCL of 5 mg/L (Figure 22). With the exception of the always wet containers, the mass of zinc released from the TDA appears to decrease exponentially from the start of the experiment (Figure 23). The leachate from the always wet containers had a higher zinc mass loss rate than the remaining operating conditions for the first half of the study, after which the rate of mass loss of zinc from the TDA slows considerably (Figure 23). The decrease in zinc concentrations observed in previous experiments supports the trend observed in this study (e.g., Brophy and Graney, 2004; Humphrey and Katz, 2001; Miller and Chadik, 1993; Selbes, 2009).

The cumulative mass over time indicates that all operating conditions show an initial period of high loss rate, followed by a slowly decreasing rate (Figure 24). In all but the always wet condition, the mass loss rate is high for the first 12 to 16 weeks of operation, and then quickly settles into a much slower, nearly constant rate for the last 30 weeks of the experiment. While there are initial differences between the loss rates among the three non-always wet conditions, after Week 20, their behavior is nearly identical as indicated by the nearly identical slope of the cumulative mass rate loss curves (Figure 24). In the always wet case, the period of high loss rate continues until Week 30, and then resembles the other operating conditions for the remainder of the experiment.

These results suggest that the highest rate of zinc loss will occur under conditions of a TDA fill below the water table. Loss rates of zinc are relatively high for the first few months of exposure to water, and then slow considerably after that. At the end of the

experiment, the TDA in the always wet containers had lost 1.7 times as much zinc as the TDA in the average of other containers.

The initial zinc loss may be from the rubber itself, rather than the wire. Zinc concentrations of a batch study with crumb rubber were at least an order of magnitude greater than those of tire chips over the course of 28 days (Selbes, 2009), which suggests the rubber is the primary source of zinc. This was further supported by the metal content results observed in this study (Table 27). An initial pulse of elevated levels of zinc followed by steady, decreased levels was reported in a crumb rubber study (Rhodes et al., 2012).

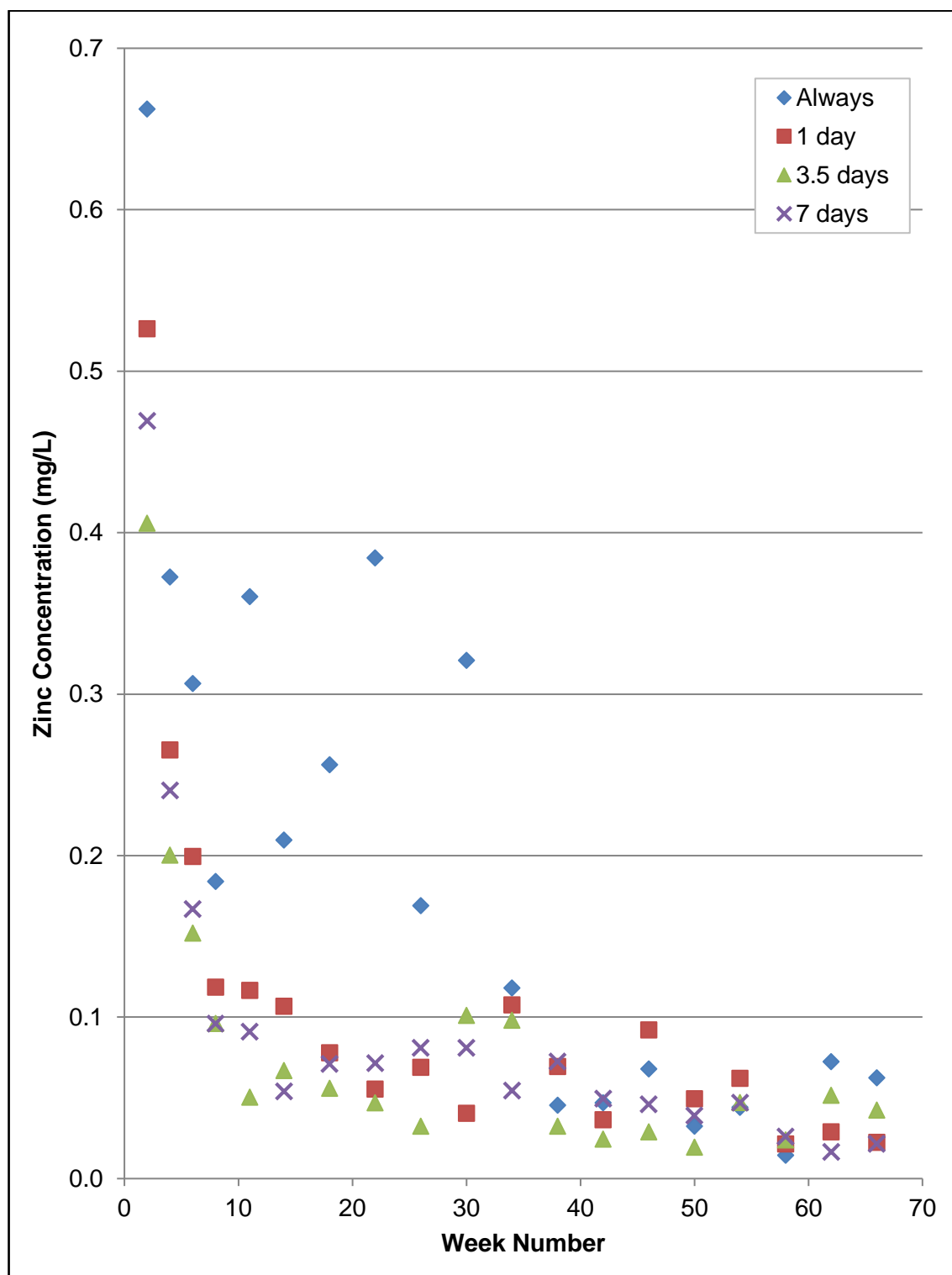


Figure 22. Zinc concentrations are always below the Secondary MCL of 5 mg/L.

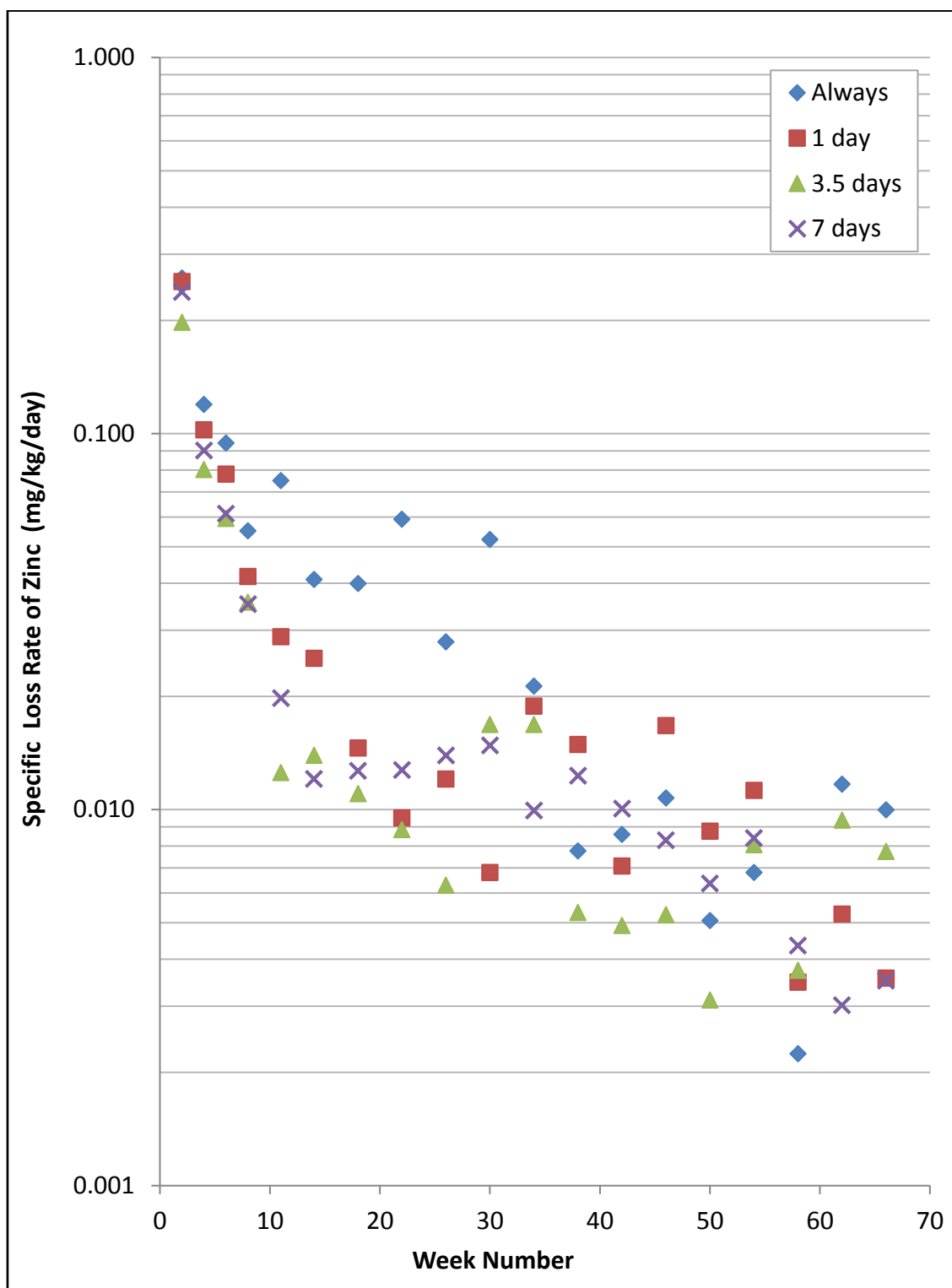


Figure 23. Zinc specific loss rate over time. (Note: logarithmic vertical scale).



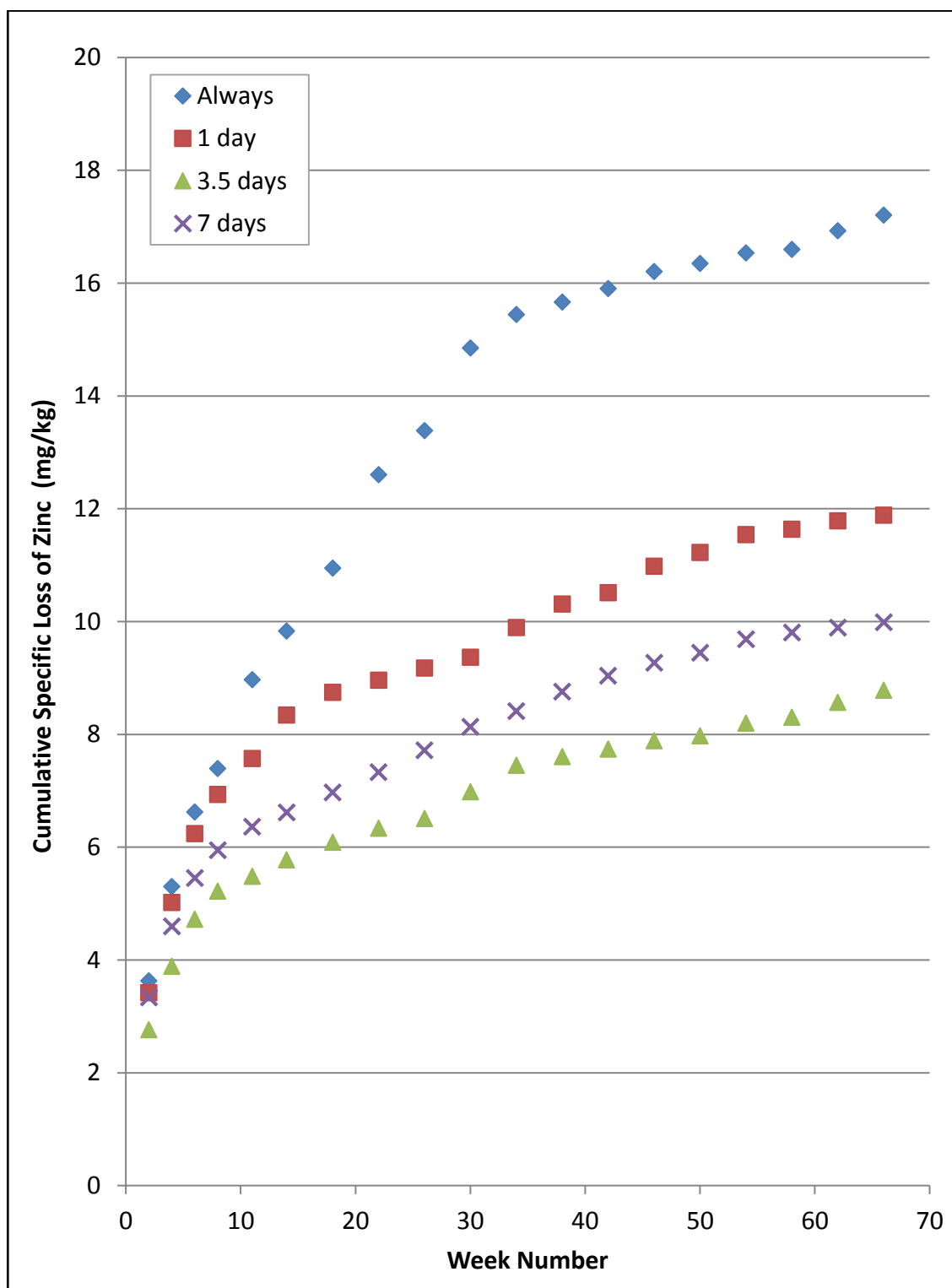


Figure 24. Zinc cumulative specific loss over time.

The concentrations of manganese and iron in the containers were frequently above their respective Secondary MCLs. Manganese concentration was above the 0.0004 mg/L detection limit for all of the operating conditions used in the experiment (Figure 25). Approximately 68% of the observed concentrations were above the Secondary MCL of 0.05 mg/L. The highest concentrations were typically observed in the always wet containers (“Always”). The higher concentration of manganese in the always wet containers compared to the remaining containers (“Others”) is not due only to the lower water volume in those containers since the rate loss is also higher in the always wet containers (Figure 26).

The cumulative mass leached from the TDA in the always wet containers confirms that the rate of mass loss decreases for all containers after Week 12, but the reduction is not nearly as dramatic as it is for the remaining containers (Figure 27). With the exception of the always wet condition, the rate of manganese released appears to be approaching zero by the end of the experiment. At the end of the experiment, the TDA in always wet containers had lost 1.6 times more manganese than the TDA in the average of the other containers.

As was observed with zinc, the rate of manganese lost from the TDA is highest during the first 12 weeks. After 12 weeks, the rate slows considerably and is a relatively constant value after Week 32 in the non-always wet containers. In addition, these same containers behave similarly over the entire sampling period. The rate of mass loss in the always wet containers is also very similar for zinc and manganese. As indicated by the slope of the cumulative specific loss curve, zinc initially has a higher rate of loss

compared to manganese (Figure 28). However, beyond Week 34 the loss rate for each metal is nearly the same.

The results of this study are supported by previous literature. For example, Downs et al. (1996), Edstrom et al. (2008), Humphrey and Katz (2001) and Sheehan et al. (2006) found manganese in the leachate from TDA, but concentrations did not generally exceed the Secondary MCL. In addition, Humphrey and Katz (2001) indicated that manganese concentrations approached background concentrations by the end of their four-year study.

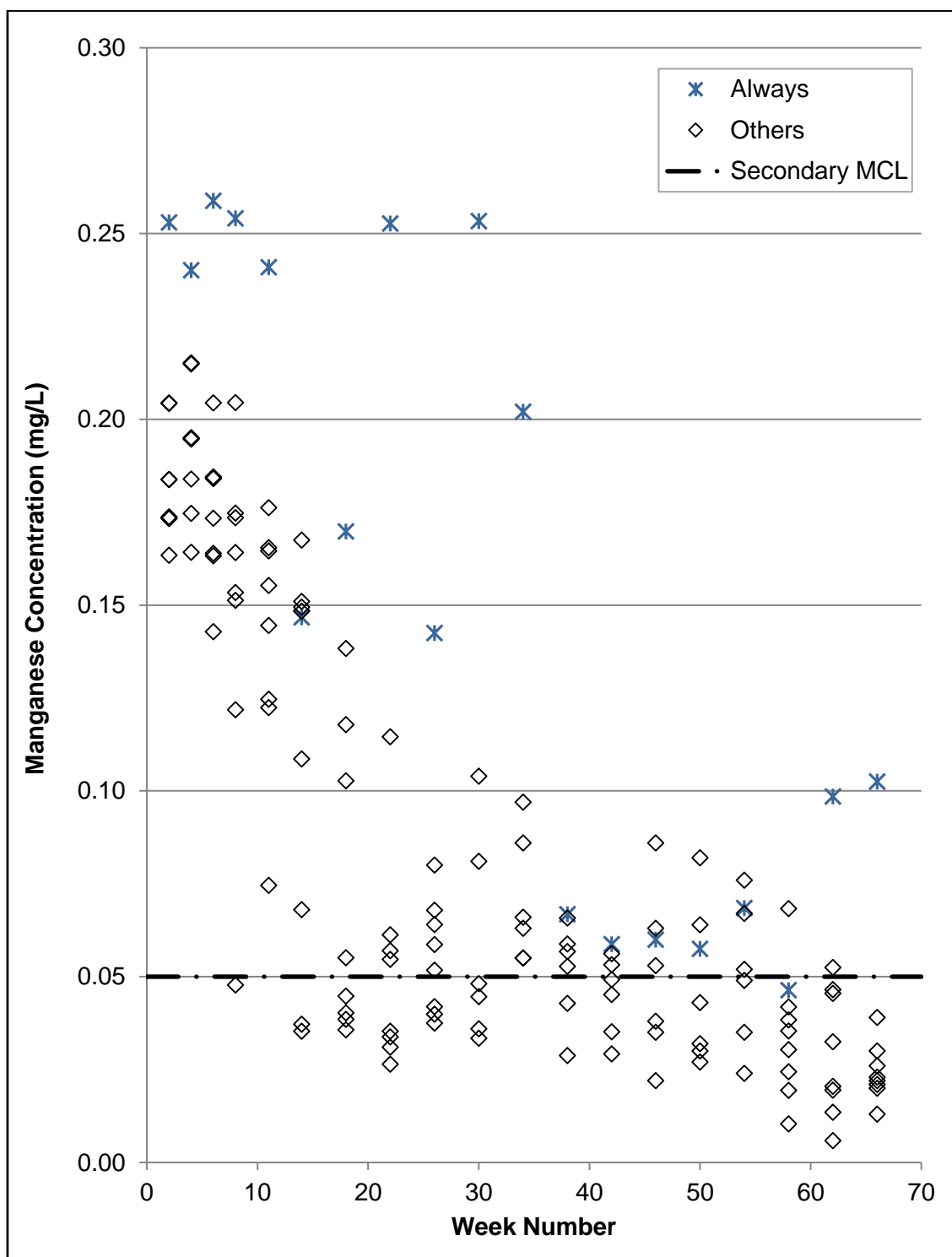


Figure 25. Manganese concentration declines over time, and always wet containers (“Always”) typically have the highest concentration.

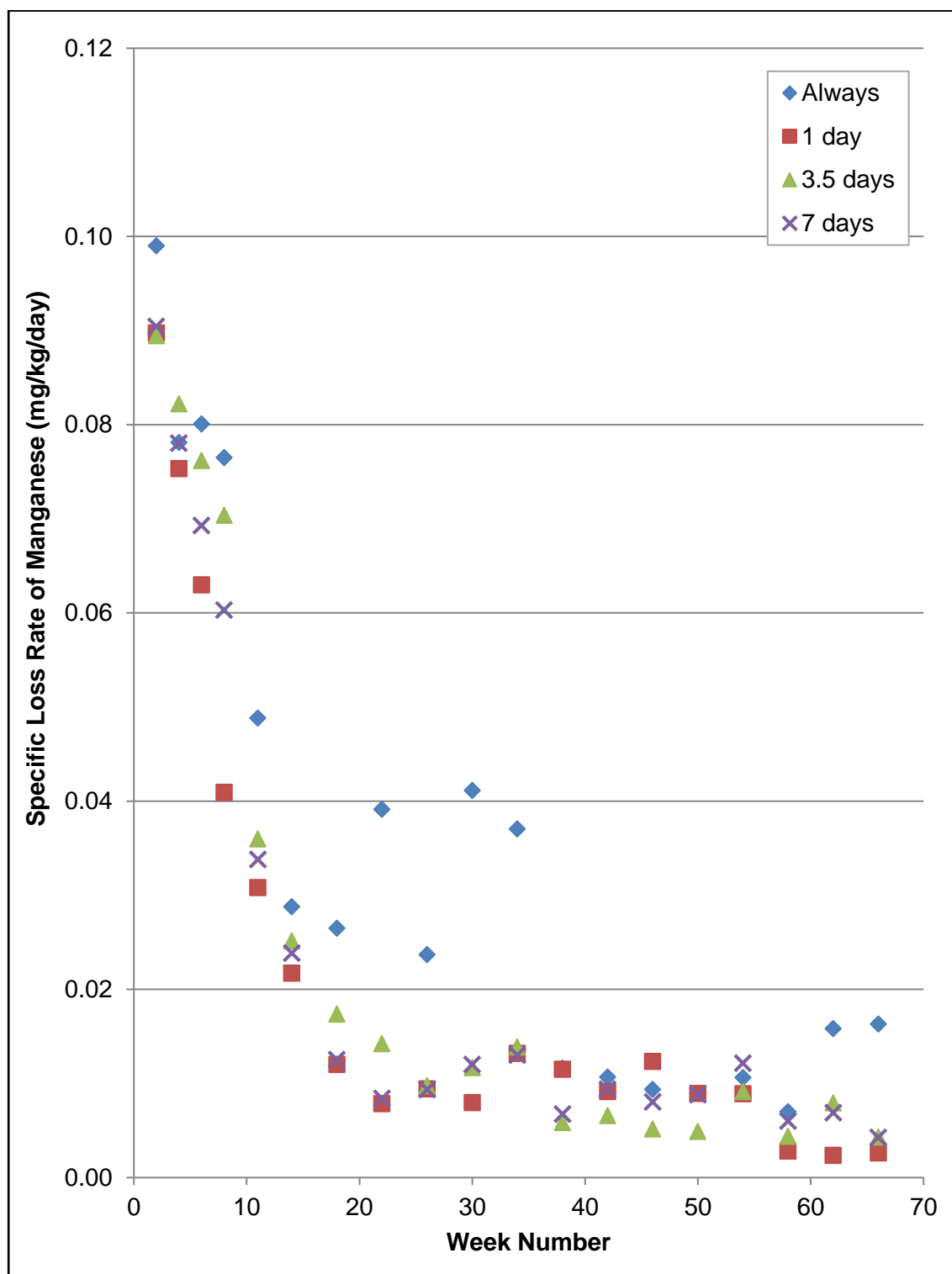


Figure 26. Manganese specific loss rate over time.

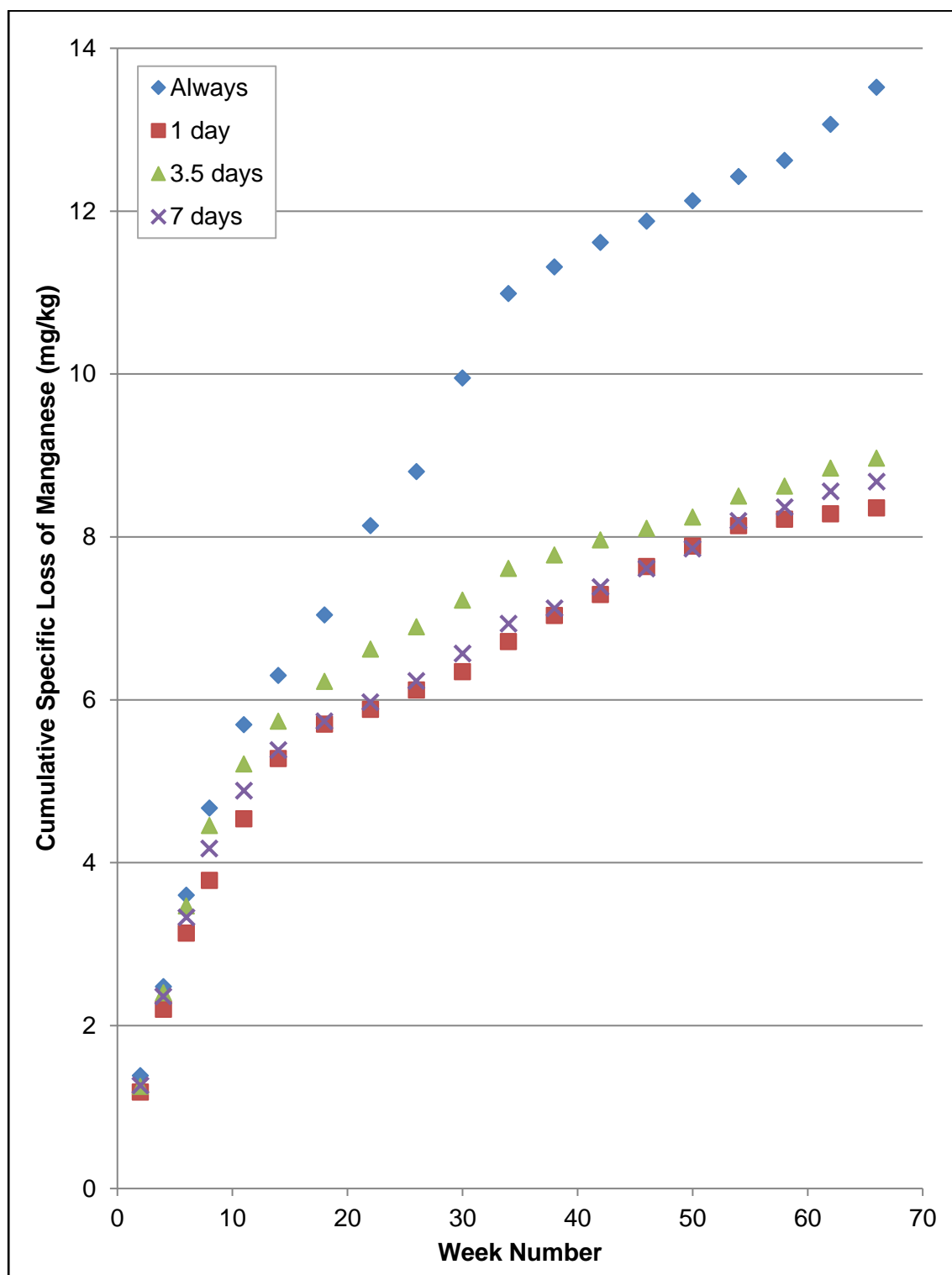


Figure 27. Manganese cumulative specific loss over time.

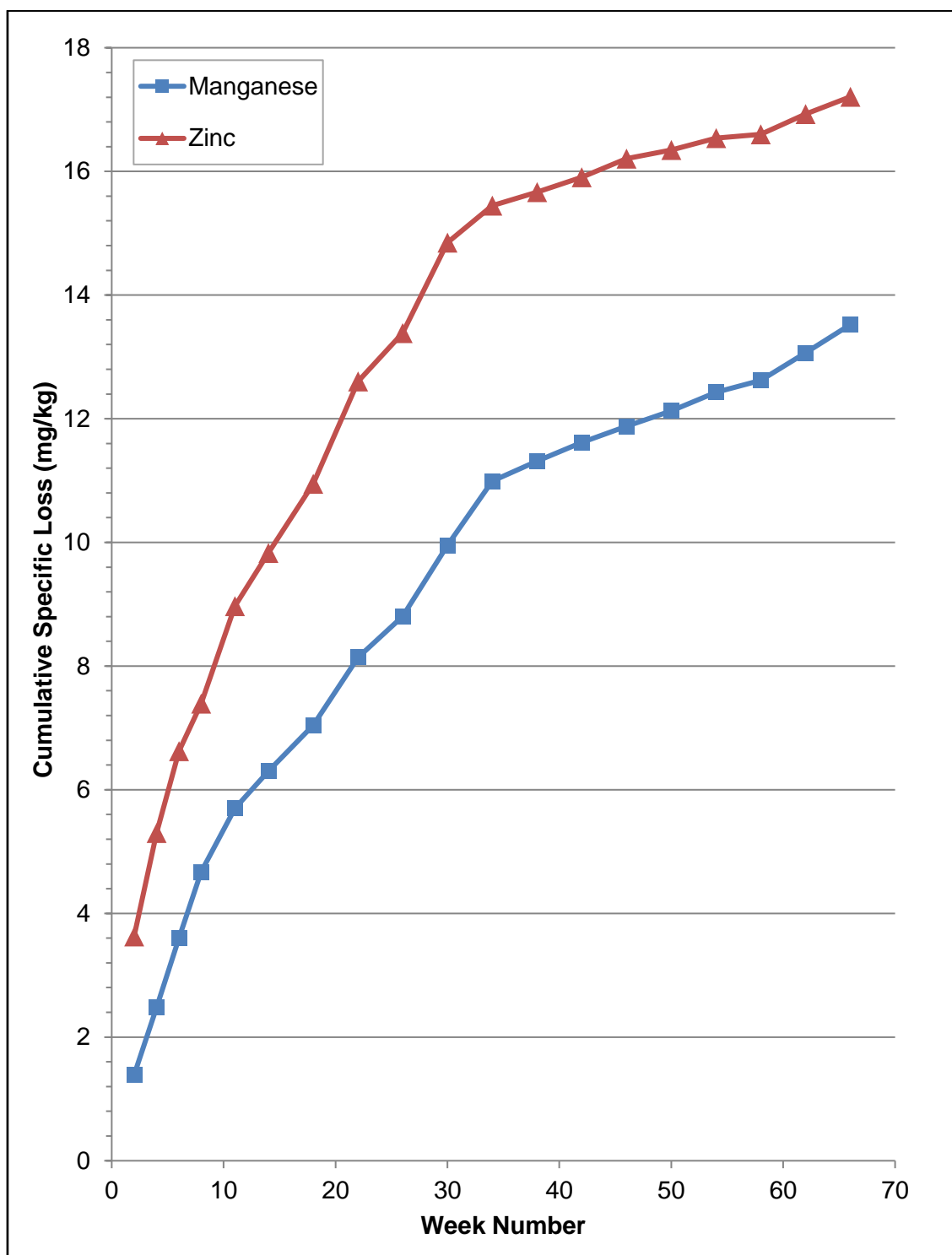


Figure 28. Comparison of cumulative specific loss of manganese and zinc for always wet containers.

Iron was detected in the containers for all sampling events and exceeded the Secondary MCL of 0.3 mg/L for 99% of the samples. The iron concentration was highest in the always wet containers for all weeks (Figure 29). Overall, the concentrations of iron in the containers decreased at each sampling date, and the two instances in which the iron concentration was below the Secondary MCL occurred in C3 and C10 at Week 62, right before the end of the experiment. A decrease in iron levels over time has been reported in the majority of previous literature (e.g., Miller and Chadik, 1993; Brophy and Graney, 2004). In all but the always wet containers, the rate of mass loss from the TDA resembled that of zinc and manganese, declining sharply after Week 12 (Figure 30 and Figure 31). The specific loss rate of iron did not significantly decline in the always wet containers until after Week 32. As a result, at the end of the experiment, the TDA in always wet containers had lost 2.6 times as much iron as the TDA in the average of the other containers. By comparison, the loss of zinc and manganese from the TDA in the always wet containers was only approximately 1.5 times higher than the loss in the other containers, suggesting the loss rate of iron is much more sensitive to periods of drying than for zinc and manganese.

As observed with the other metals, the non-always wet containers exhibited similar behavior over the entire experiment, and considerably different behavior than the always wet containers. This suggests that having a dry period of at least a day results in a much lower rate of metals loss from TDA, and that having a dry period is more important than the length of the dry period in determining the rate of metals' losses.



In general, iron, manganese and zinc demonstrated similar temporal variations, as illustrated by the always wet containers (Figure 32). With the exception of the relatively large initial zinc loss, the timing of the peak losses observed for the three metals was similar. This trend was also observed for the other operating conditions except for the 7 day condition, in which zinc and manganese losses were relatively constant with few peaks after the first sampling event (Figure 33).

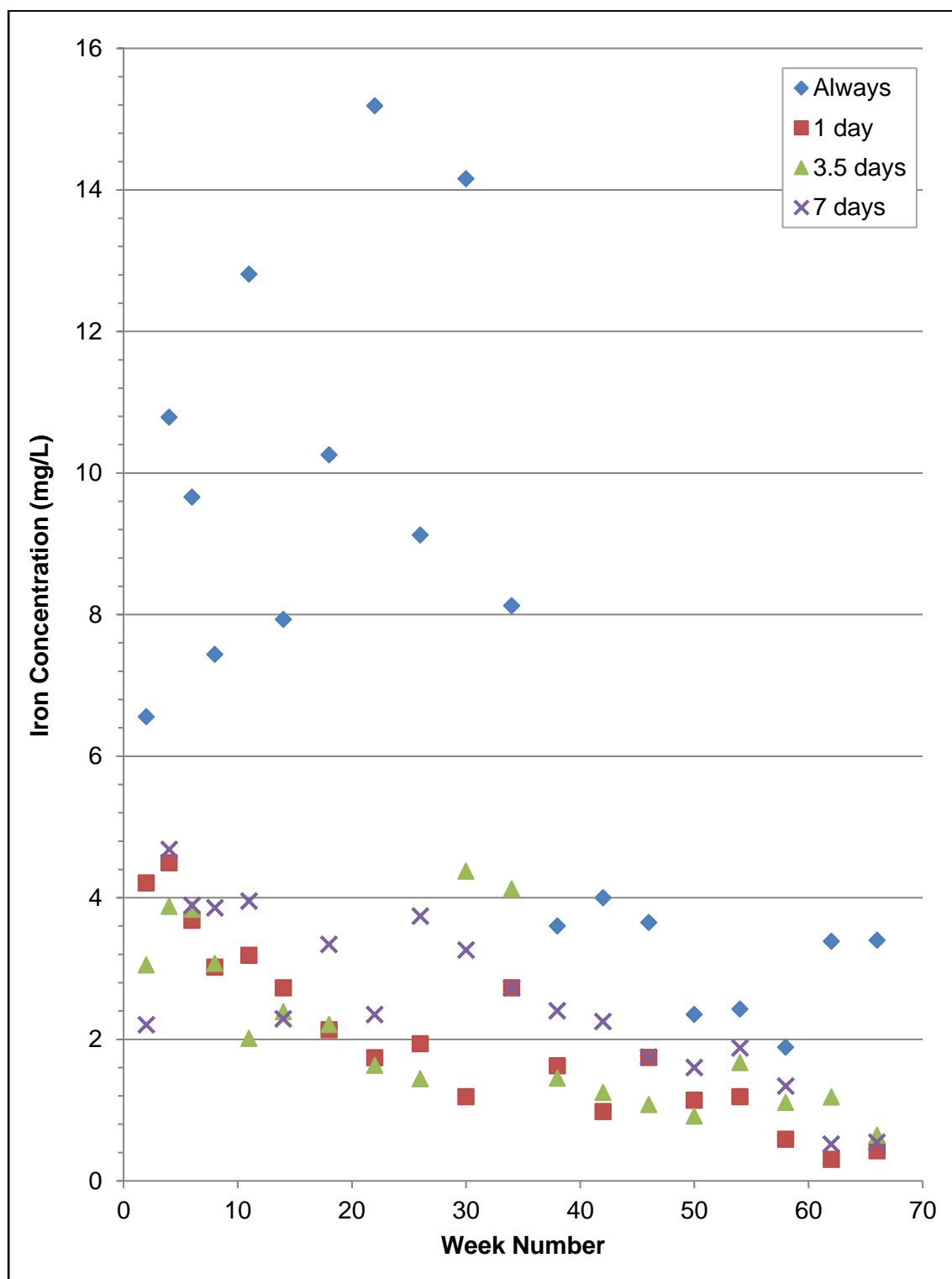


Figure 29. Iron concentrations over time. California MCL (not shown) is 0.3 mg/L.

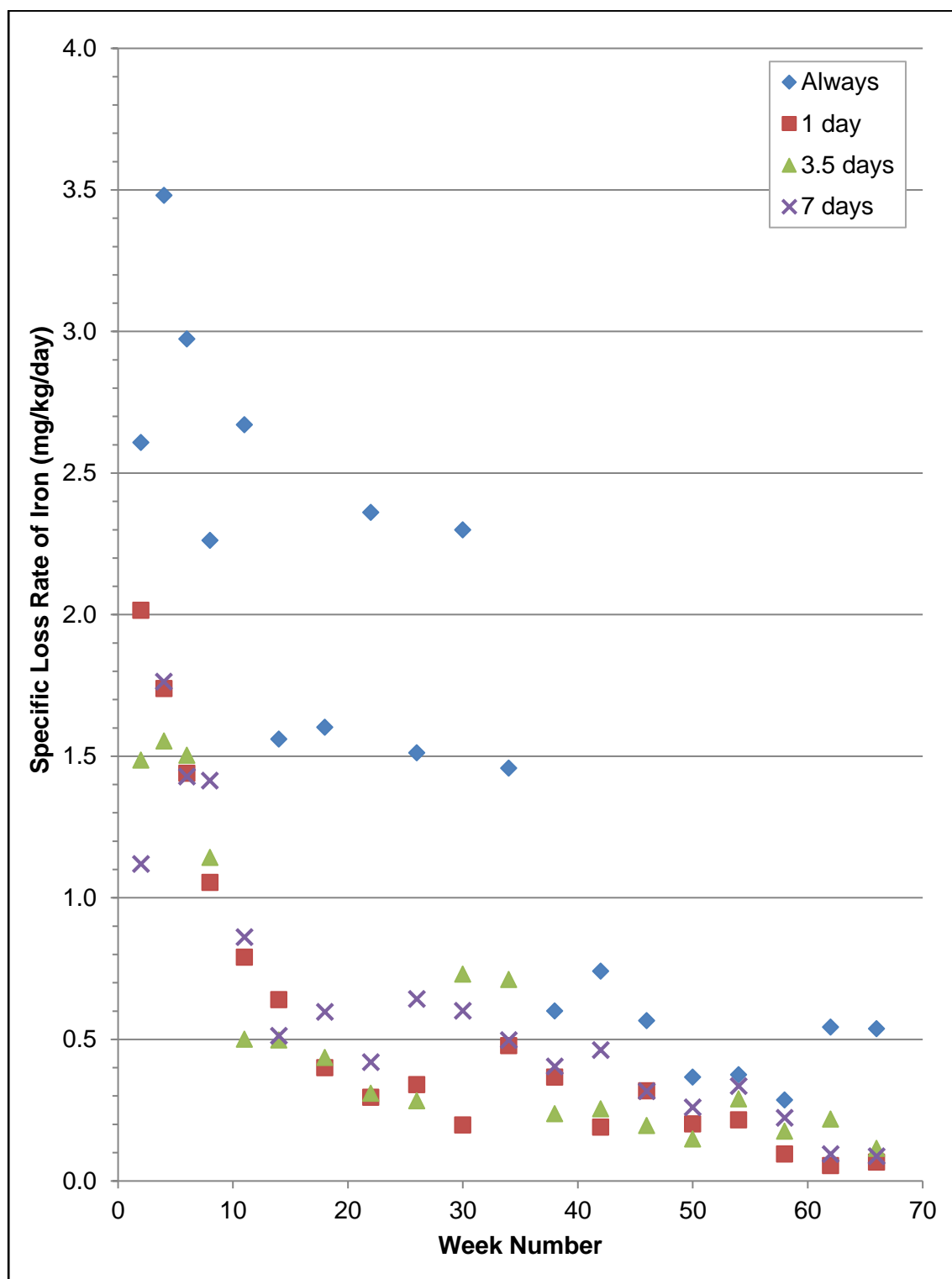


Figure 30. Iron specific loss rate over time.

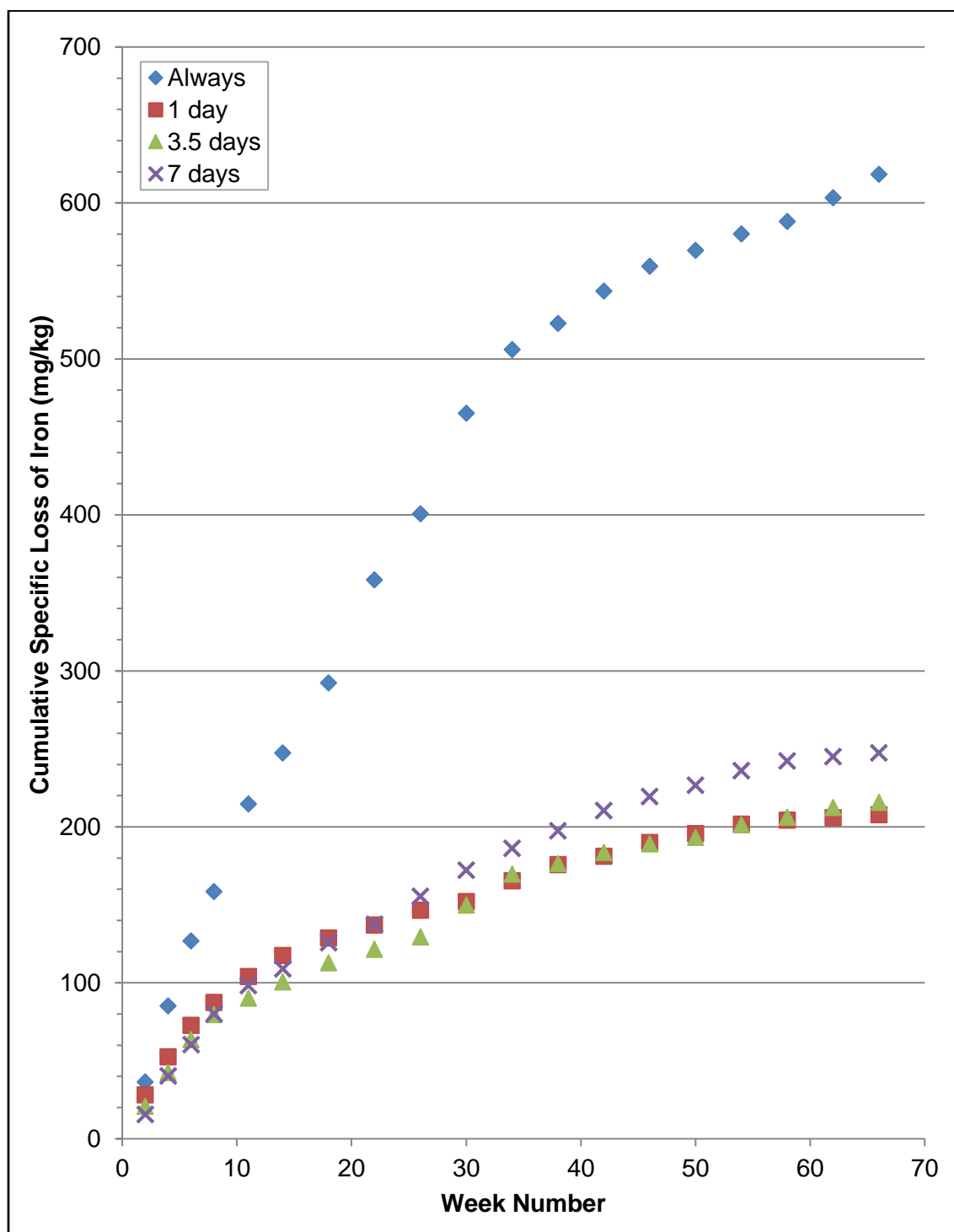


Figure 31. Iron cumulative specific loss over time with 'Always' (always wet) containers significantly higher than remaining containers.

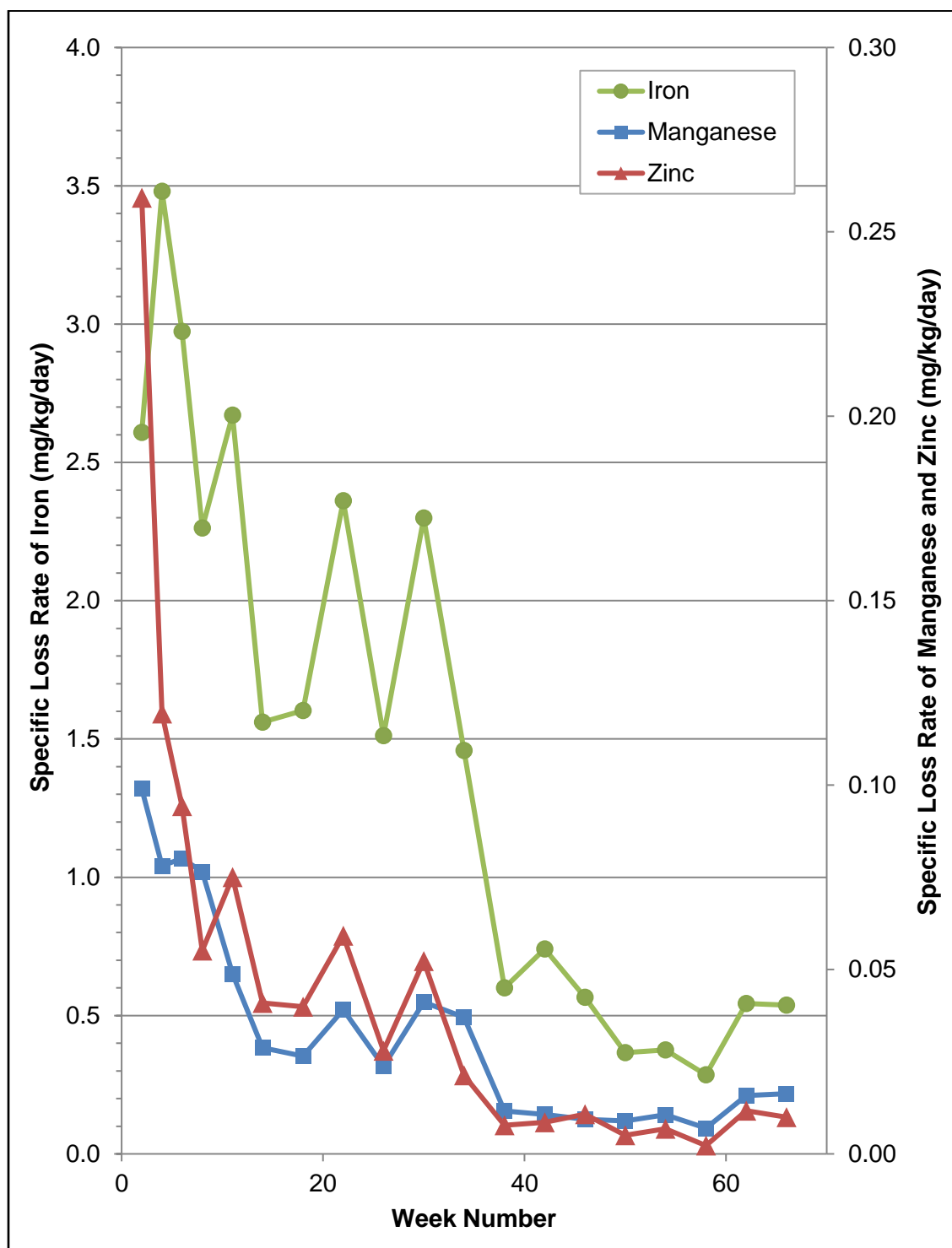


Figure 32. Comparison of specific loss rates for iron, manganese, and zinc for always wet operating condition. (Note: secondary axis for manganese and zinc).

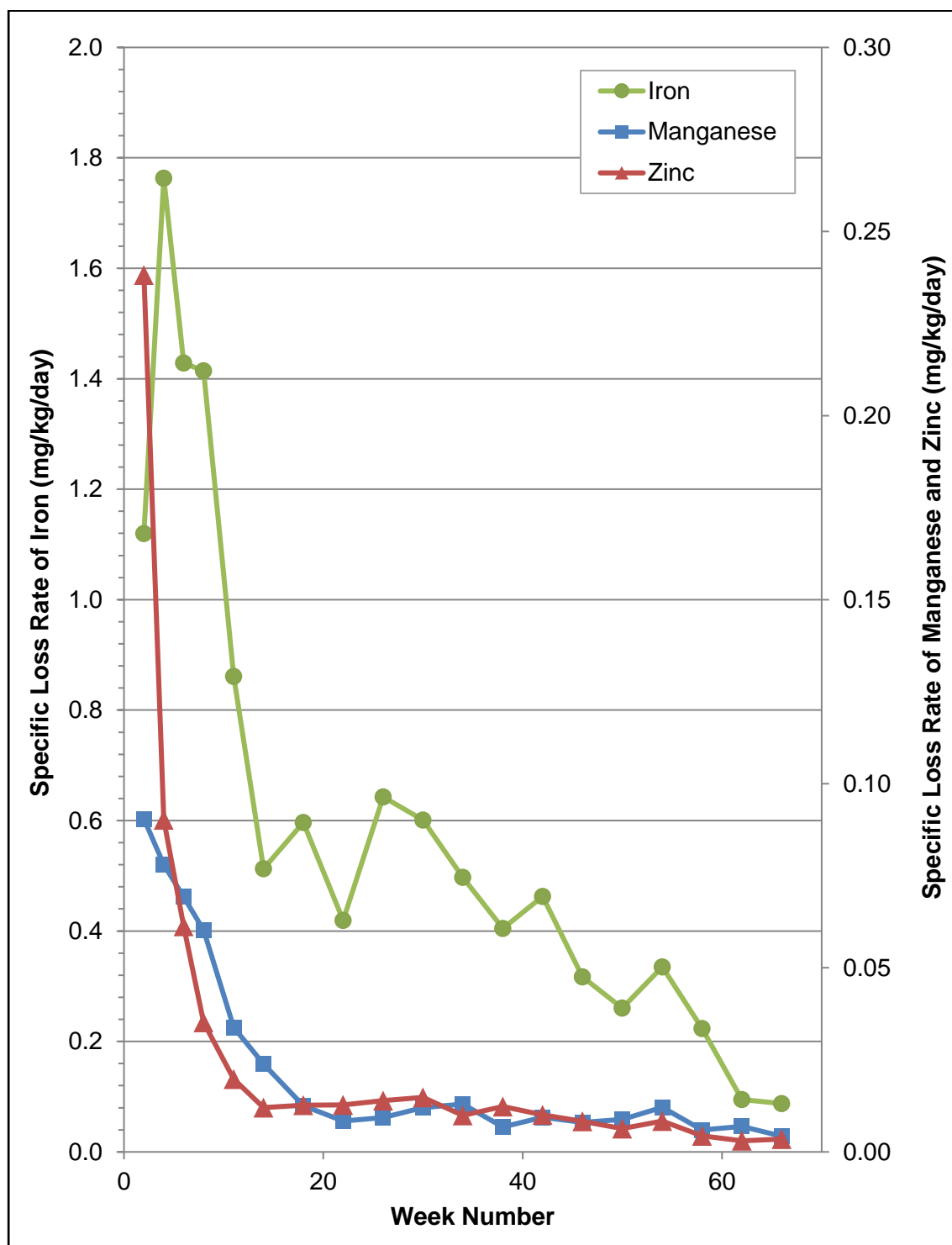


Figure 33. Comparison of specific loss rates for iron, manganese, and zinc for 7 day operating condition. (Note: secondary axis for manganese and zinc).

*Effects of Seasonality*

One objective of this study was to evaluate the effects that seasonal meteorological conditions might have on the leaching rate of compounds from a TDA fill. For this study, a dry period was simulated by leaving two containers (C9 and C10) without water and undisturbed for six months. After the six-month period, water was reintroduced into the containers. This provides insight into the inorganic leaching behavior in locations that experience extended periods of dry weather, and in applications in which a TDA fill may alternate between being above and below a seasonally-varying groundwater table.

The recirculation tubing for C9 and C10 was scrubbed for the first time during the experiment on Week 58, four weeks after resuming the regular operational condition of alternate one day wet and one day dry. However, because the 'post-scrub' values account for accumulation in the tubing back to the beginning of the experiment (including the six month dry period), these values were not used. Instead, to estimate the specific loss rate during the four week period between resumption of operation and the Week 58 sample date, iron and manganese masses proportional to the containers that operated similarly to C9 and C10 (C3 and C4) were added to the 'pre-scrub' values of the first sampling date after the dry period. As with other operating conditions, four milligrams of zinc was added to the result report for the first sample on Week 2.

The release of manganese and iron from TDA showed similar behavior to the effects of the simulated seasonal dry period, with iron serving as an illustrative example for these constituents. A comparison of the specific loss rate of iron for the two

containers that were dry for six months ('Seasonal') with the two containers that followed the same operating condition, but without a dry period ('Constant') shows a higher initial specific loss rate after the dry period followed by a decrease that appears to approach the 'Constant' data (Figure 34). The higher iron loss observed in the seasonal containers at Week 58 was likely due to one, or both, of two possible causes. First, oxidation facilitated by moisture in the air while the TDA was 'dry' may have occurred and the accumulated oxidized material was flushed out when water was reintroduced. Second, the TDA used in the Seasonal containers may have had more exposed wire than the constant containers, as indicated by the higher cumulative specific loss of iron in the seasonal containers prior to the extended dry period (Figure 35). These results suggest a pulse of iron and manganese mass may occur after an extended dry period, but the specific rate loss would approach that of a constantly submerged TDA fill within several months. Further, the initial pulse after an extended dry period would not exceed the initial mass losses observed at the onset of water exposure.

#### *Expected Metal Losses over Time*

As indicated earlier, approximately 2.1% of the steel wire in the TDA used in this experiment was protruding from the rubber and therefore easily oxidizable. According to the Rubber Manufacturer's Association (not dated), approximately 0.55% by weight of the steel wire used in tires is manganese and 98.5% is iron. Over the 15-month experiment, in the always wet containers, only approximately 3.1% of the total mass of iron in the exposed wire was accounted for in the leachate. In addition, the rate of iron



loss is decreasing with time, with 50% of the mass recovered in the leachate occurring during the first third of the experiment. For the non-always wet containers, the mass of the exposed iron recovered in the leachate ranged from 0.9% to 1.2%, and again approximately half of the mass was recovered during the first third of the experiment. The small fraction of the available mass actually recovered in the leachate during the 15-month period, and the relatively slow and decreasing rate, suggest that iron would likely be released from TDA during the lifetime of typical TDA fill applications. This is supported by data from a 34,000 gallon/day aerated lagoon wastewater treatment plant with a tire-shred-filled constructed wetland, which observed elevated effluent iron concentrations exceeding 0.5 mg/L eight years after construction (Mackinnon, 2015).

Relative to the expected mass ratio, manganese appeared to leach from the TDA at a higher rate than iron, with the always wet containers leaching 11.9% of the manganese mass in the exposed wire and the non-always wet containers leaching between 5.1% and 7.8%. The reason that manganese appears to leach from the exposed wire at a higher rate than iron is unknown, but this phenomenon has been observed by other researchers (Grefe et al., 1989 as cited in Tatsilo, 2006; Gunter et al., 1999; Selbes, 2009).

Estimating the rate and long-term total mass of zinc leached from TDA is complicated because zinc is contained in the wire and the rubber. Because the rate and extent that the rubber degrades and exposes fresh rubber to the water that zinc can leach into is unknown, the total mass of zinc that potentially could enter the receiving water is difficult to quantify. However, the highest zinc concentrations were observed at the

beginning of the experiment and were an order of magnitude below the Secondary MCL.

In addition, the concentrations were two orders of magnitudes below the regulatory standard by the end of the fifteen-month experiment, suggesting that while zinc may leach from the TDA for many years, the rate will be very low after the first year of exposure to water.

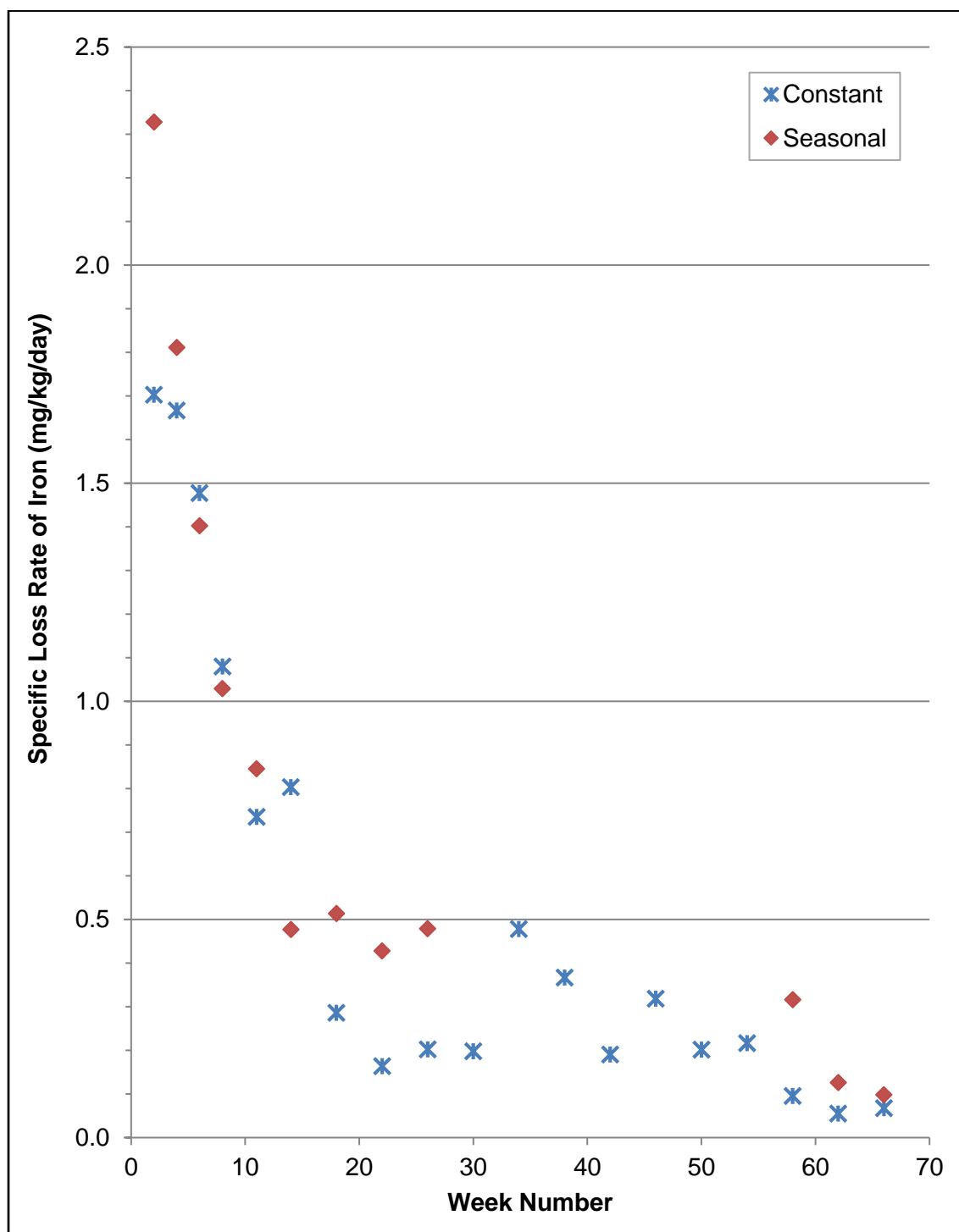


Figure 34. Specific loss rate of iron for 'Seasonal' (C9 & C10) compared to that of the 'Constant' (C3 & C4).

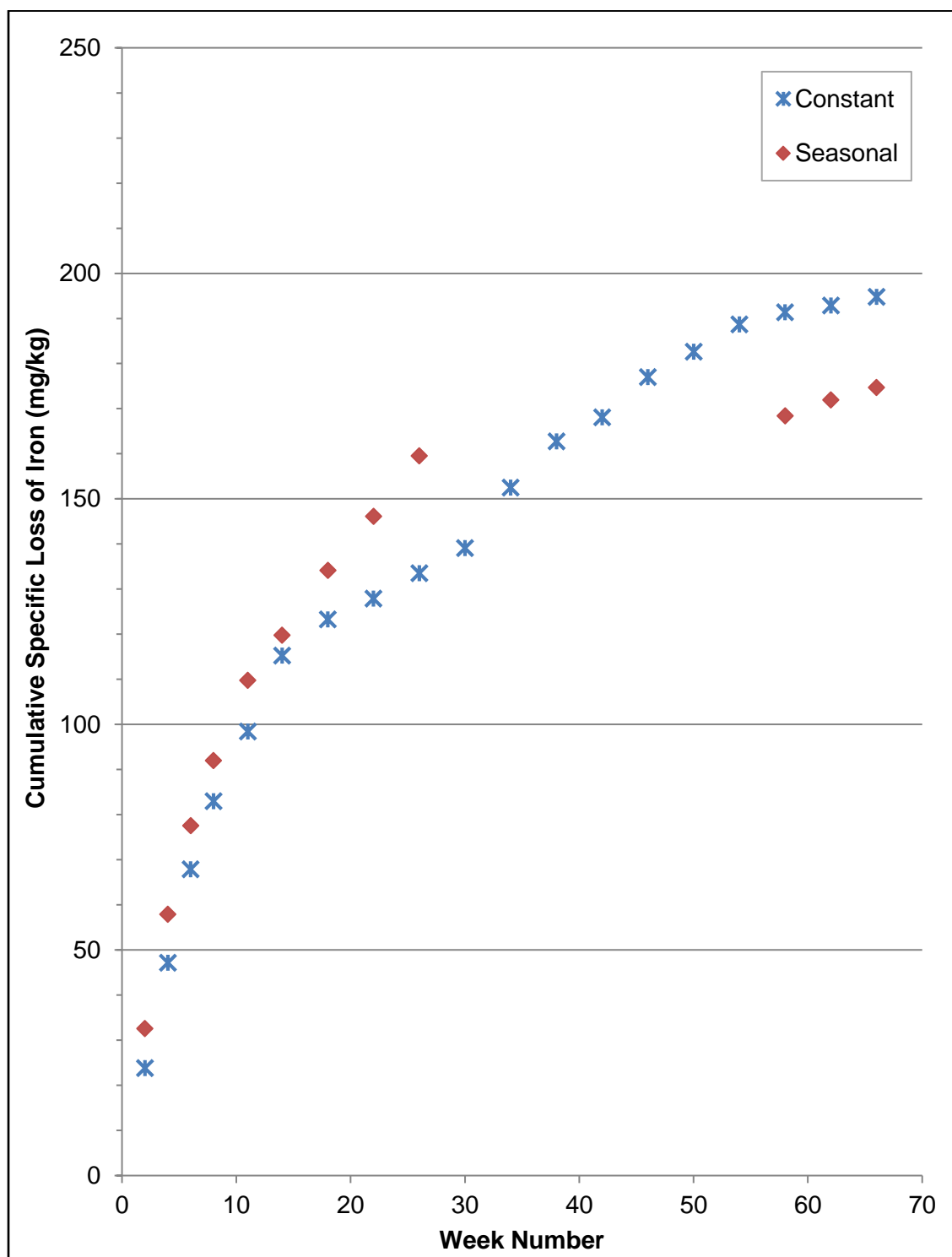


Figure 35. Cumulative specific loss of iron for Constant and Seasonal data.

### Volatile Organic Compounds

Only two operating conditions were used to evaluate the impact that wet-dry cycles might have on the rate that selected volatile organic compounds (VOCs) leach from TDA. The always wet containers (C1 and C2) and containers C7 and C8, which had one week wet followed by one week dry conditions were analyzed for organic compounds. Sampling began on Week 4, with a composite sample of C1 and C2, and then continued starting at Week 6 for both operating conditions on the same schedule used for the inorganic constituents. Sampling of the source water began on Week 8 and the concentrations of the source water for Week 4 and Week 6 were assumed to be equal to the average of the concentrations over the remaining weeks of the experiment. After the Week 18 sample results were available, a review of the data to date determined that there was no evidence that the concentration of any of the tested constituents was consistently higher in C7 and C8 as compared to C1 and C2. However, for several compounds such as benzene, the results suggested that the always wet containers released higher levels of organics than the alternating wet/dry containers (Figure 36). These results suggest that the always wet operating condition provides the best estimates of the maximum expected concentrations of organic compounds leaching from TDA in typical civil engineering applications, and this operating condition was the only one sampled for VOCs for the remainder of the experiment.

The data in the following sections describe organic compounds results for C1 and C2. Results from C7 and C8 can be found in Appendix D. The aforementioned Week 4 composite sample of C1 and C2 is presented as Container 1 data for all organic

compounds. A list of all VOCs included in the testing and the detection limit for each constituent is given in Appendix A.

Only three VOCs had concentrations consistently above the test detection. A number of constituents were sporadically detected at seemingly random intervals and from random containers. A discussion of these constituents is not included here, but a full set of data is in Appendix D. The source of the three remaining VOCs is likely the containers or the TDA itself, and a more detailed discussion of these VOCs is presented in the section below.

#### *VOCs suspected to be released from TDA or Experimental Equipment*

The concentration of methyl isobutyl ketone (MIBK) decreased over the 15-month experiment and was not detectable in the final sample from one of the two containers (Figure 37). MIBK was only detected in the source water once (Week 18) at 0.61 ug/L. While there is not currently an MCL for MIBK, it is recognized as a carcinogen by the California Office of Environmental Health Hazard Assessment. Although an increase in MIBK released was observed starting at Week 18 in C1, the rate loss was similar to the low levels in C2 by Week 42 (Figure 38). These results suggest that MIBK is likely released from TDA, but may only appear for the first several months if constantly submerged. MIBK is not known to be used in the manufacturing of tires, so it may be introduced during a tire's use or after its disposal. Aydilek et al. (2006), who also detected the compound, postulated that municipal refuse is the source of MIBK.

Gunter et al. (1999) detected MIBK in their laboratory experiment, but reported that concentrations decreased to insignificant levels after seven months.

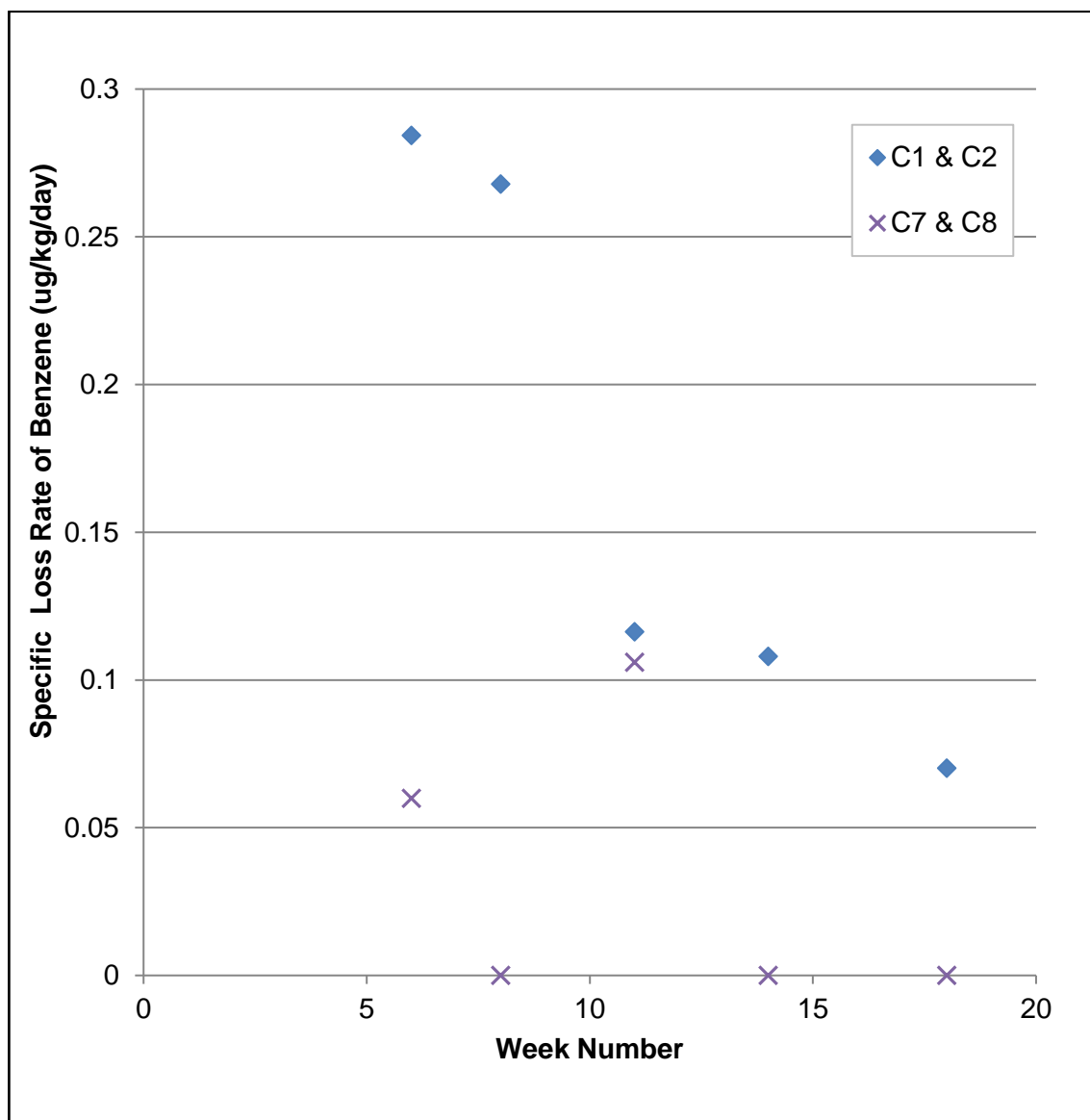


Figure 36. Comparison of average benzene concentrations in always wet containers (C1 & C2) and alternating week of wet and week of dry (C7 & C8).

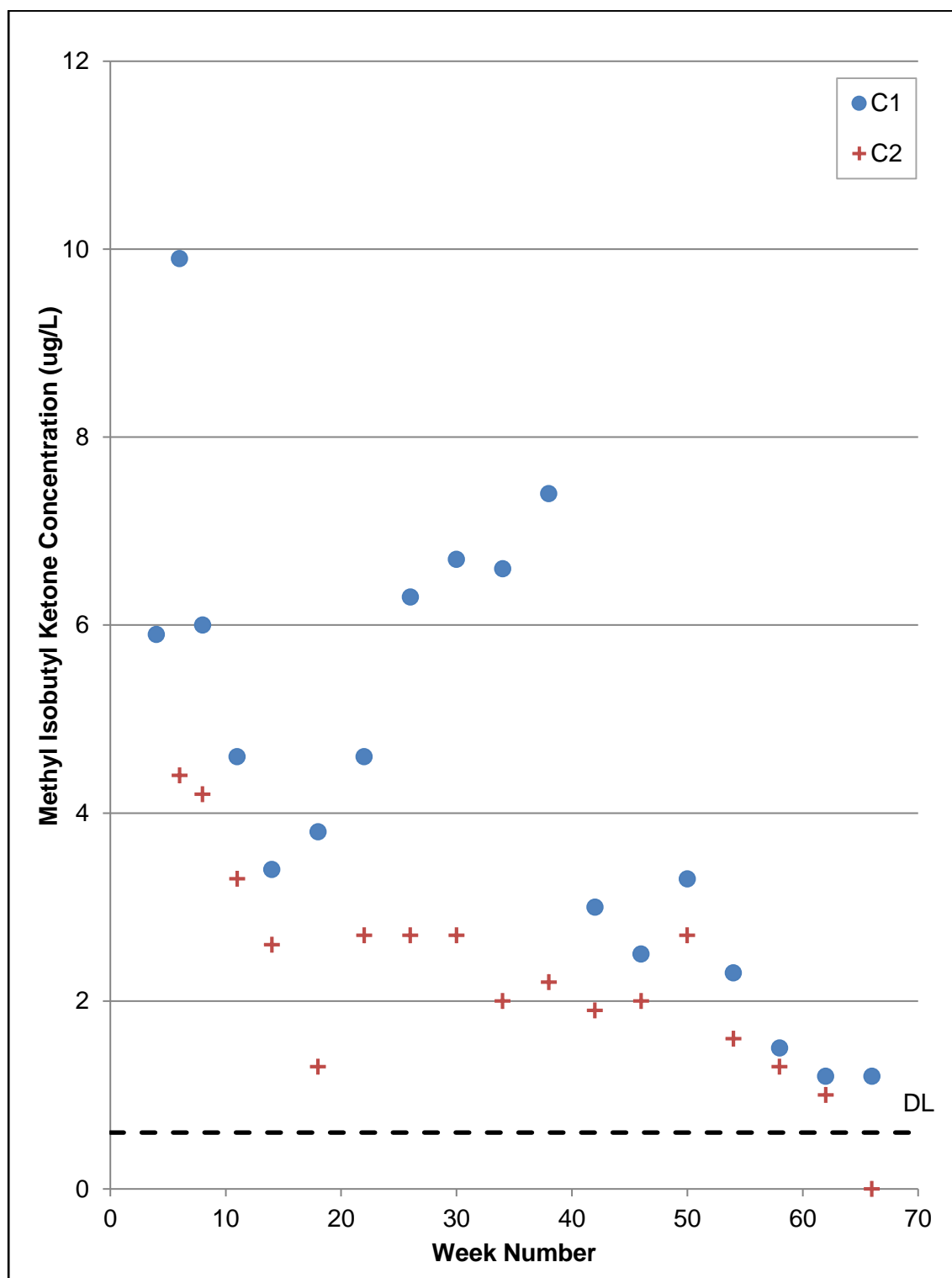


Figure 37. Methyl isobutyl ketone concentrations over time.



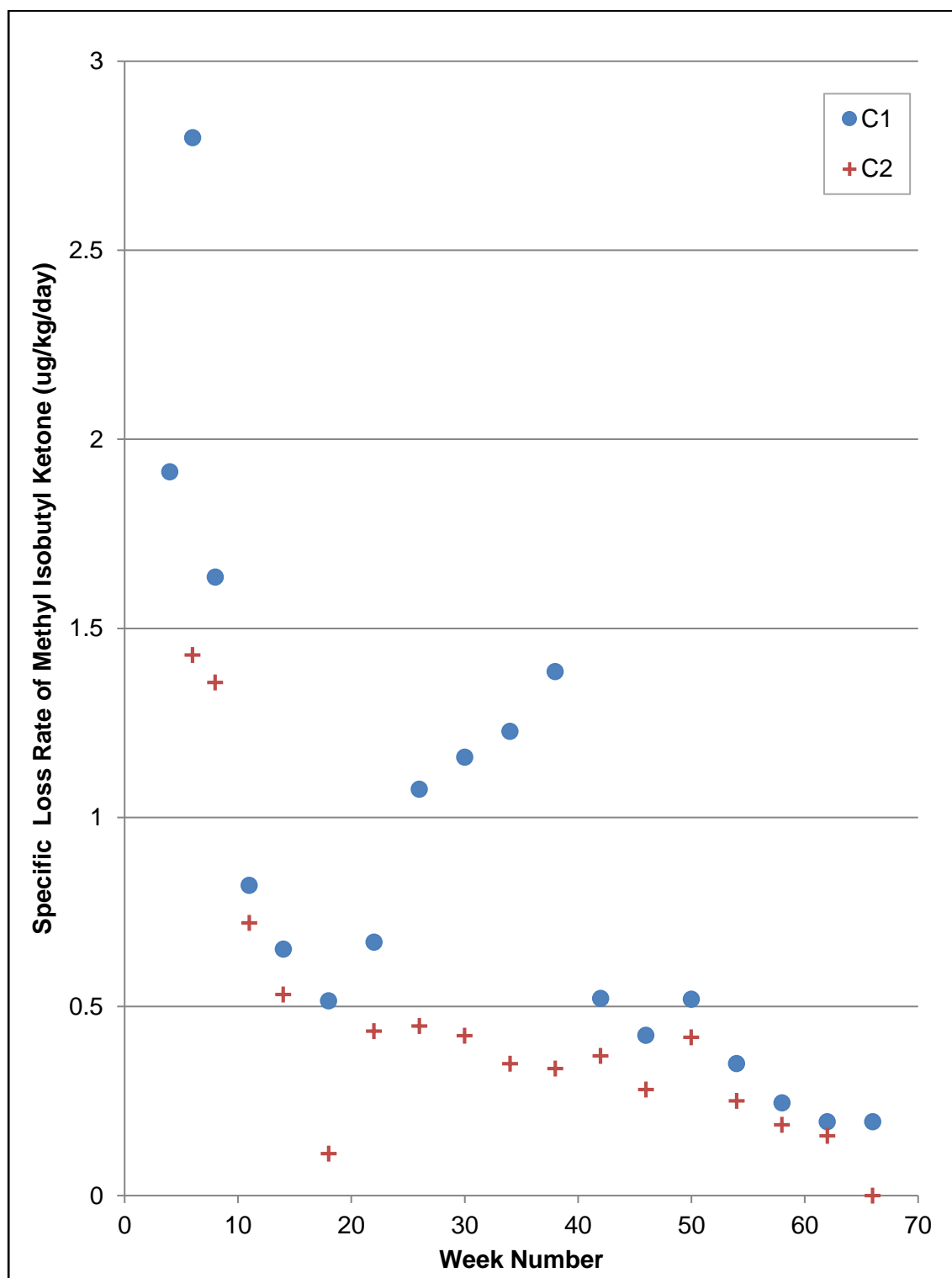


Figure 38. Methyl isobutyl ketone specific loss rate over time.

Results for benzene suggest that the compound is immediately released from the TDA when it is submerged (Figure 39). The highest concentrations (maximum = 0.97 ug/L) nearly exceeded its CA MCL of 1.0 ug/L (more stringent than the EPA's MCL of 5 ug/L), but levels dropped below the detection limit of 0.3 ug/L by Week 34. The specific loss rate of benzene suggests a rapid decrease in the amount of benzene leached from the TDA with the largest decrease occurring between Week 8 and Week 11 (Figure 40). The specific loss rate decreased by an average of approximately 45% for the two containers from Week 8 to Week 11. A similar behavior over time was also observed by Miller and Chadik (1993), who reported a rapid, exponential decrease over their 90-day study. Other laboratory and field studies suggest that benzene may be released at trace levels (Gunter et al., 1997; Humphrey and Katz, 2001).

Although acetone was detected in the leachate, results from the control experiments indicate that acetone is released from the containers, tubing, or pump (Figure 41). Results from the control experiments (B1 and B2) are circled in Figure 41. The source of the acetone is likely the plastic containers. A subtle odor was noticed for some of the containers. The amount of acetone released from the containers is likely dependent upon the age of the container, a possible explanation for the variability in acetone concentration in the two control experiments. The time of manufacturing of the containers, and therefore age of the containers, cannot be determined. The levels detected in the TDA containers (C1 and C2) are comparable or less than that of the control experiments (B1 and B2). Although previous literature indicates TDA may release

acetone initially (Gunter et al., 1999; Humphrey and Katz, 2001), the results of this study do not suggest TDA is the source of the compound.

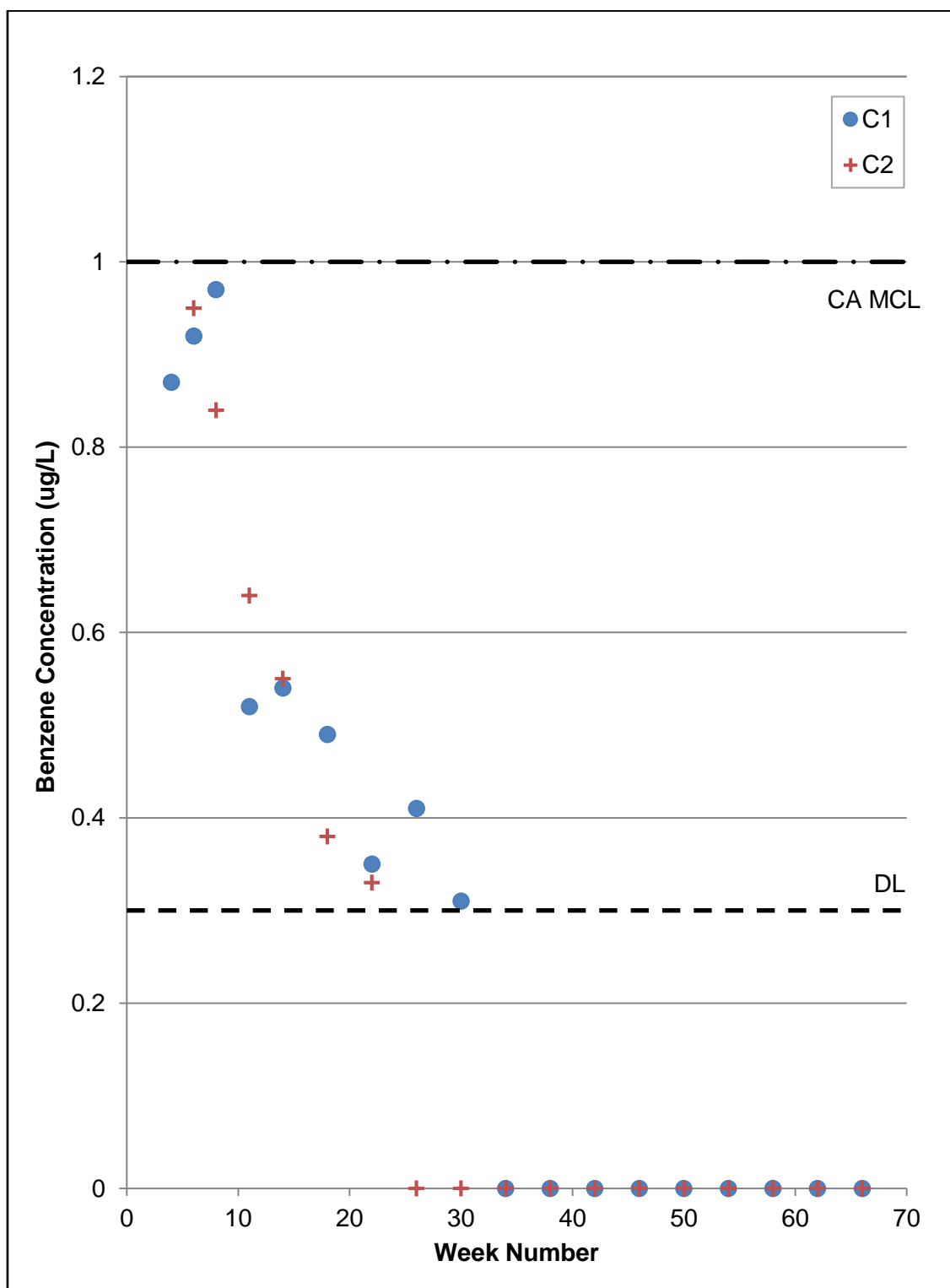


Figure 39. Benzene concentration drops below detection limit (0.3 ug/L) by Week 34.

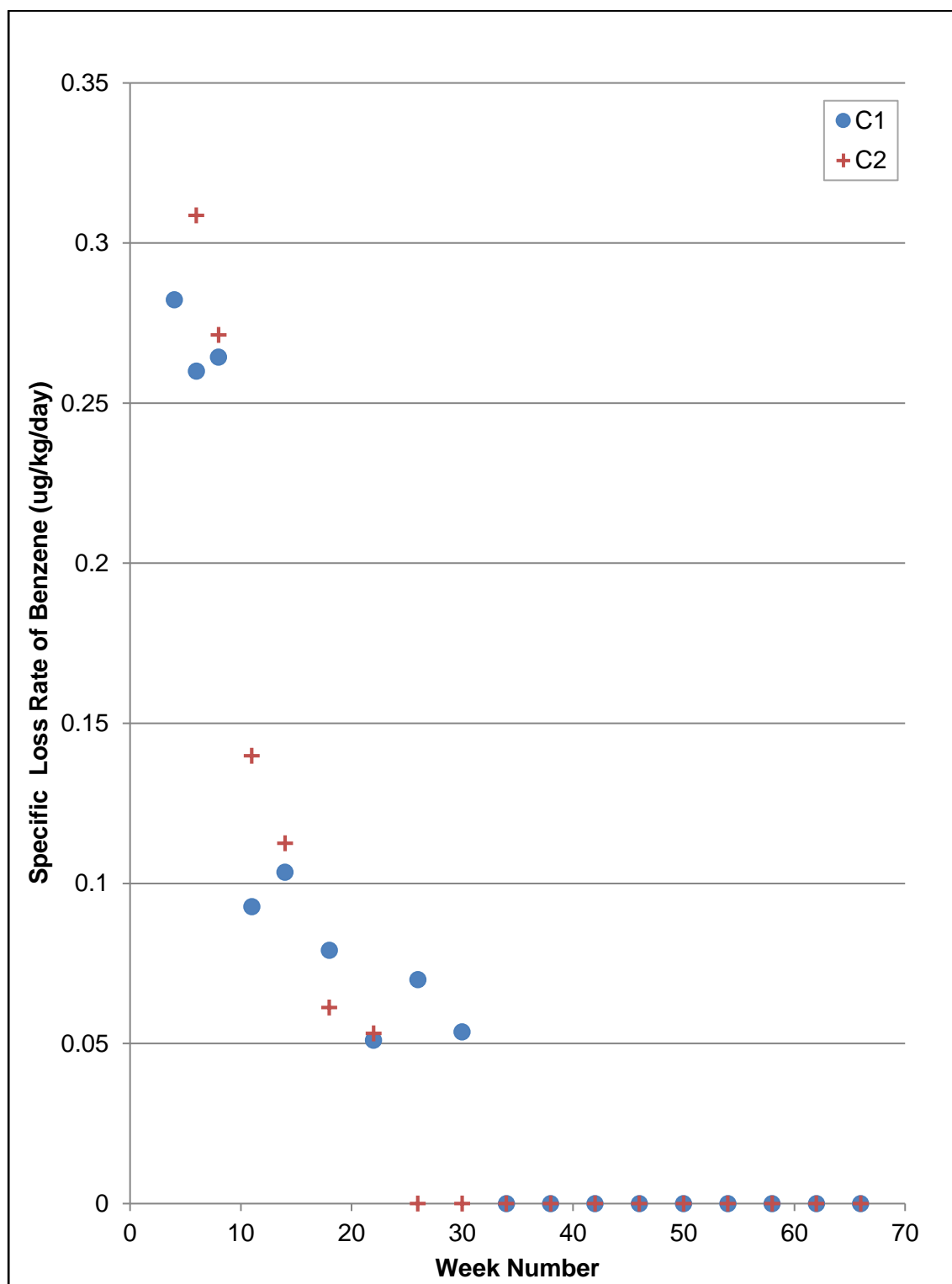


Figure 40. Benzene specific loss rate over time.

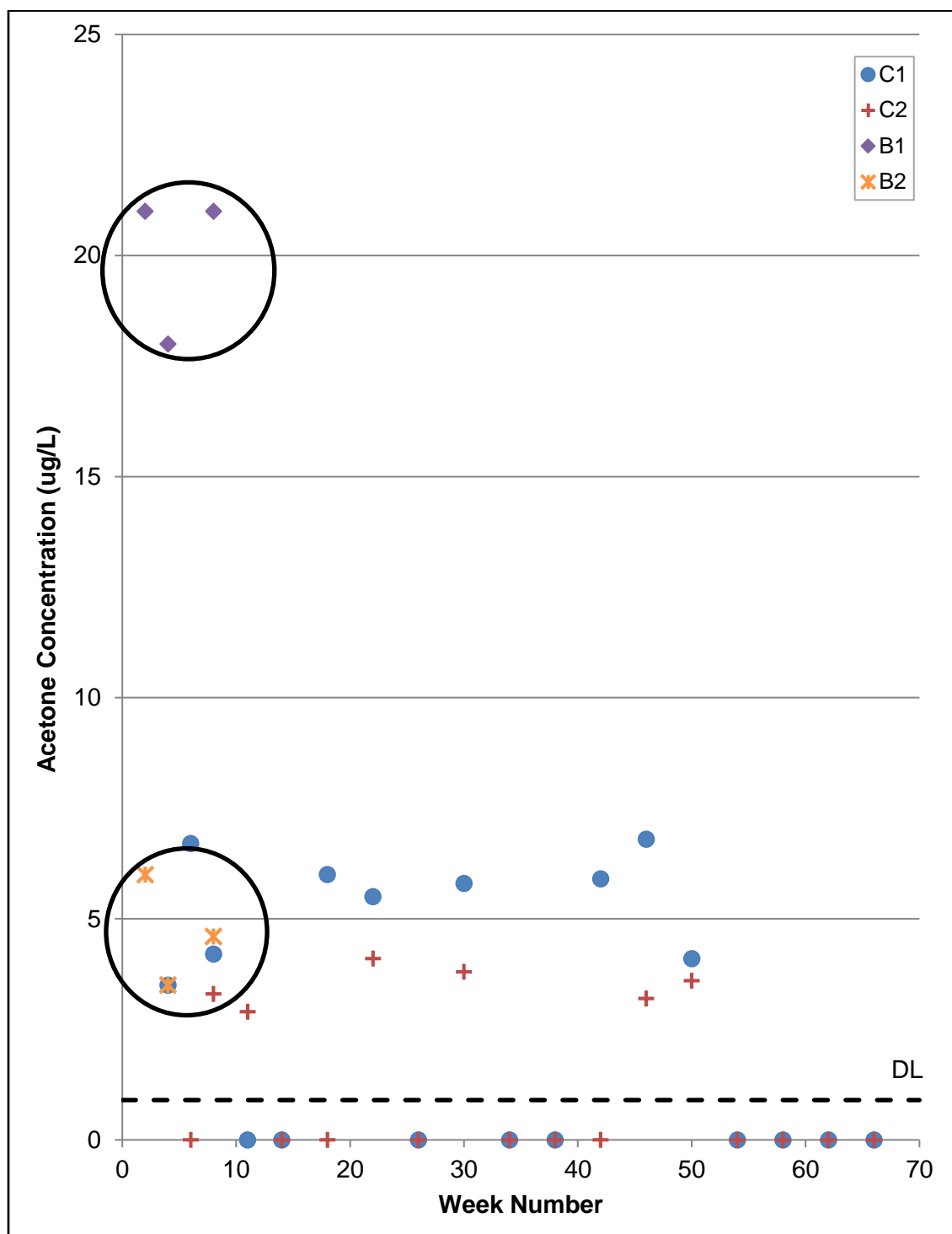


Figure 41. Acetone concentration in always wet containers (C1 & C2) compared to control experiments (B1 and B2) circled in black.

### Common Water Quality Index Parameters

The sampling regime for common water quality parameters followed that of VOCs. Sampling began at Week 4 with a composite sample of C1 and C2, followed by individual samples for the remainder of sampling events.

#### *Parameters Originating in Source Water*

Nitrate was detected in the containers, but, with the exception of a single anomalous point, at concentrations lower than that of the source water (Figure 42). The literature suggests that the compound is not used in the manufacturing of tires, so it is not typically included in TDA studies. One study that analyzed for nitrate in a four-year study did not detect it in any samples (Aydilek et al., 2006). This information suggests that compound is introduced from the source water, not from the TDA. While dissolved oxygen concentrations in the containers were always above 4 mg/L, pockets of anaerobic zones where denitrification was occurring may be responsible for the lower concentrations of nitrate in the containers compared to the source water.

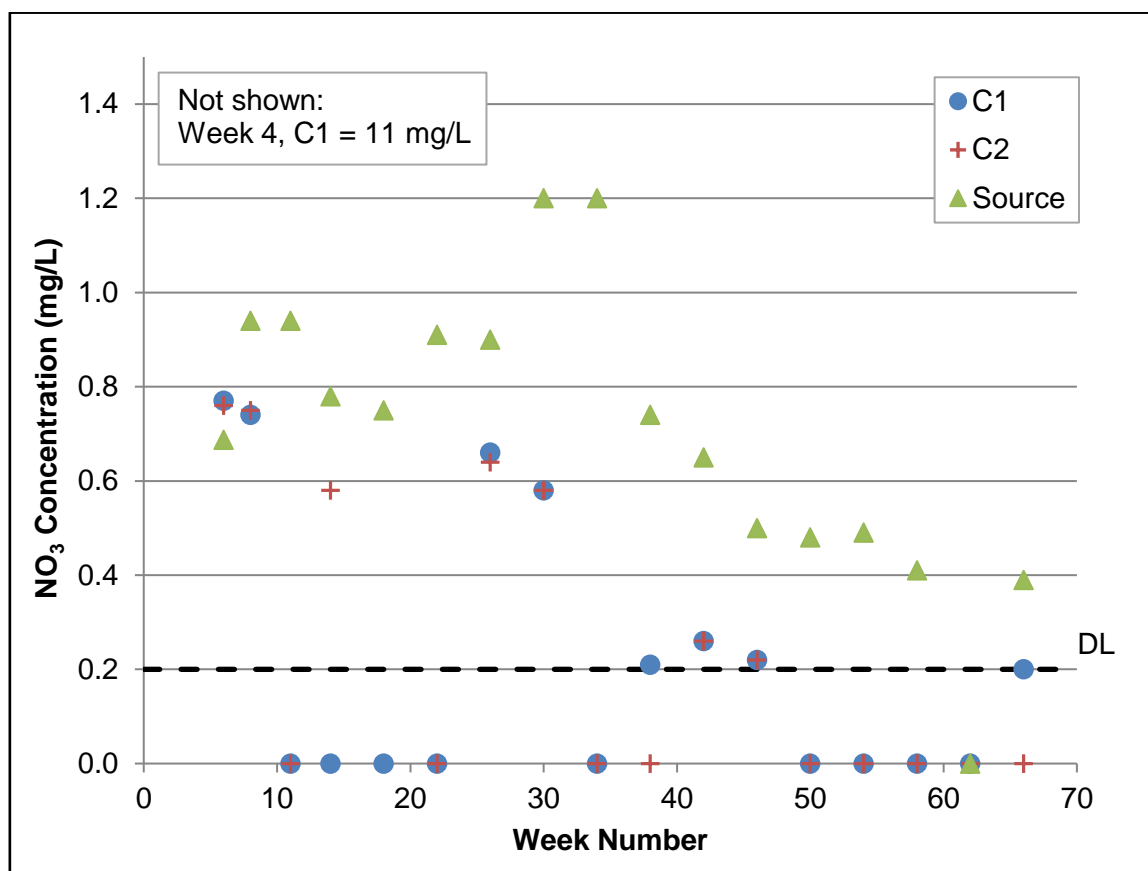


Figure 42. Nitrate concentration in containers is nearly always less than that of the source water.

Oil and grease was above the detection limit in the containers for approximately 90% of the samples and approximately 95% of the source water samples (Figure 43).

With the exception of Week 4, C2, all oil and grease results not shown were below the detection limit. Excluding the anomalous result in the source water (Week 50), only one result in the containers (C2, Week 22) exceeded the typical range of the source water.

Another potential source of oil and grease is the recirculation pumps and the containers since in the control setups, oil and grease concentrations ranged from ND to 2.0 mg/L.

These results suggest that the source water or the experimental equipment, and not the



TDA, introduced oil and grease. A previous study also detected oil and grease in their laboratory experiment, but concentrations were higher in the control setups, suggesting that TDA was not the source (Gunter et al., 1999).

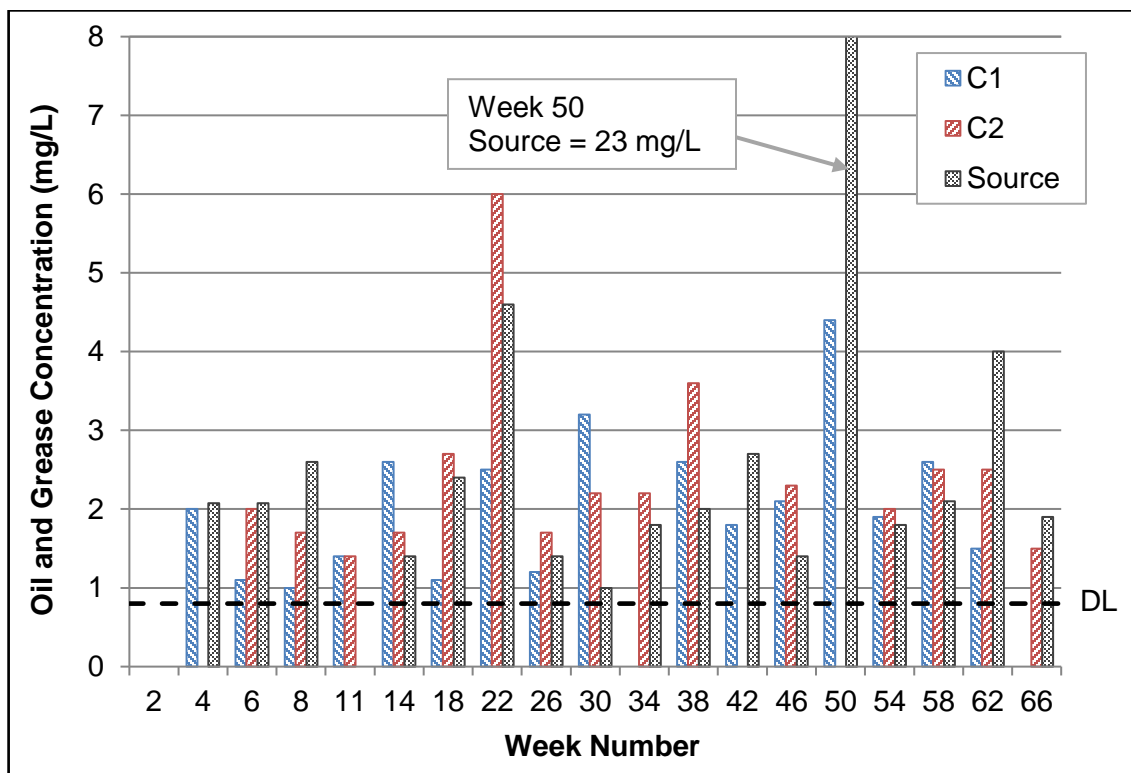


Figure 43. Oil and grease concentrations in containers is typically comparable to that of the source water.

Sulfate results were above the detection limit for all container and source water samples (Figure 44). The highest concentrations in the containers were observed for the first two sample dates (Week 4 and Week 6), dates for which the source water was not sampled. With the exception of the anomalous result (Week 14, C2), sulfate levels in the containers were not appreciably higher than (and typically lower than) that of the source water. This suggests that leachate from TDA is unlikely to cause elevated levels of

sulfate in typical applications. This is supported by a TDA leach field study that reported effluent sulfate levels were lower than those of the influent, which was likely a result of biological growth facilitated by the TDA (Finney et al., 2013).

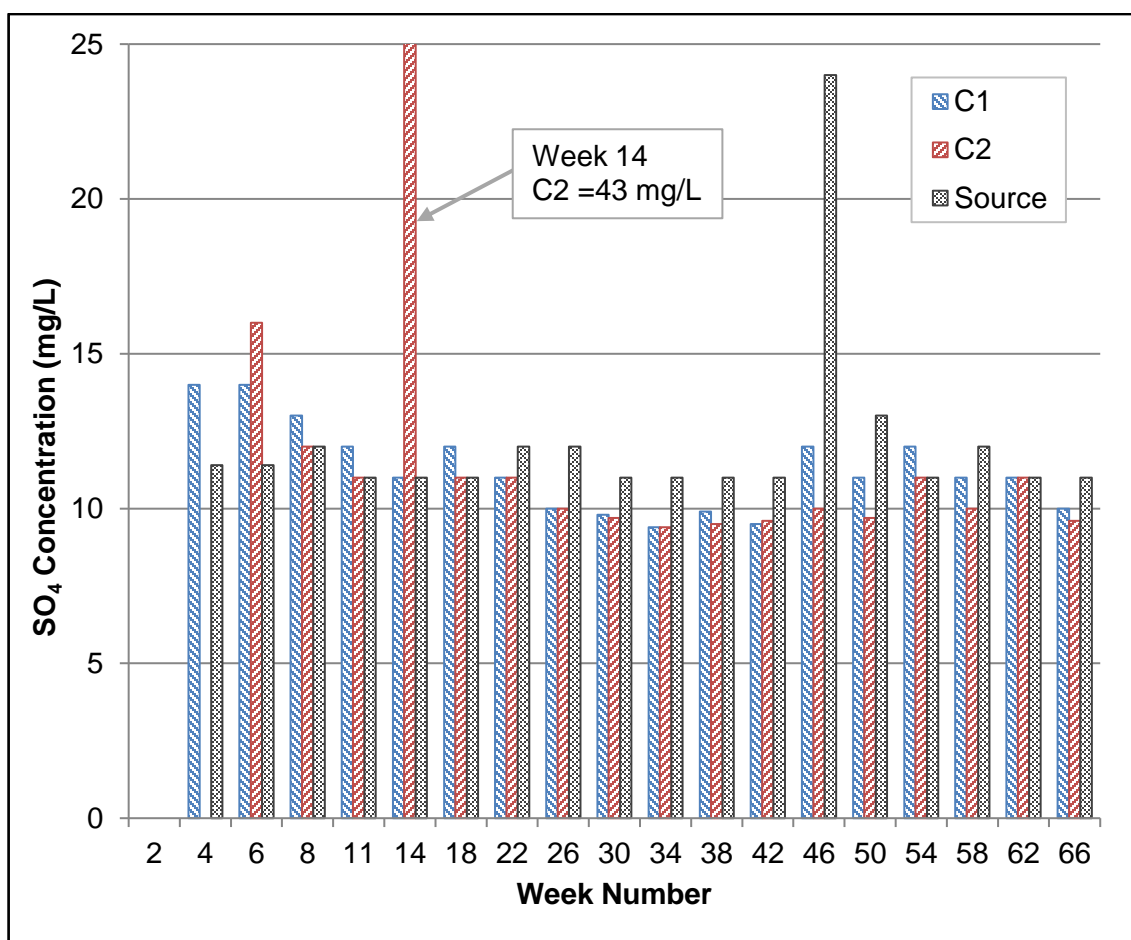


Figure 44. Sulfate concentration in containers is typically comparable to that of the source water.

The specific conductance of water is dependent on the concentration and mobility of dissolved solids in the water. Given the metal ions that TDA leaches into the water, it was expected that the TDA containers' specific conductance would be higher than the source water. However, for this study, the specific conductance of the source water was

typically higher than that of the containers (Figure 45). Total dissolved solids (TDS) of the source and container water was not measured, but it is possible that the metal ions from the TDA acted as a coagulant, sweeping out some of the TDS and lowering the conductance. Further investigation of this hypothesis could be examined in a future study.

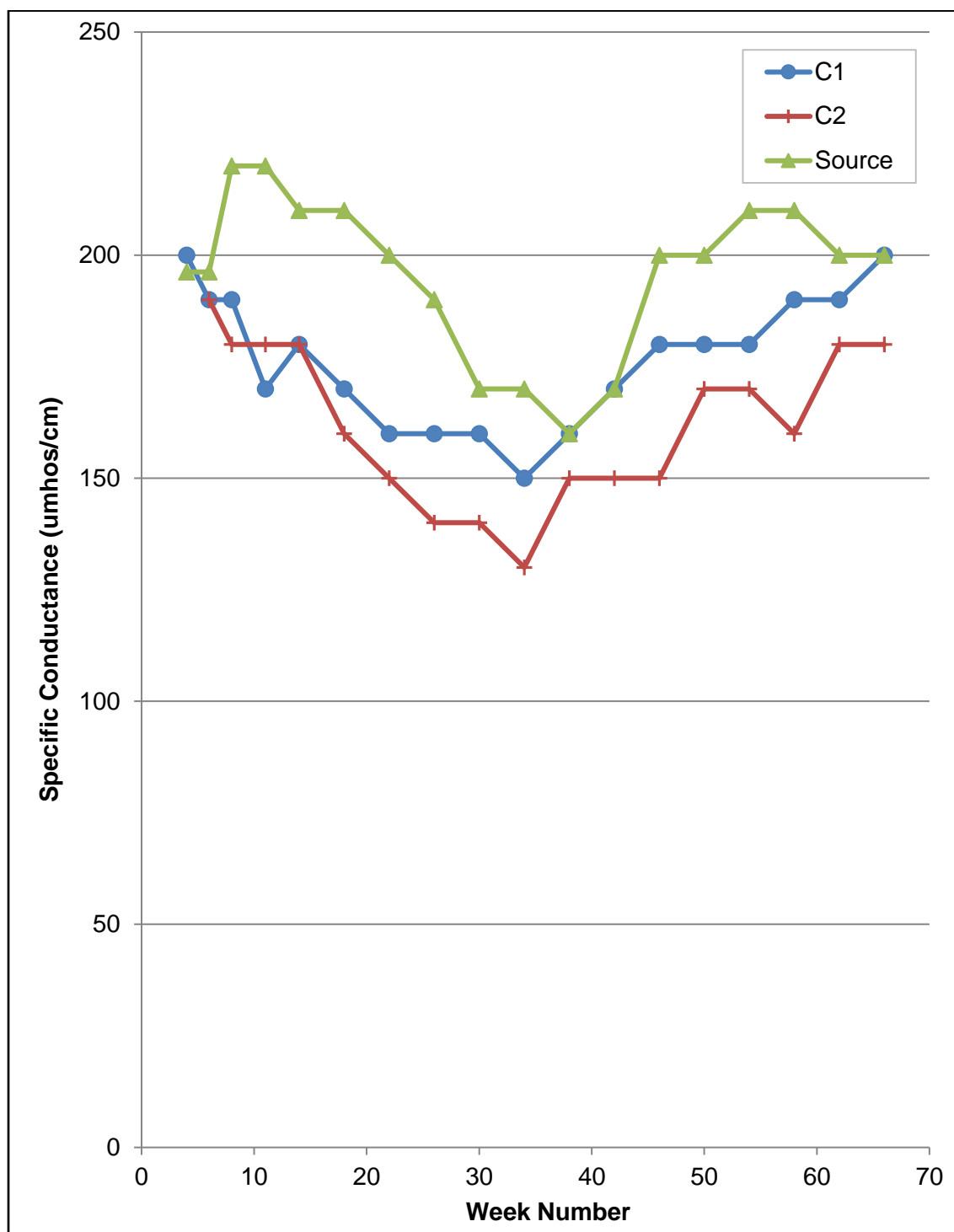


Figure 45. Specific conductance in containers is typically comparable or less than that of the source water.

*Parameters with an Undetermined Origin*

Chemical oxygen demand (COD) appeared in the containers above the detection limit of 9 mg/L for approximately 70% of the samples and in 30% of the source water samples (Figure 46). Unlike the other organic compounds, the average COD concentration of collected source water data was not used to fill in the missing concentrations for Week 4 and Week 6. Of the three sampling collections for the control experiments, COD was only detected during Week 8 (circled in black in Figure 46), which suggests the containers, tubing, or pumps may increase COD levels. No discernible trend is observed in the COD. Possible sources of increased levels of COD are contamination such as debris in the containers, experimental equipment, and chemicals adsorbed on the surface of the rubber while used as a vehicle tire.

To remain within the EPA's hold time of 15 minutes, the pH of the containers and source water was measured on site rather than tested at Alpha Laboratories. The pH of the source water was inadvertently not measured for Week 2 and Week 11. Although a general increase over the course of the experiment is observed in the pH of the TDA leachate, a similar trend is also observed in the source water (Figure 47). The maximum pH measured in the containers was 8.3, below the Secondary MCL of 8.5. There is not an overwhelmingly consistent relationship recognized between the pH of the source water and that of the containers. The pH in the containers was higher than that of the source water for 11 of the 17 sampling dates with data available for comparison. An increase in pH was also observed in the control containers (pH = 8.2) in comparison to the source water (pH = 7.8) for one of the two sets of data (Appendix D). The lack of evidence that

TDA alters the pH in this study is supported by Humphrey and Swett (2006) who reported neutral (6.79 to 7.51) conditions in five field studies. Similar results were reported by O'Shaughnessy and Garga (2000) and Aydilek et al. (2006). Other studies, however, observed a decrease in pH (Edstrom et al., 2008; Miller and Chadik, 1993). In general, the results of this study and previous literature suggest that the use of TDA is unlikely to result in a major change in the pH of water flowing through a TDA fill.

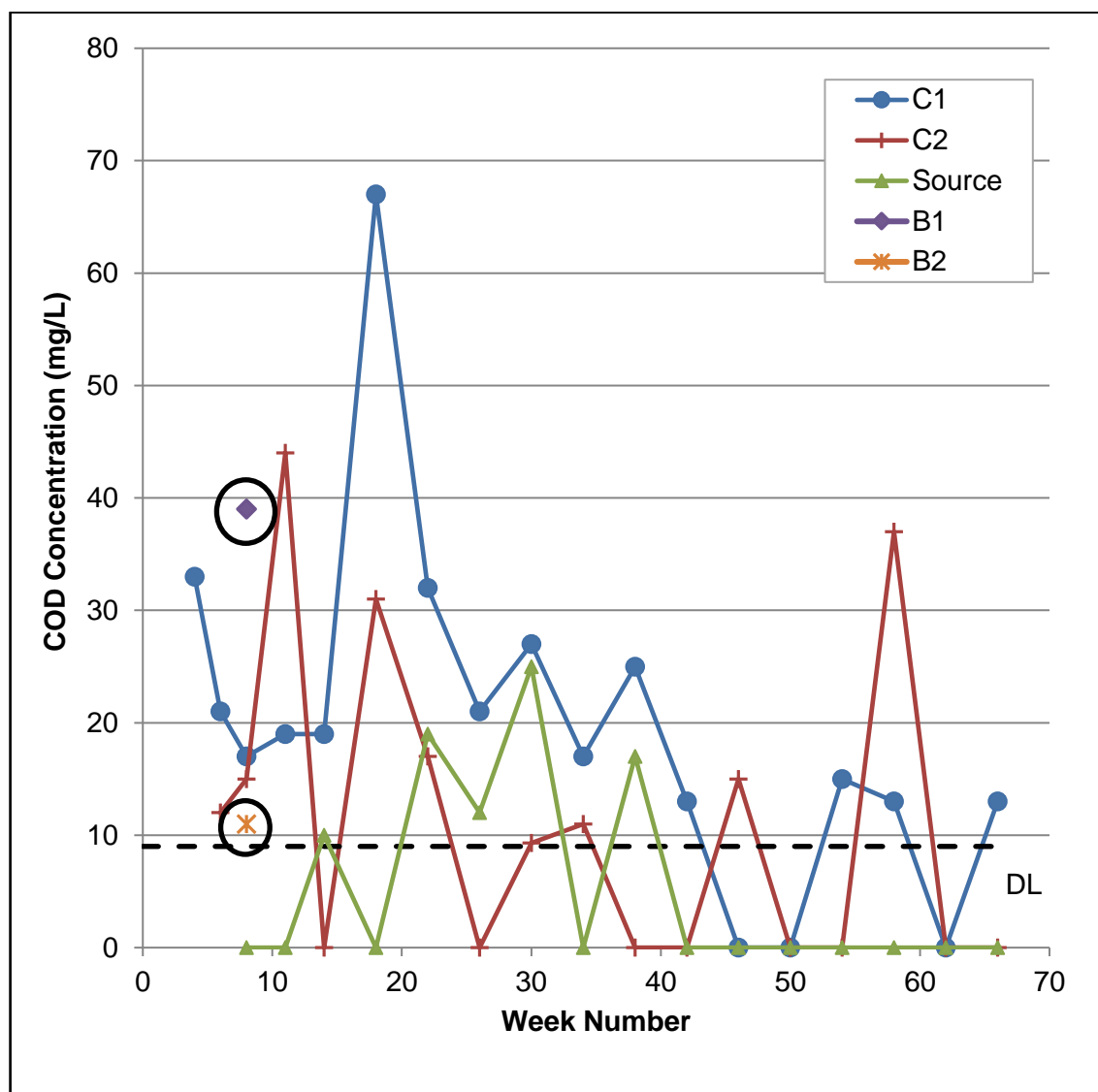


Figure 46. Chemical oxygen demand in always wet containers (C1 & C2), control containers (B1 & B2) circled in black, and source water has an inconsistent relationship.

#### *Parameters Likely Altered by TDA*

Weekly dissolved oxygen (DO) measurements suggest TDA may cause an initial decrease in DO, but levels increased considerably by Week 18 (Figure 48). The average DO of all of the containers is presented since there was no apparent difference from one

operating condition to the others; a full set of data is provided in Appendix D. The reduction in DO concentrations below saturation is likely due to oxidation reactions occurring in the TDA wire and aerobic biological activity in the biofilm on the surface of the TDA. Based on the water temperatures measured during the experiment, the saturation DO ranged from 9 to 11 mg/L. While 100 percent saturation was never observed, the reduction in DO never resulted in an anaerobic environment in the containers. The minimum concentrations were approximately 3 mg/L, sufficient to support oxidation-reduction reactions.

The concentration of total suspended solids (TSS) in the containers was above the detection limit (1.0 mg/L) for all samples (Figure 49). It was detected in the source water for two sample dates, Week 11 (1.3 mg/L) and Week 58 (1.6 mg/L). These values were deducted from the corresponding containers to determine the TSS specific loss rate (Figure 50). An increase followed by a rapid decline is observed for C1. A general increase in the TSS concentration was observed in C2 from Week 11 to Week 30, which corresponds to increases in the concentration of several of the inorganics and VOCs. While there were time periods where the TSS concentration did increase, over the full course of the experiment, a decrease in TSS concentration was observed. This corresponded with the visual observation of a decrease in “debris” in the water near the end of the experiment compared to the first few sampling dates.

Total phosphate levels were above the detection limit (0.06 mg/L) for approximately half of the container samples, with all but one result (and one anomalous result – Week 50, C1) occurring in the first half of the 15-month experiment (Figure 51).



The low levels of total phosphate suggest that a TDA fill is unlikely to cause total phosphate levels to increase to a concerning concentration. This conclusion is supported by a TDA leach field study that did not observe increased levels of phosphate (Finney et al., 2013). The loss rate of phosphate from the TDA declines rapidly past Week 32 (Figure 52), suggesting any phosphorus load on the receiving environment from TDA leachate would not persist beyond a year after placement of the material.

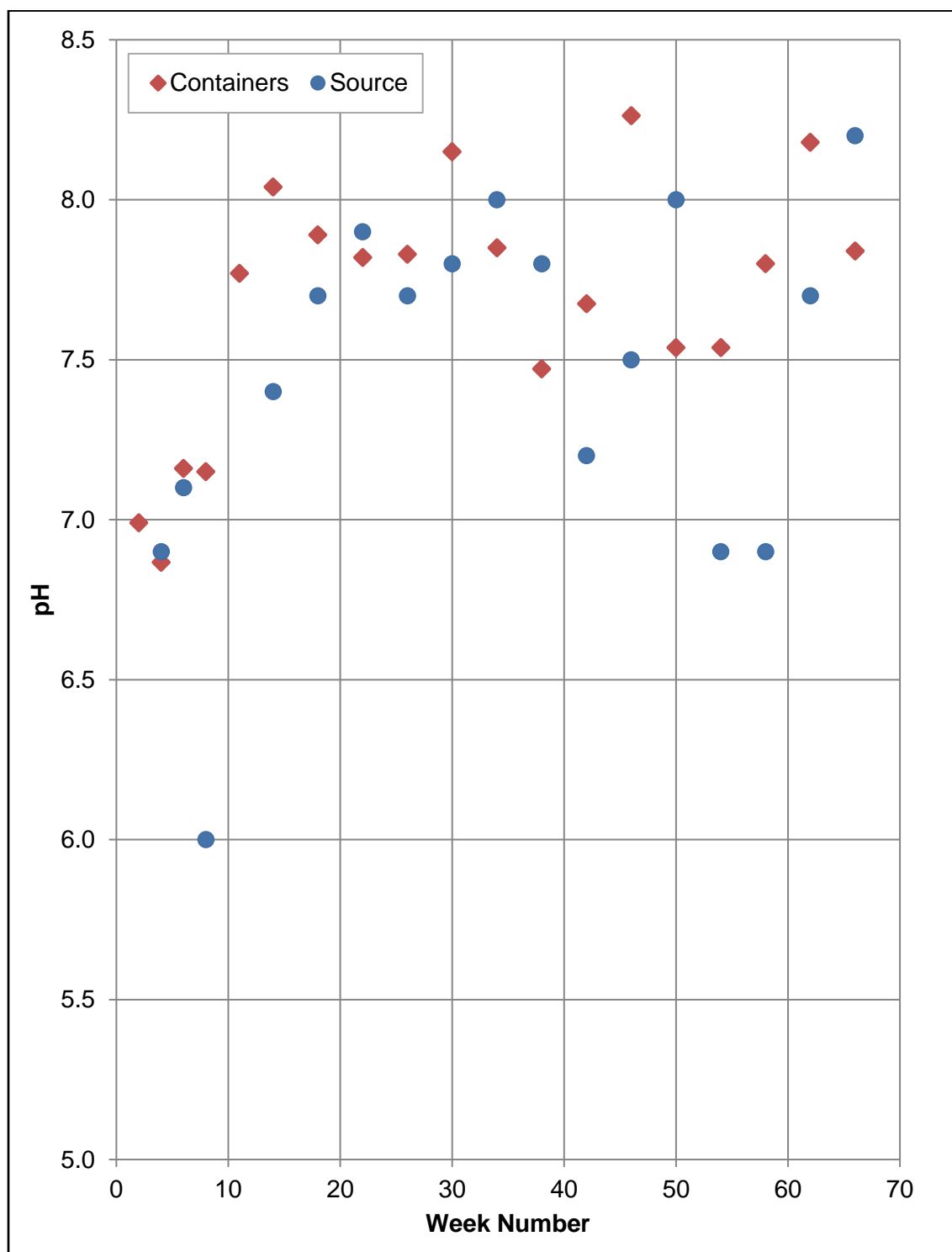


Figure 47. Average pH in containers has an inconsistent relationship with pH in source water.

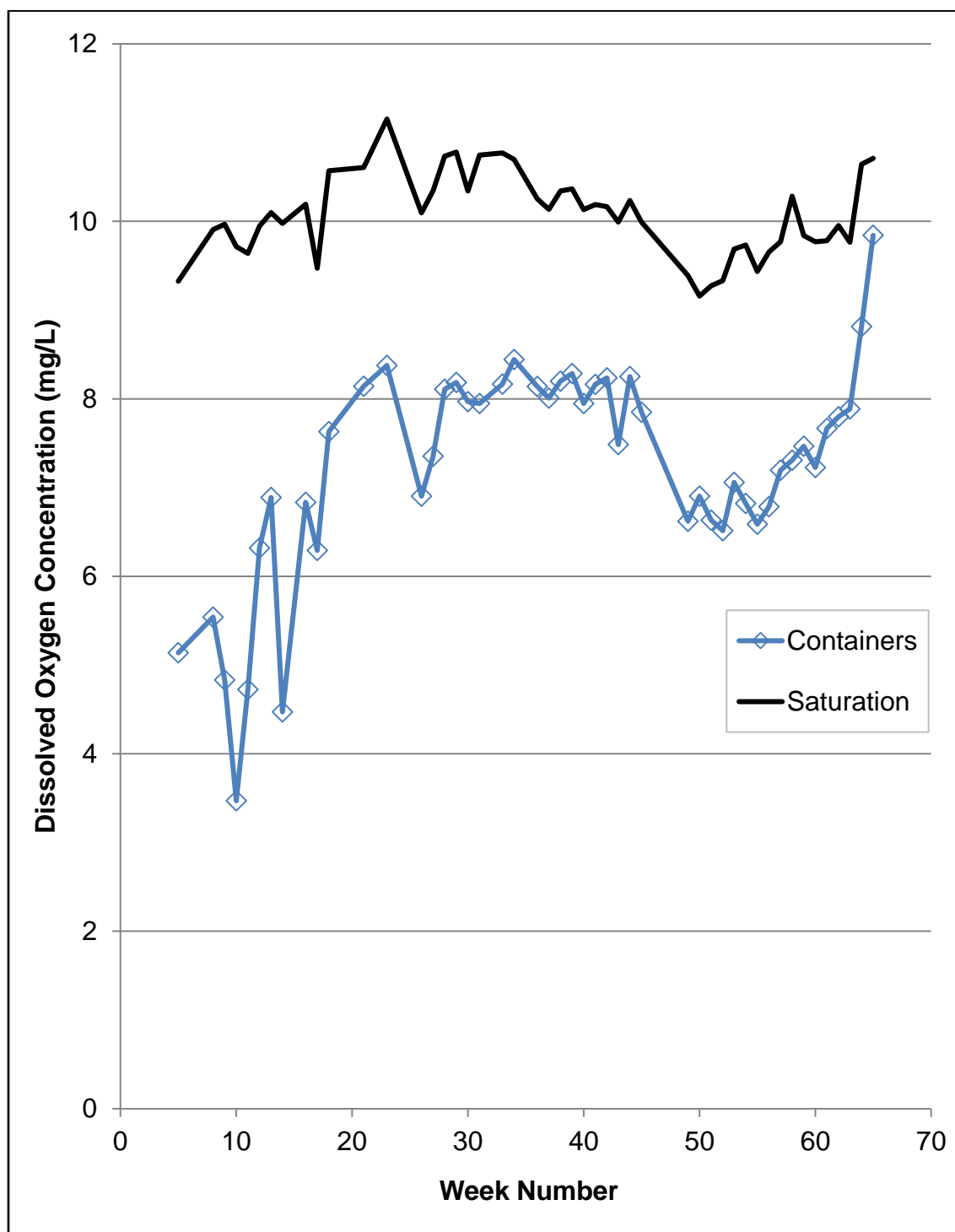


Figure 48. Average dissolved oxygen concentration in all containers with saturated dissolved oxygen concentration.

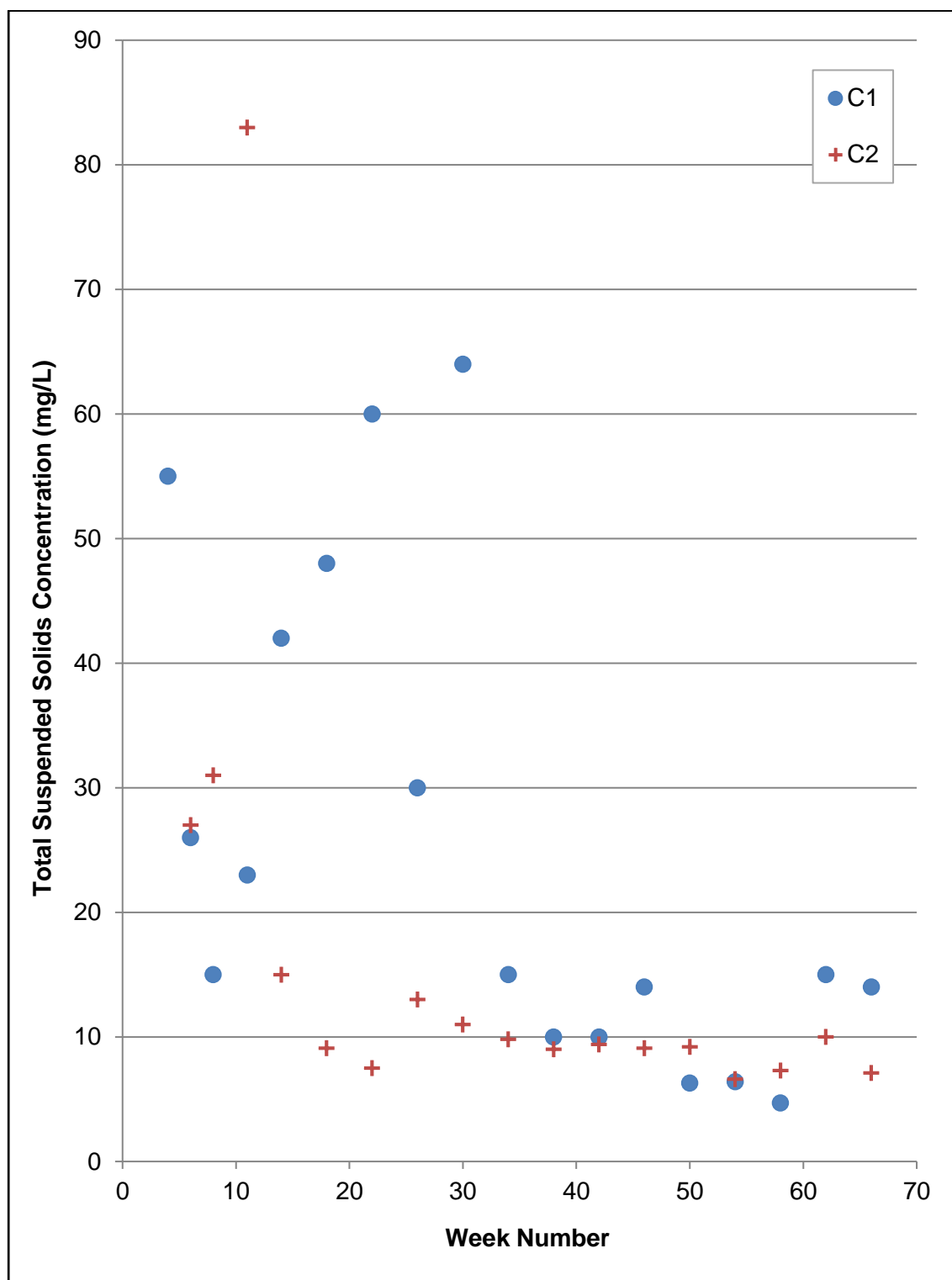


Figure 49. Total suspended solids concentration over time.

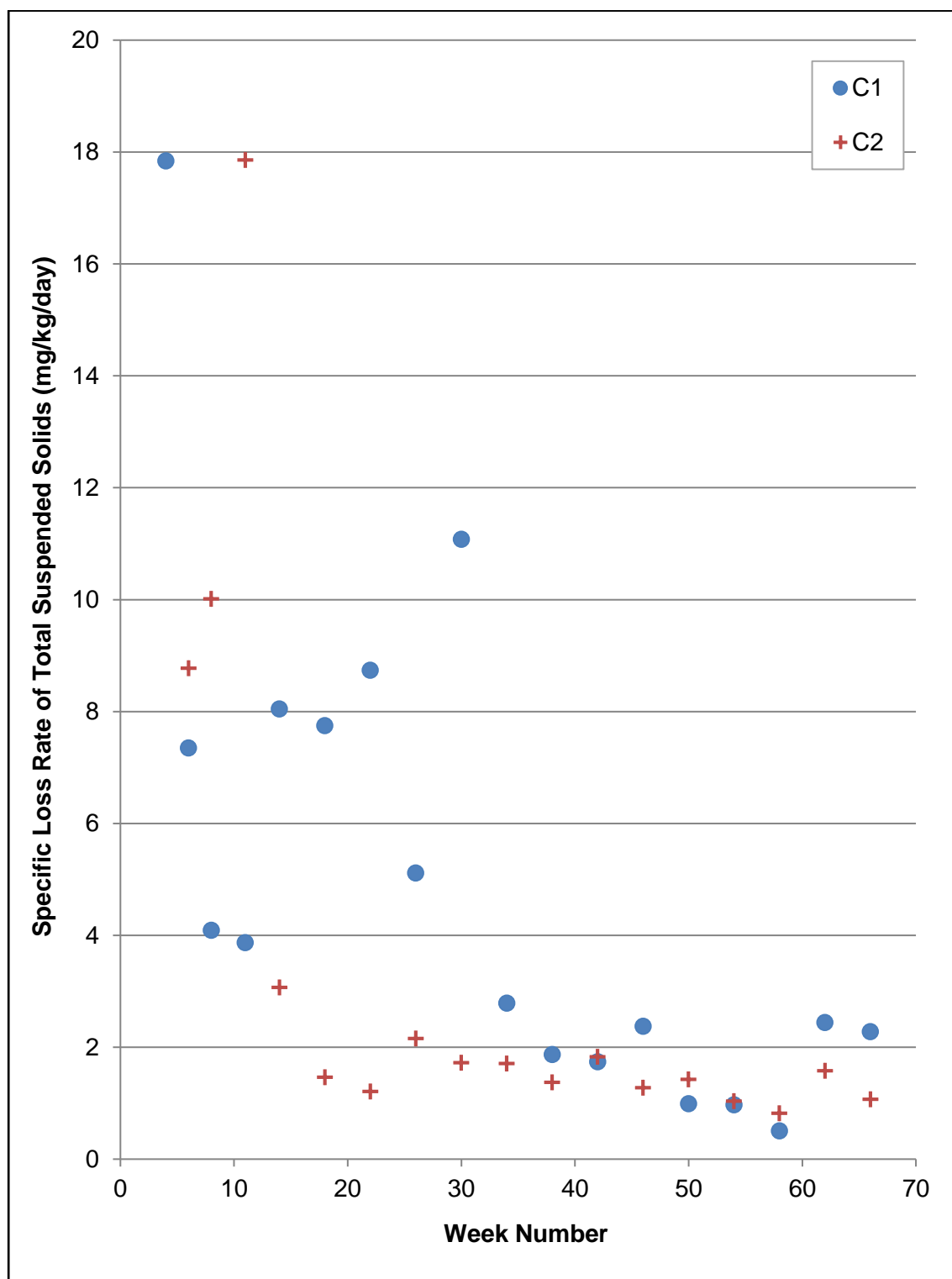


Figure 50. Total suspended solids specific loss rate over time.

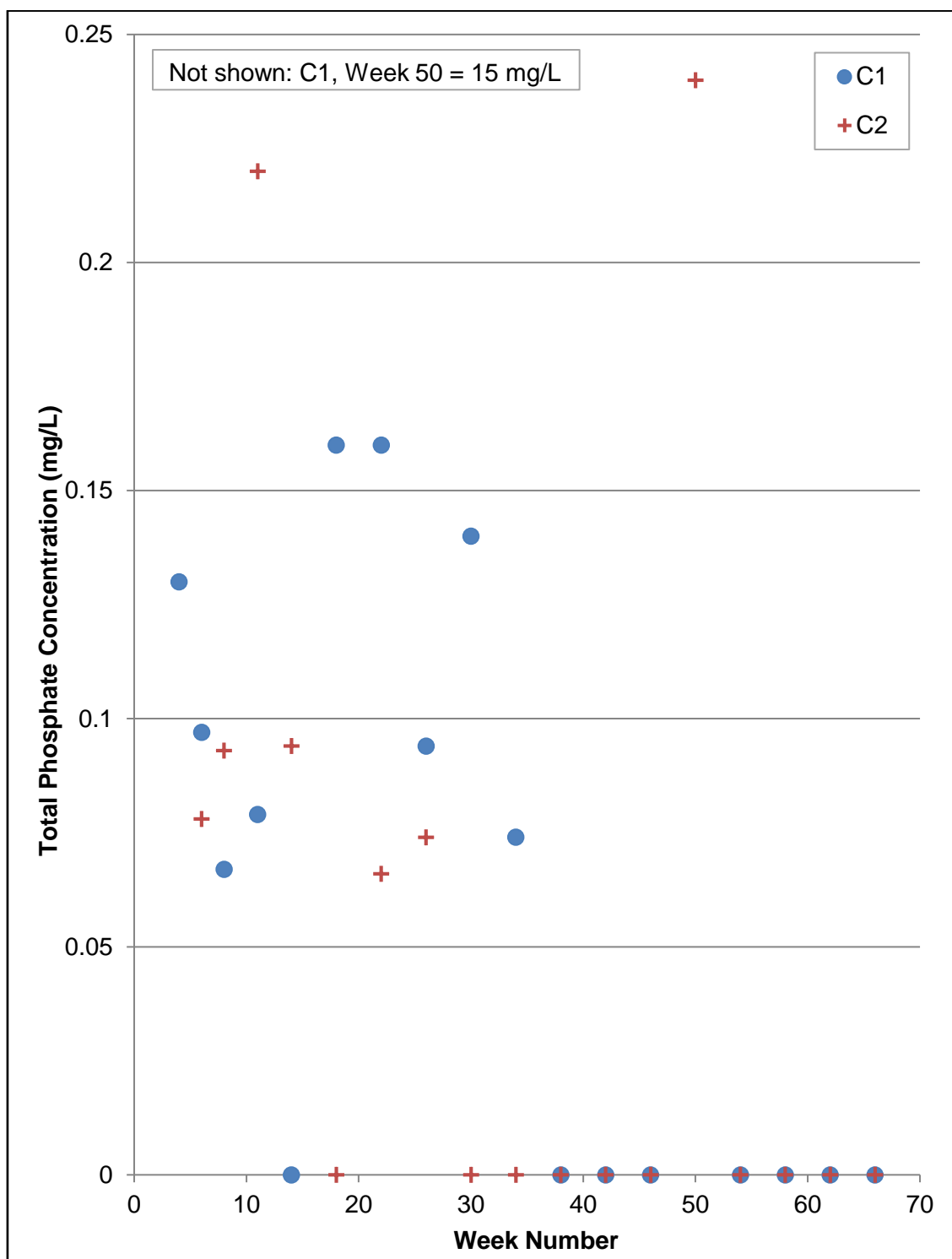


Figure 51. Total phosphate concentration drops below the detection limit (0.06 mg/L) by Week 38.

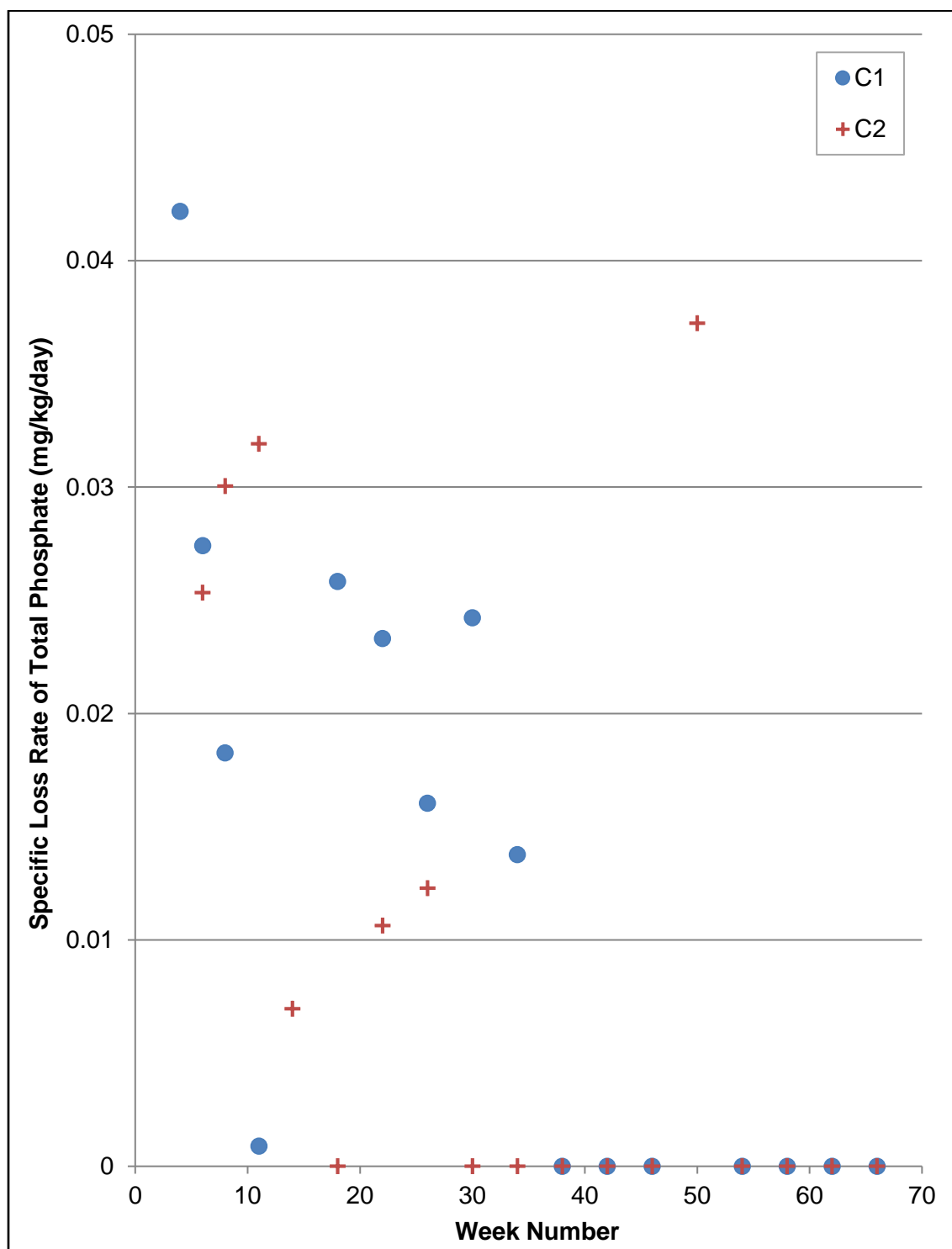


Figure 52. Total phosphate specific loss rate over time.

### Summary of Constituents Suspected to Originate in the TDA

The results of the laboratory experiment identified constituents that are suspected to originate from TDA. These include: benzene, methyl isobutyl ketone (MIBK), total phosphate, total suspended solids, cadmium, iron, manganese, and zinc. Concentrations detected in the laboratory are compared to select drinking water standards (Table 28). Benzene and MIBK concentrations decreased rapidly. Benzene levels were below the detection limit (0.3 ug/L) by Week 34. A rapid decrease in benzene concentration was also observed in previous studies (Gunter et al., 1999; Miller and Chadik, 1993). Miller and Chadik (1993) suspect that benzene accumulates from gasoline contamination during a tire's use as a vehicle tire and will therefore leach from the media when first exposed to an aquatic environment. MIBK levels were below the detection limit (0.6 ug/L) by the end of the study. This downward temporal trend was also observed by Gunter et al. (1999). Phosphate concentrations ranged from nondetect (detection limit = 0.06 mg/L) to 0.24 mg/L for the first six months, after which all but one sample were below the detection limit. Similar to the majority of detected constituents, a downward trend over time in total suspended solids was observed.

When above the detection limit, cadmium concentrations were typically at least two orders of magnitude less than the Secondary MCL of 0.005 mg/L. Iron exceeded its Secondary MCL of 0.3 mg/L in nearly all samples. Manganese concentrations often exceeded the Secondary MCL of 0.05 mg/L. With the exception of the always wet containers, concentrations were below 0.05 mg/L by the end of the study. Zinc concentrations were initially an order of magnitude less than its Secondary MCL of 5



mg/L, and two orders of magnitude less by the end of the study. Previous literature suggests that elevated levels of cadmium, iron, manganese, and zinc are typical of TDA leachate (e.g., Downs et al., 1996; Edstrom et al., 2008; Finney et al., 2013; Humphrey and Katz, 2001; Miller and Chadik, 1993; Sheehan et al., 2006).

Table 28. Concentrations of constituents suspected to leach from TDA compared to regulatory standards. Blank cells indicate no applicable level for indicated constituent.

<b>Constituent</b>	<b>CA MCL</b>	<b>EPA MCL</b>	<b>EPA Secondary MCL</b>	<b>Maximum</b>	<b>Average</b>	<b>Minimum</b>
Benzene (ug/L)	1	5		0.97	0.58*	<0.30
Cadmium (mg/L)	0.005	0.01		0.0018	0.000088*	<0.00002
Iron (mg/L)			0.3	26.3	3.4	0.1
Manganese (mg/L)			0.05	0.39	0.11	0.01
MIBK (ug/L)				9.9	3.55	<1.0
Total Phosphate (mg/L)				15	0.7*	<0.06
TSS (mg/L)			500	83	18	2.5
Zinc (mg/L)			5	0.686	0.134	0**

\*Average computed with values above the detection limit, \*\*concentration in container less than that of source water

## Field Results

The water quality constituents identified to originate from the TDA based on the laboratory portion of this study are the focus of the field experiment analysis. Other tested constituents will also be discussed, but the laboratory experiment demonstrates that these constituents are not suspect of leaching from TDA.

The TDA fill was placed on August 13<sup>th</sup>, 2014 and sampling began with a rain event on October 14, 2014. A total of 12 events were sampled (Table 29). A groundwater sampling port was installed during the dry season on September 18<sup>th</sup>, 2015 and three samples were collected and analyzed before a significant rain event. The TSS results suggest that disturbance from construction affected the groundwater quality for the first two sample dates (Table 30). The third sample date (10/7/15) will therefore be used as the dry season background groundwater concentration for this site. Groundwater was also sampled from this location during rain events. The concentration of water quality constituents in the pan and lysimeter sample locations below the TDA fill during rain events appear to be independent of the concentrations found in the groundwater sample location. For example, with the exception of a single data point, the concentration of tetrachloroethane in the groundwater samples is considerably higher than observed in the pan or lysimeter (Figure 53).

Table 29. Sampling event number with corresponding date.

<b>Sampling Event Number</b>	<b>Date Sampled</b>
1	10/14/2014
2	10/23/2014*
3	11/19/2014
4	12/3/2014
5	12/10/2014
6	2/5/2015
7	3/15/2015
8	3/22/2015
9	11/15/2015
10	11/24/2015
11	12/2/2015*
12	12/9/2015*

(\*) = Pan and/or lysimeter samples taken the following day

Table 30. Concentrations for groundwater samples during dry season.

<b>Compound</b>	<b>9/20/2015</b>	<b>9/23/2015</b>	<b>10/7/2015</b>
Cadmium (mg/L)	0.00047	0.00040	ND
COD (mg/L)	270	27	ND
EC (umhos/cm)	290	240	240
Iron (mg/L)	56	6.6	0.7
Lead (mg/L)	0.0280	0.0050	0.0001
Manganese (mg/L)	1.4	0.58	0.51
Nitrate as NO <sub>3</sub> (mg/L)	4.6	6.1	6.3
pH	6.87	6.55	6.72
Phosphate (mg/L)	8.7	0.8	0.2
Sulfate (mg/L)	17	15	15
Tetrachloroethene (ug/L)	42	36	26
TSS (mg/L)	250	150	21
Zinc (mg/L)	0.12	0.12	0.08

A failure of the physical integrity of the pan occurred in March of 2015; therefore all subsequent sampling events do not include results from this location. For some rain events, insufficient pore soil water was collected to allow testing of all constituents in the pan and lysimeter. Missing samples will be noted in text. A few other considerations should be noted for interpreting the results:

- The results from this portion of the study reflect the effects of a TDA fill and approximately one foot of soil, a configuration that would be typical of a TDA application. The TDA and soil system will be referred to as 'the TDA system'.
- The concentration of constituents typically found in a particulate form (the metals in particular) may vary in the pan and lysimeter due to a variation in the pore size opening of the sampling equipment.
- Effects of dilution from direct rainfall onto the rain garden was considered, but a consistent decrease in concentration from the gutter to the pre-TDA was not observed. Because areas were comparable between the gutter and pre-TDA to that between the pre-TDA and the location of the pan and lysimeter, precipitation dilution effects from the pre-TDA to the pan and lysimeter were likely insignificant.
- The referenced regulatory standards are applicable for drinking water. The comparison of the data from the field experiment to these regulatory standards serves only as a reference point to known standards. The selected drinking water regulations are not applicable to typical TDA applications.

The detected constituents will be presented in one of two categories based on results from the laboratory analysis: constituents that are suspected to come from the TDA and those that are not. Other constituents were occasionally observed above their respective detection limits, including chloroform, cis-1,2-dichloroethene, methyl ethyl ketone, toluene, tetrachloroethene, trichloroethene, and vinyl chloride. These constituents will not be further discussed here, but a full set of data can be found in Appendix E.

Precipitation data from the Nation Weather Service office in Eureka (Figure 54) provides a reference for when the TDA fill may be wet, but the values are cumulative daily amounts and therefore do not serve as an indication of when the TDA fill is submerged. To identify times and the level at which the TDA fill was submerged, five-minute water levels from one of the two pressure transducers were plotted (Figure 55). A comparison of water levels at the two pressure transducers during a few storm events shows that the water level in the entire TDA fill is generally uniform (Figure 56).

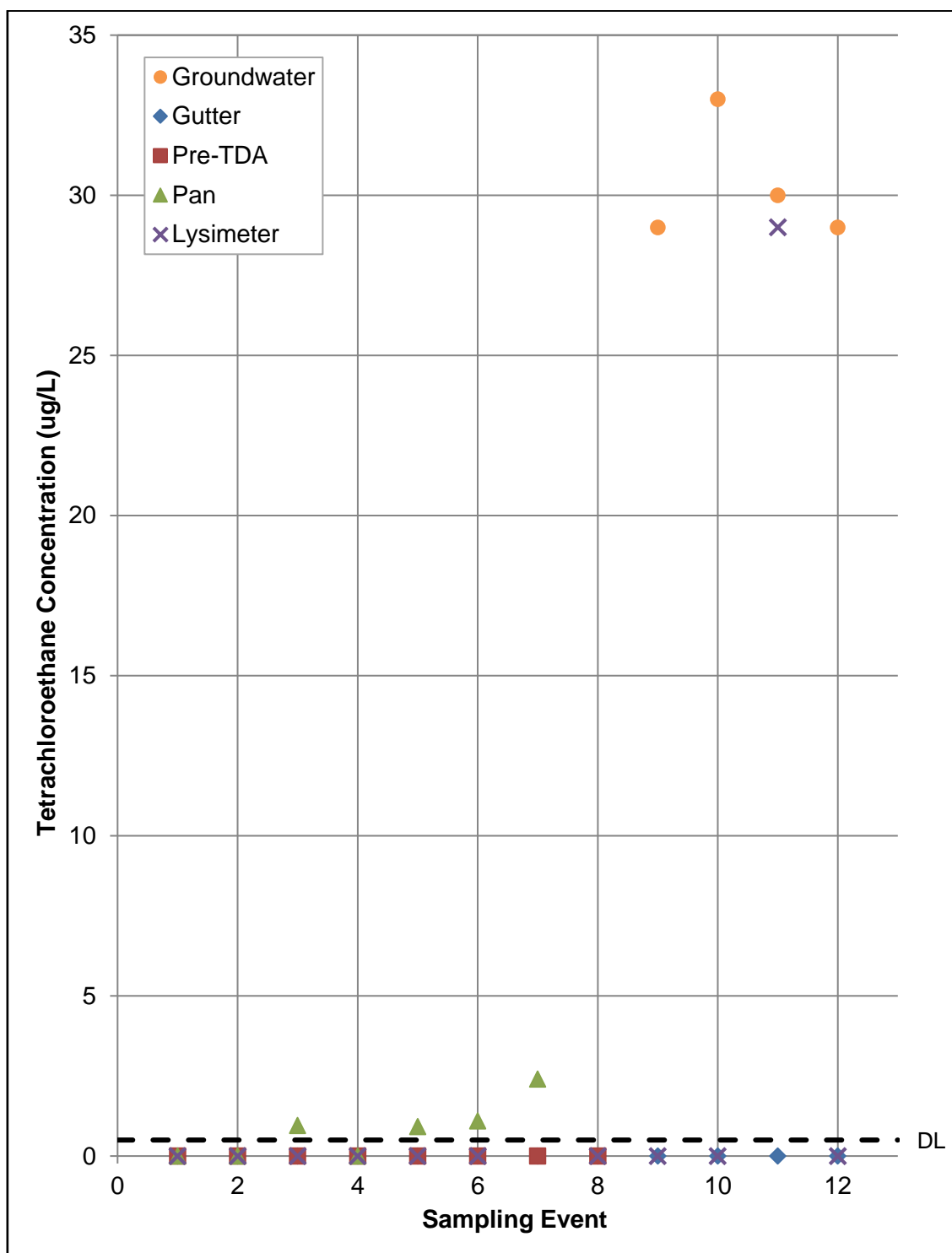


Figure 53. With the exception of a single event, the concentration of tetrachloroethane suggests groundwater does not enter sampling points below the TDA-soil system.

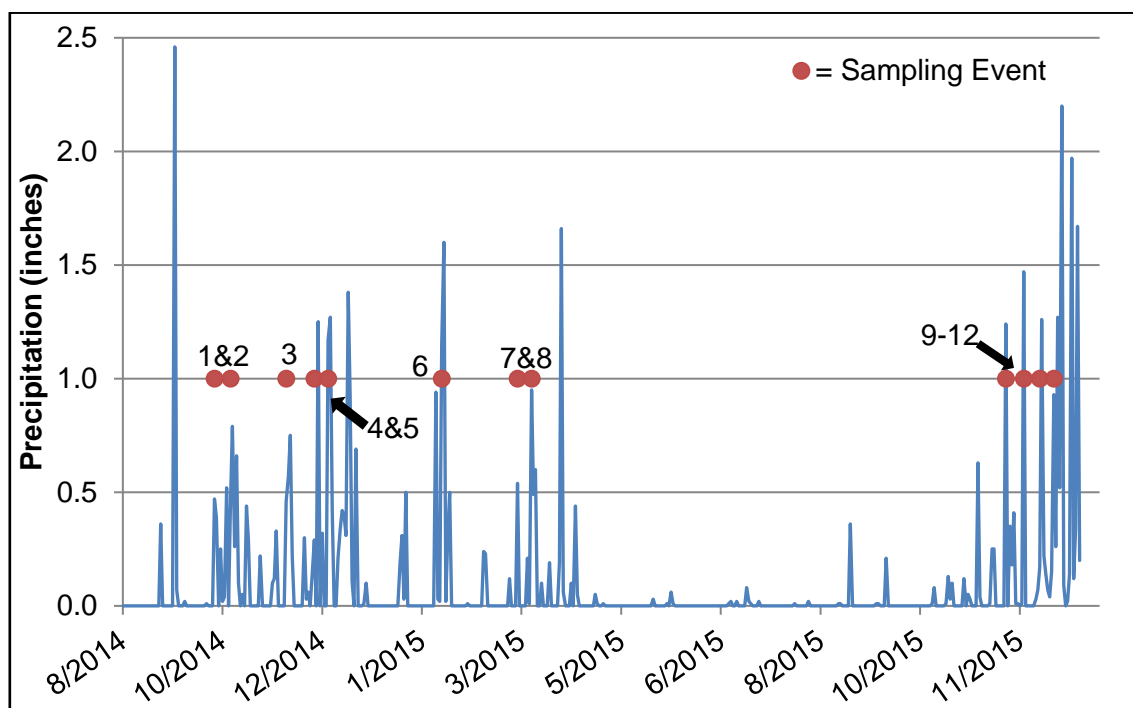


Figure 54. Precipitation with Sampling Events (NOAA, 2016).

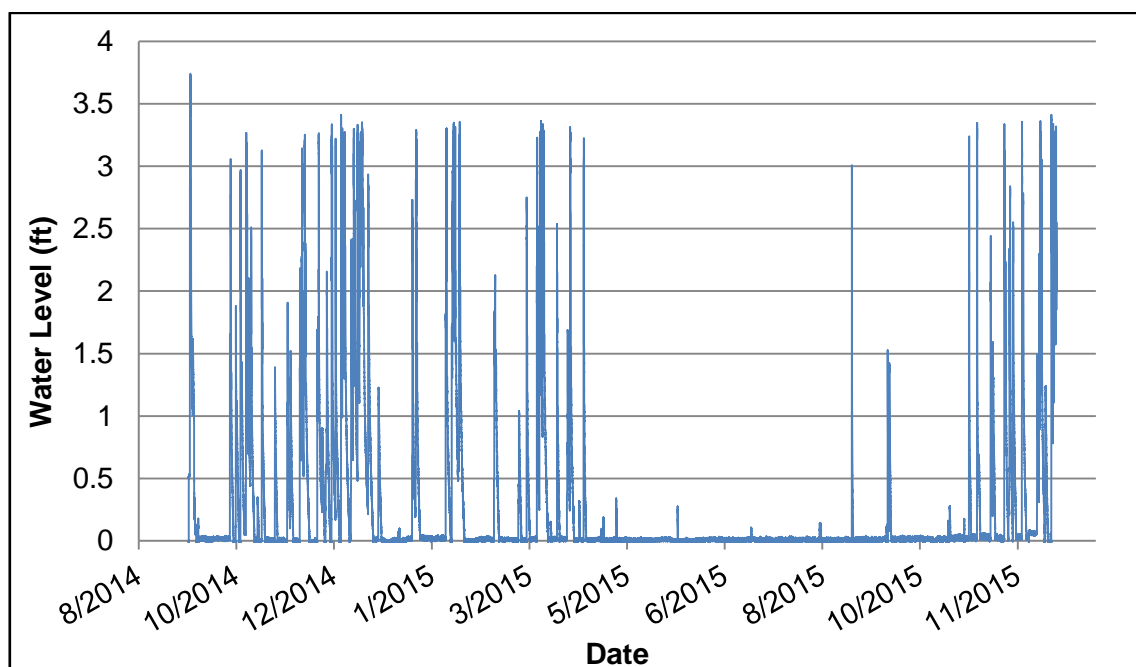


Figure 55. Water level of TDA fill where zero is the base of the fill and levels above 2.7 feet indicate the fill is completely submerged.

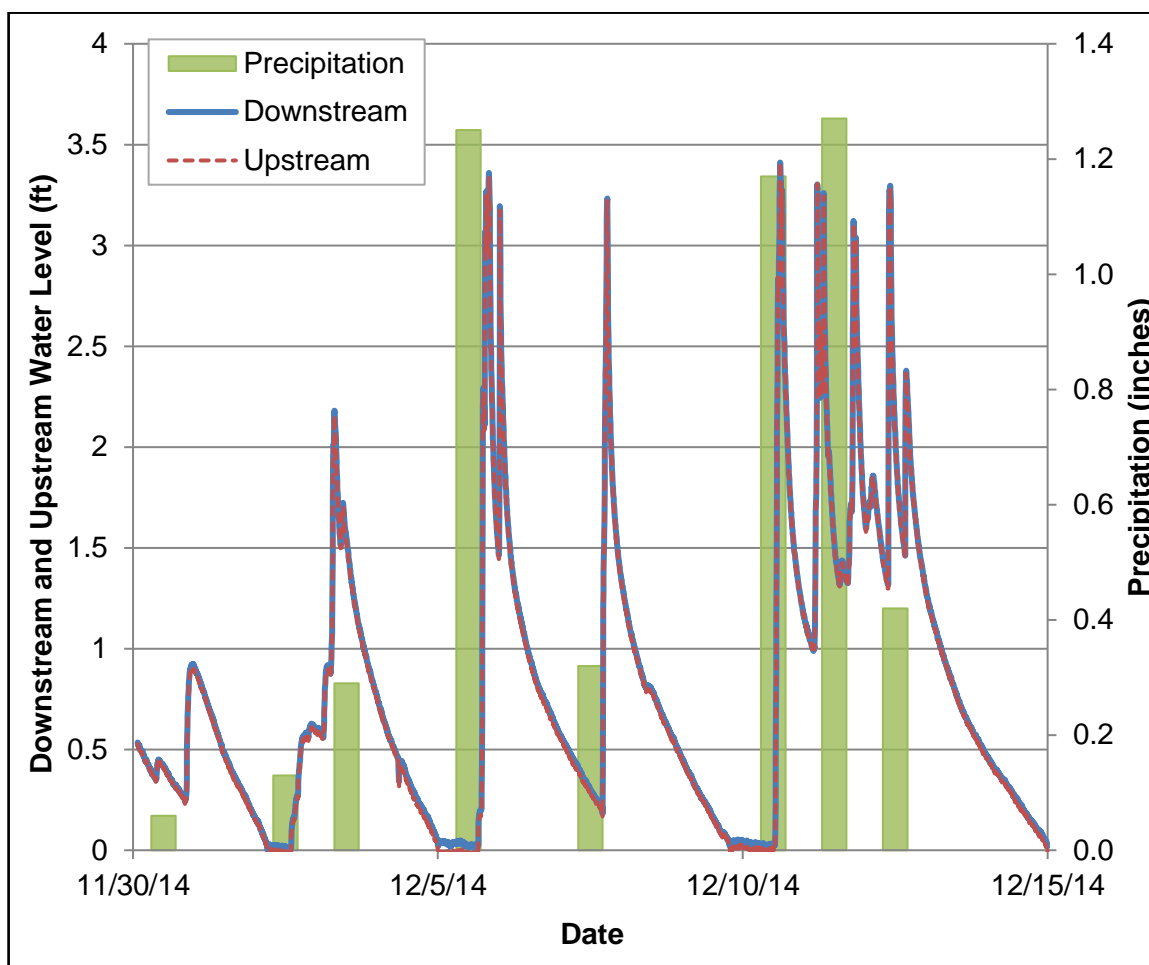


Figure 56. Five-minute water level and daily precipitation data for selected time interval. Trace amounts of precipitation were observed on 12/6/14 and 12/14/14.

#### Constituents Suspected to Originate from TDA

Results from the laboratory analysis identified several compounds that likely originate from the TDA. The field results for these constituents are presented in the following sections.



### *Iron*

With the exception of the last two sampling events for the lysimeter, all iron concentrations were above the detection limit. Concentrations in the pan and lysimeter were below those of the gutter and pre-TDA for all sampling events, with two instances in which the pan concentration was greater than the Secondary MCL (0.3 mg/L) (Figure 57). However, all samples for the gutter, pre-TDA and groundwater exceeded the Secondary MCL, suggesting that the system removes iron from the stormwater runoff. Furthermore, the system removes iron to levels below that of the surrounding groundwater during a rain event and to levels below the detection limit for the last two sampling events. With the exception of Sampling Event 7 in the pan, the concentration of iron in the pan and lysimeter were always less than the dry season background groundwater value of 0.69 mg/L.

### *Manganese*

Manganese concentrations were typically lower in the pan and lysimeter as compared to those of the gutter and pre-TDA (Figure 58). All results were above the detection limit (0.0004 mg/L) with the exception of the lysimeter for Sampling Event 11. The highest concentrations observed in the pan and lysimeter occurred in the first two sampling events, all subsequent results for these locations were less than those of the gutter and pre-TDA with the exception of a single data point (Sampling Event 5 in the lysimeter). Concentrations in the pan and lysimeter were all within or below those of the groundwater and all but two data points from the first two sampling events were below

the Secondary MCL (0.05 mg/L). All results shown in Figure 58 are below the measured dry season background of 0.51 mg/L.

### *Zinc*

With the exception of a single sampling event (Sampling Event 9), all zinc concentrations in the pan and lysimeter were less than those of the gutter and pre-TDA (Figure 59). All samples were above the detection limit (0.0005 mg/L). The maximum concentration detected below the system was in the lysimeter during Sampling Event 9 at 0.083 mg/L. This value falls within the range of the surrounding groundwater and is well below the Secondary MCL of 5 mg/L. The lower values found in the pan and lysimeter suggest that the TDA system removes zinc from the stormwater runoff. Zinc is typically removed to concentrations less than that of the surrounding groundwater, and less than the dry season background concentration of 0.081 mg/L.

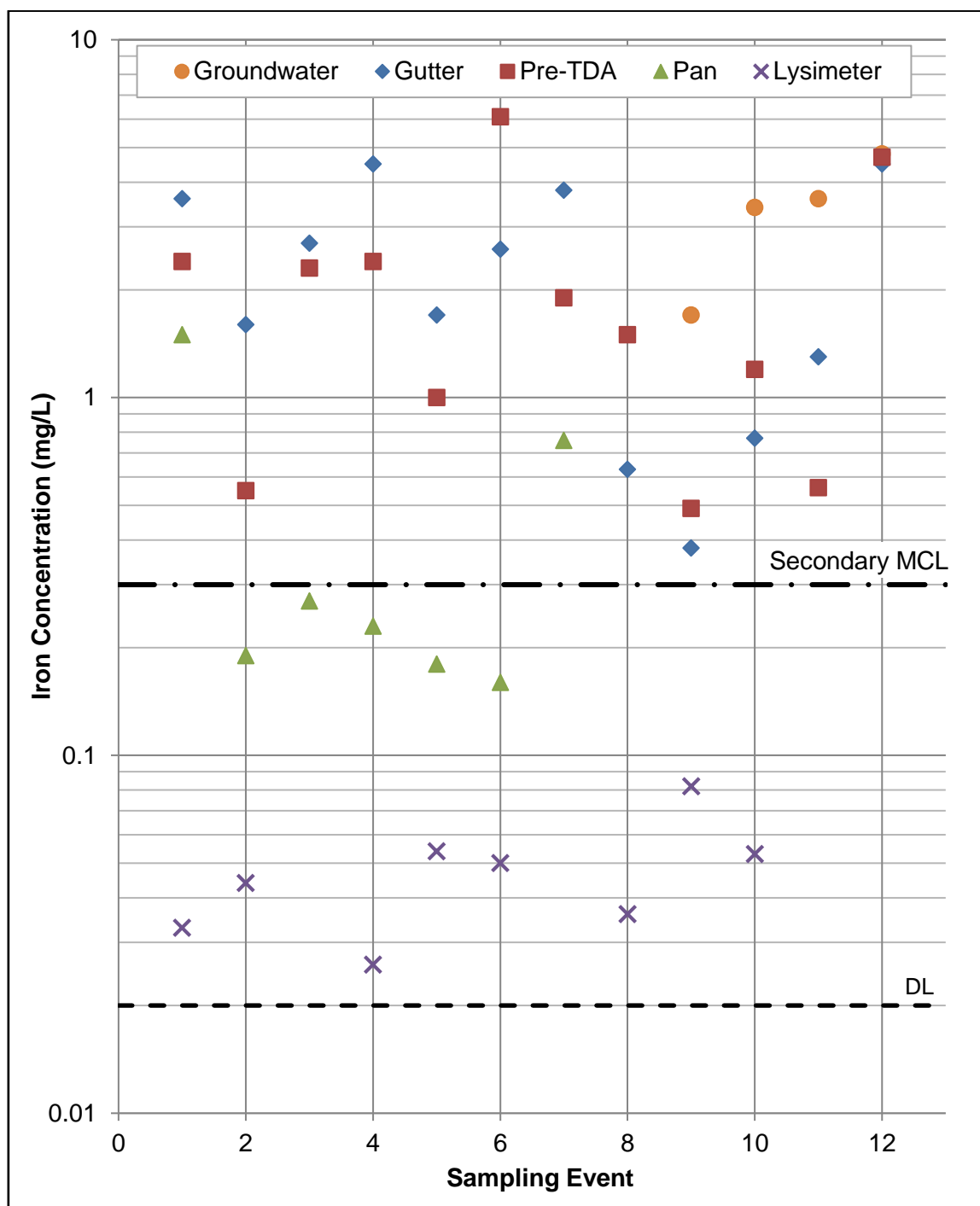


Figure 57. Iron concentrations at sampling locations below the TDA fill (pan and lysimeter) are typically below those of the gutter and pre-TDA. The last two results for the lysimeter were below the detection limit. All other missing data points were samples not collected. (Note: logarithmic vertical scale).

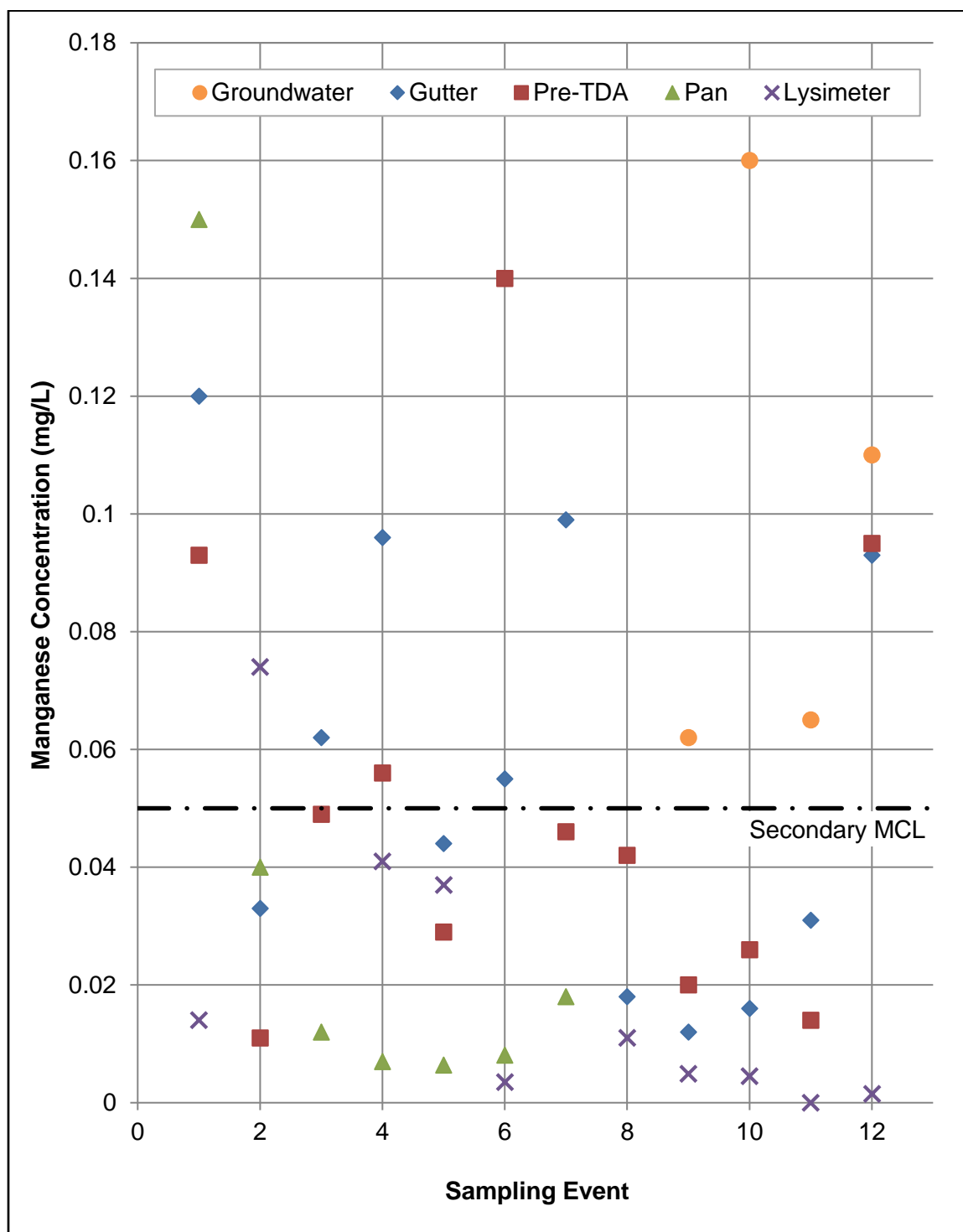


Figure 58. Manganese concentration at sampling locations compared to Secondary MCL (0.05 mg/L).

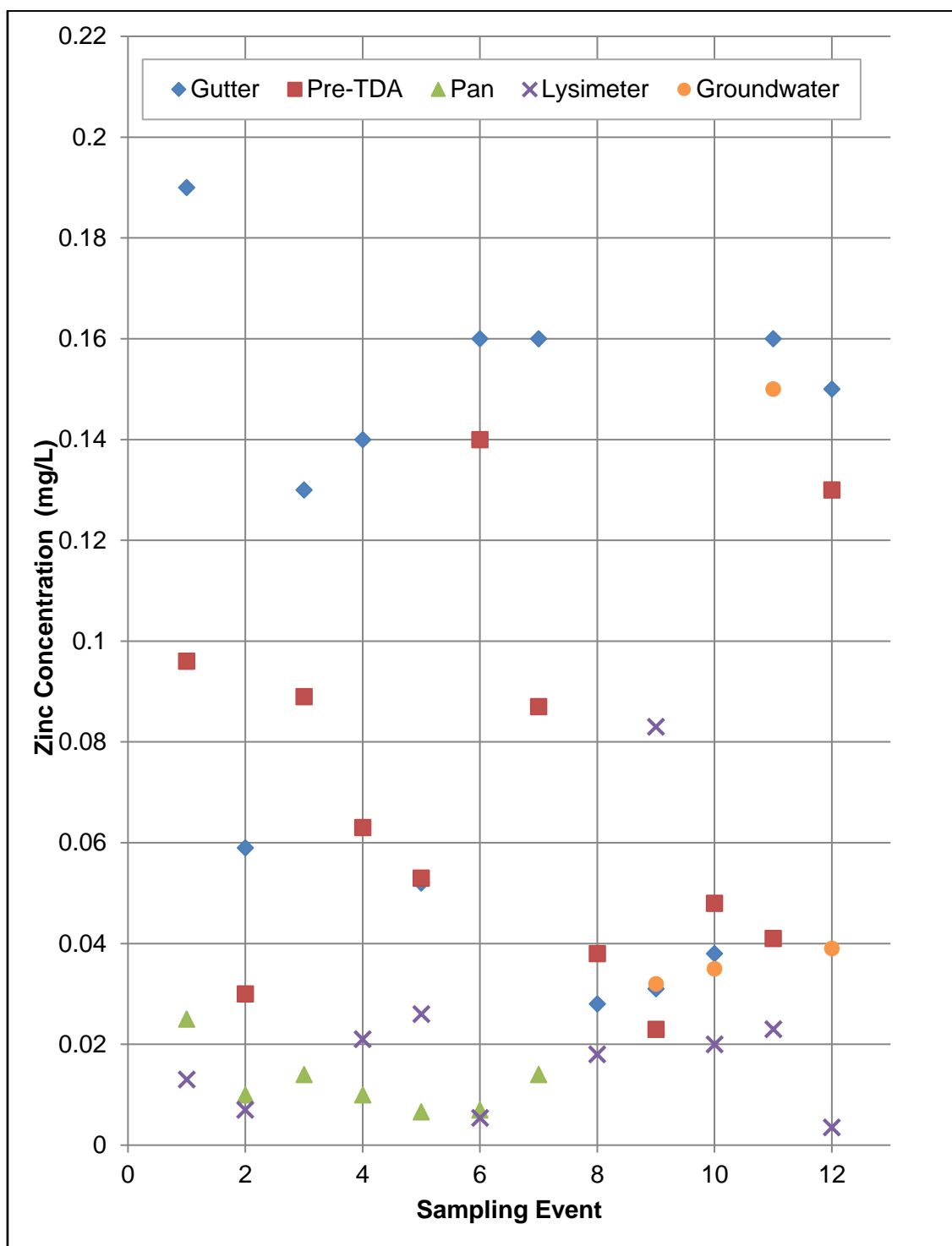


Figure 59. All zinc concentrations at sampling locations are below the Secondary MCL (5 mg/L). Detection limit (not shown) varied between 0.0005 mg/L and 0.002 mg/L.

### *Cadmium*

Cadmium was detected in the pan and lysimeter for the first two sampling events, after which the compound was only detected in the gutter, pre-TDA, and groundwater (Figure 60). For the first sampling event, concentrations in the pan and lysimeter were less than those of the gutter and pre-TDA. For the second sampling event, concentrations were the same in the lysimeter and gutter, and not detectable in the pre-TDA and pan. The detection limit increased fourfold after Sampling Event 2 with the exception of the pan for Sampling Event 6 and the gutter for Sampling Event 8. Since cadmium concentrations in the sampling points below the TDA system during the first two sampling events were below the increased detection limit, a decrease in concentration cannot be confirmed. However, the increased detection limit is two orders of magnitude less than the CA MCL of 0.005 mg/L and groundwater concentrations for the last three sampling events are higher than any samples below the TDA system.

### *Methyl Isobutyl Ketone*

Methyl isobutyl ketone (MIBK) was detected in the gutter and pre-TDA before the TDA system in approximately 85% of the samples and below the TDA system in only a single sample (Sampling Event 3 in the lysimeter) at 1.2 ug/L (Figure 61). The MIBK concentrations in the gutter and pre-TDA were more than twice as high compared to that of the lysimeter for Sampling Event 3. All subsequent MIBK concentrations were above the detection limit in the gutter and pre-TDA, and below the detection limit for the pan and lysimeter. These results suggest the TDA system provides MIBK removal. Levels of

MIBK for the groundwater samples both during rain events and in the dry season were below the detection limit.

#### *Total Phosphate*

Total phosphate was detected in all collected samples. For Sampling Events 8, 9, and 10, insufficient soil pore water was collected in the pan and lysimeter to allow determination of the total phosphorus below the TDA system. When sampled, the concentration of total phosphate below the TDA system was less than that of the sampling locations before the system (Figure 62). The highest concentration detected below the TDA system was 0.36 mg/L (Sampling Event 1 in the pan), less than all rain event groundwater samples and only slightly greater than the dry season background (0.22 mg/L). Results from this portion of the study indicate that the TDA system removes total phosphate found in the stormwater runoff to levels less than those of the groundwater.

#### *Total Suspended Solids*

All samples analyzed for total suspended solids (TSS) were above the detection limit of 1.0 mg/L. Concentrations in the pan and lysimeter were less than those of the gutter and pre-TDA for all sampling events. The maximum concentration detected below the TDA system was 37 mg/L (Sampling Event 1 in the pan) with typical concentrations ranging from 2-15 mg/L, less than the concentration range of 30 to 63 mg/L for the groundwater samples.

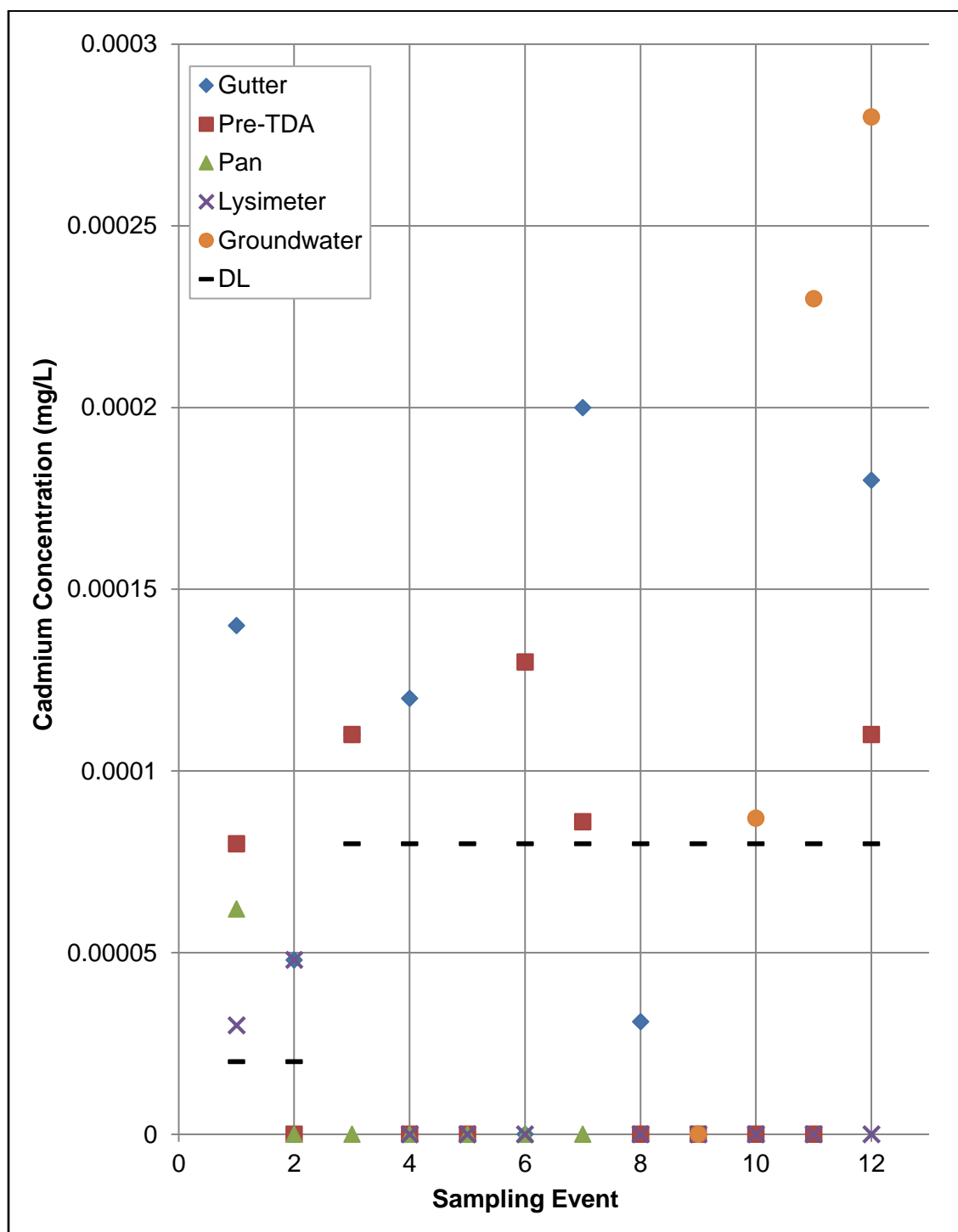


Figure 60. All cadmium concentrations at sampling locations were below the California MCL of 0.005 mg/L. The detection limit varied between 0.00002 mg/L and 0.00008 mg/L.



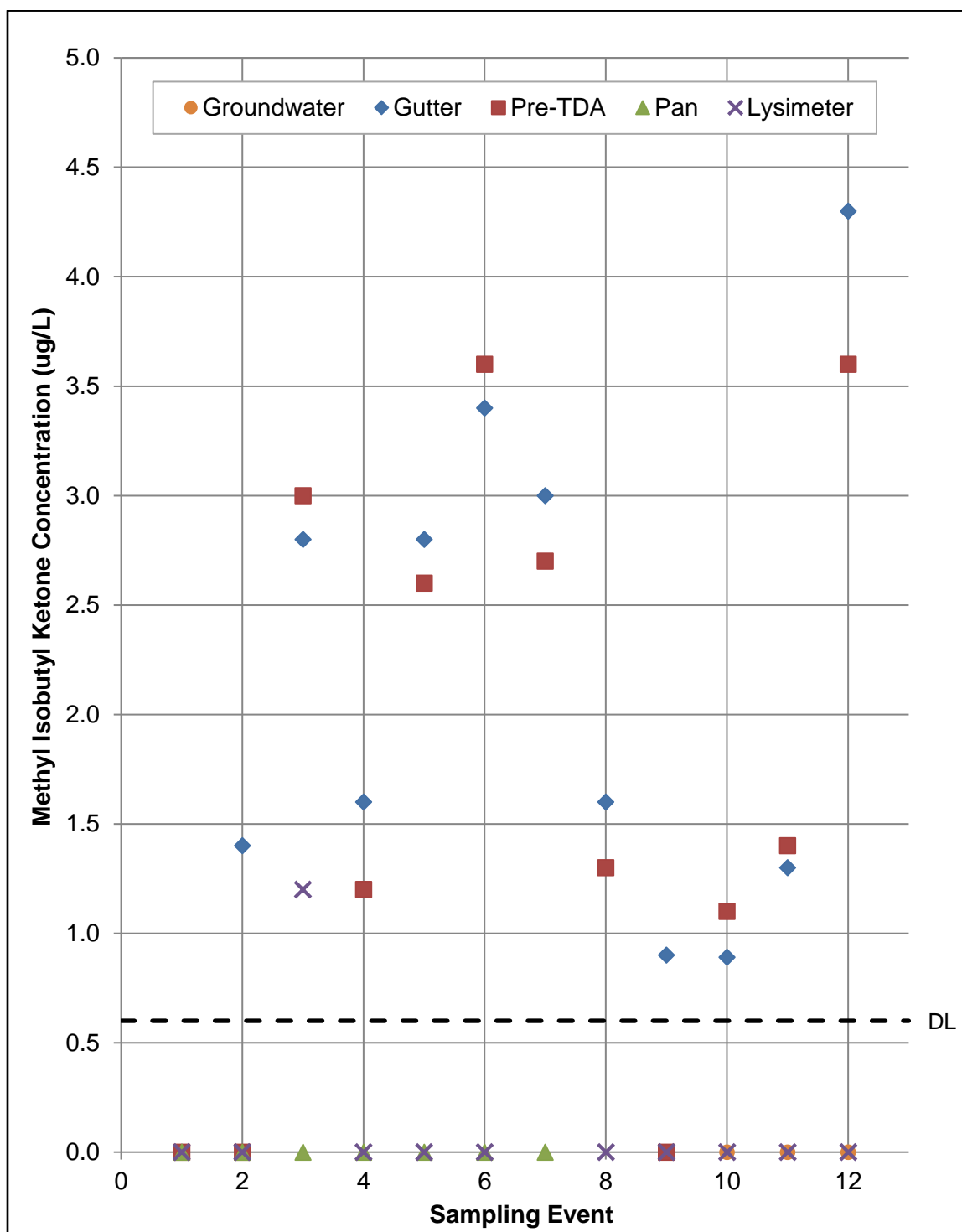


Figure 61. Methyl isobutyl ketone concentrations at sampling locations with shown detection limit (0.6 ug/L).

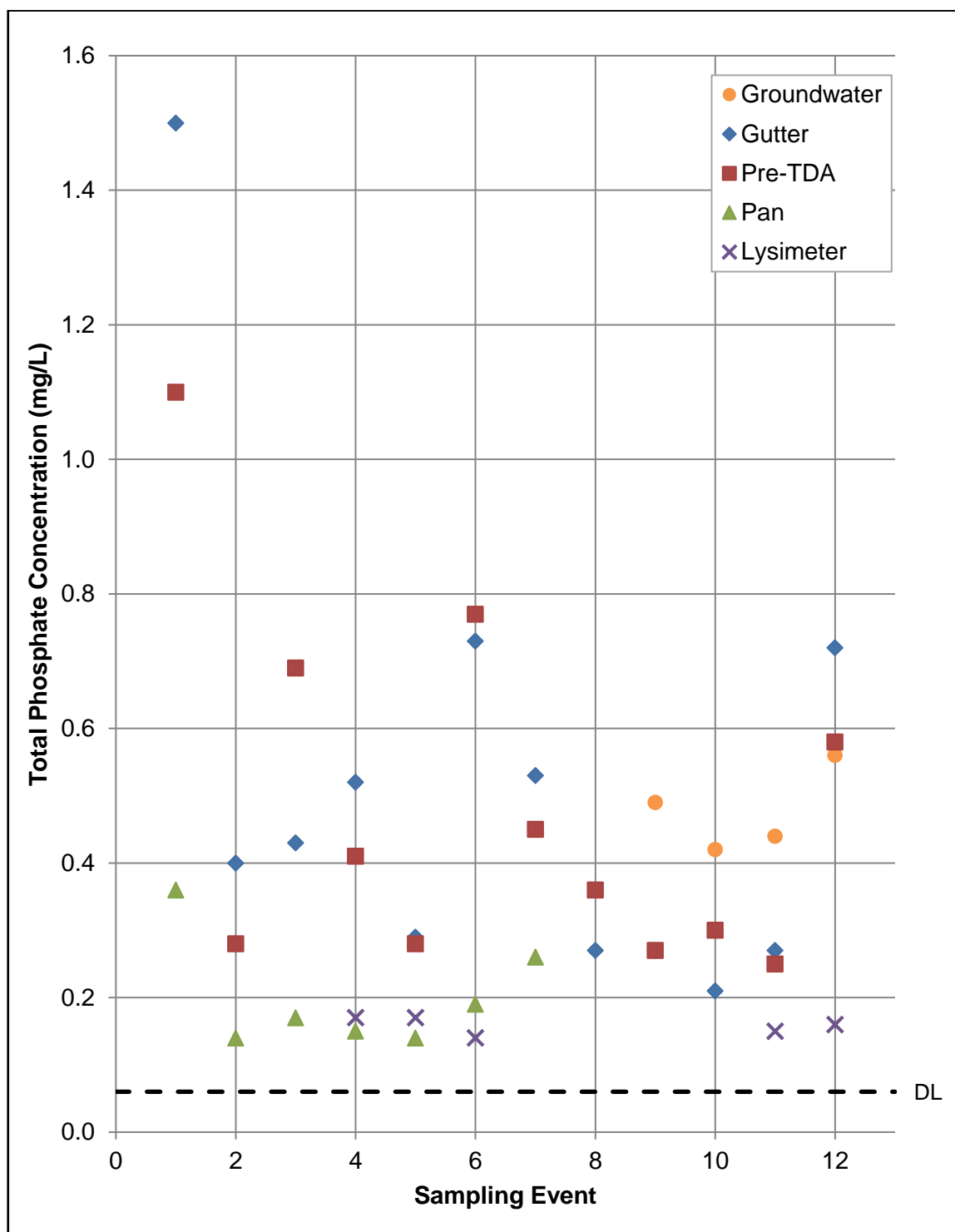


Figure 62. Total phosphate concentrations at sampling locations with all samples above the detection limit (0.06 mg/L).

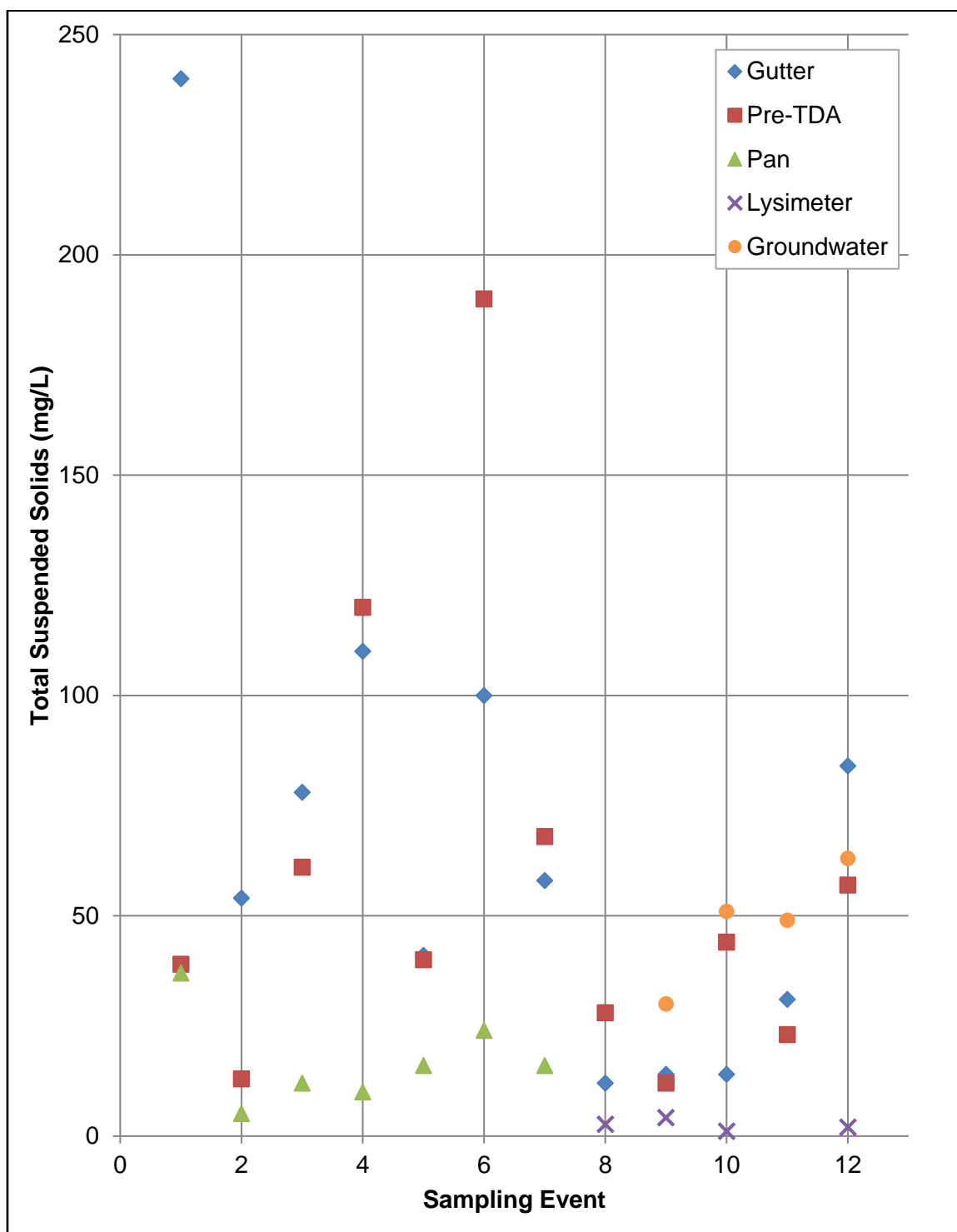


Figure 63. Total suspended solids concentrations at sampling locations with all samples above the detection limit (not shown) of 1.0 mg/L.

### Compounds not Suspected to be Originating from TDA

Although several of the following compounds were observed at higher concentrations after the TDA system, the TDA cannot be confirmed as the source of these constituents. The composition of the soil and a layer of sand beneath the cobble is unknown and may be the source of these constituents.

#### *Sulfate and Specific Conductance*

For all sampling events, sulfate concentrations in the pan and lysimeter were higher than those of the gutter and Pre-TDA (Figure 64). All samples collected were above the detection limit (0.09 mg/L). Of all the samples, the highest concentration appeared in the lysimeter during Sampling Event 9 at 29 mg/L. The highest concentration found in the groundwater (14 mg/L) corresponds with this sampling event.

Approximately half of the samples in the pan and lysimeter exceeded the dry season background of 15 mg/L, however, all concentrations are an order of magnitude below the Secondary MCL of 250 mg/L. Although these field results suggest sulfate may leach from the system, the laboratory results did not provide any evidence that TDA leaches sulfate. Other than the possibility that the soil layer below the TDA fill is contributing the sulfate, the source of sulfate is unidentifiable. All trends observed with sulfate were also observed in specific conductance, which is not suspected to originate from the TDA (Figure 65).

### *Lead*

Lead appeared above the detection limit (0.00002 mg/L) in all samples throughout the experiment (Figure 66). The maximum concentration detected after the system appeared in the lysimeter during Sampling Event 10 at 0.0012 mg/L, an order of magnitude less than the CA MCL of 0.015 mg/L. With the exception of a single sampling event in which the concentration in the lysimeter and gutter were equal, concentrations were typically more than an order of magnitude lower in the pan and lysimeter than those of the gutter and pre-TDA samples. In addition, all the post-system concentrations were less than groundwater concentrations, and fewer than 15% of the post-system concentrations exceeded the dry weather background concentration of 0.00064 mg/L. The results suggest that the system provides treatment of lead for stormwater runoff.

### *Chemical Oxygen Demand*

With the exception of a single sample (Sampling Event 5 in the lysimeter), all samples analyzed for chemical oxygen demand (COD) were above the detection limit of 9 mg/L (Figure 67). The highest concentration detected below the TDA system appeared during Sampling Event 6 in the pan at the same 120 mg/L value as that of the pre-TDA. Instances in which a data point does not appear in the figure indicates the sample was not analyzed for COD. Of the eight sampling events with data available for comparison, there were six sampling events in which COD concentrations were lower in the pan and lysimeter than in the gutter and pre-TDA. In general, concentrations below the TDA system were within the range observed in the groundwater during rain events.

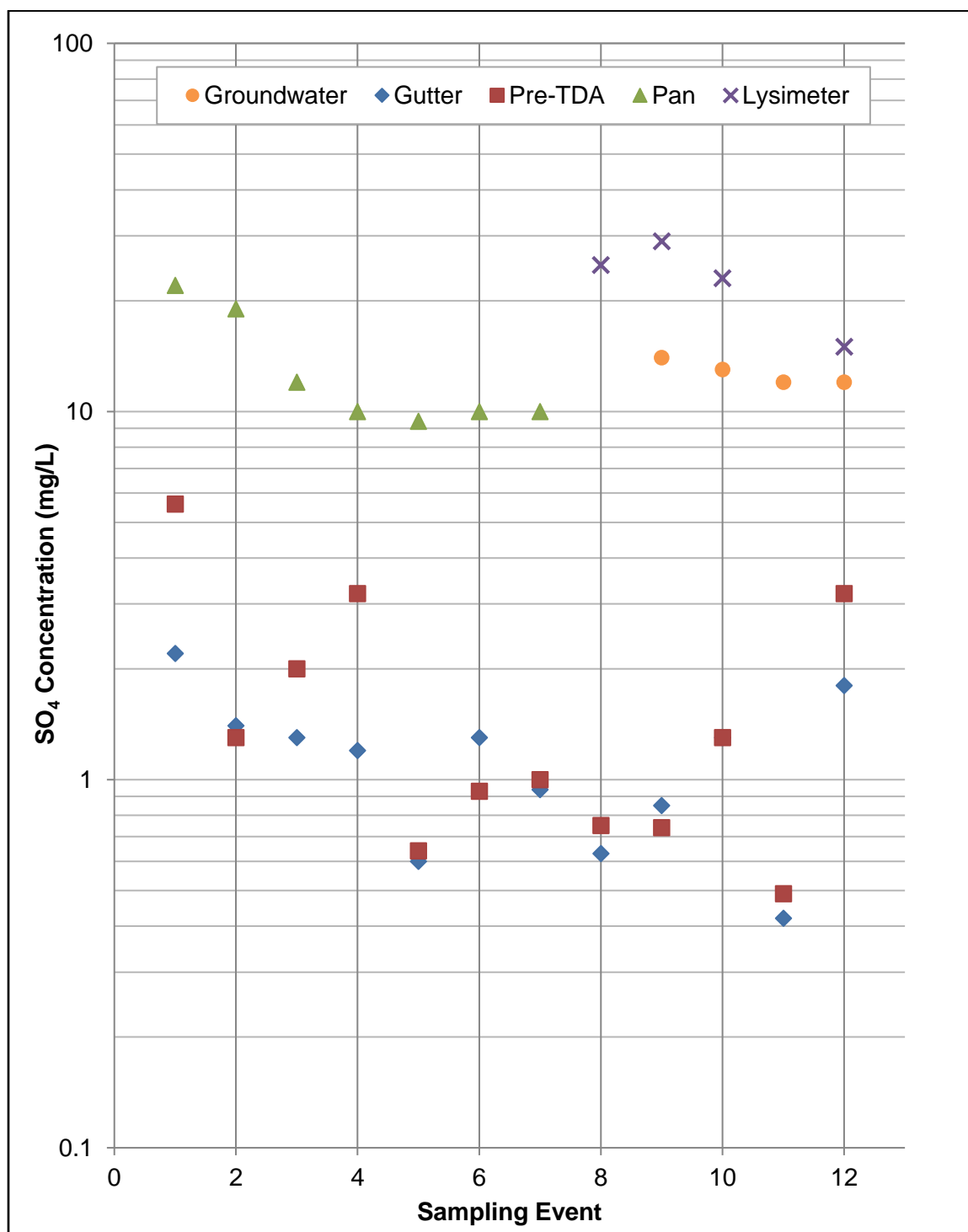


Figure 64. Sulfate concentrations at sampling locations with all samples above the detection limit of 0.09 mg/L. (Note: logarithmic vertical scale).

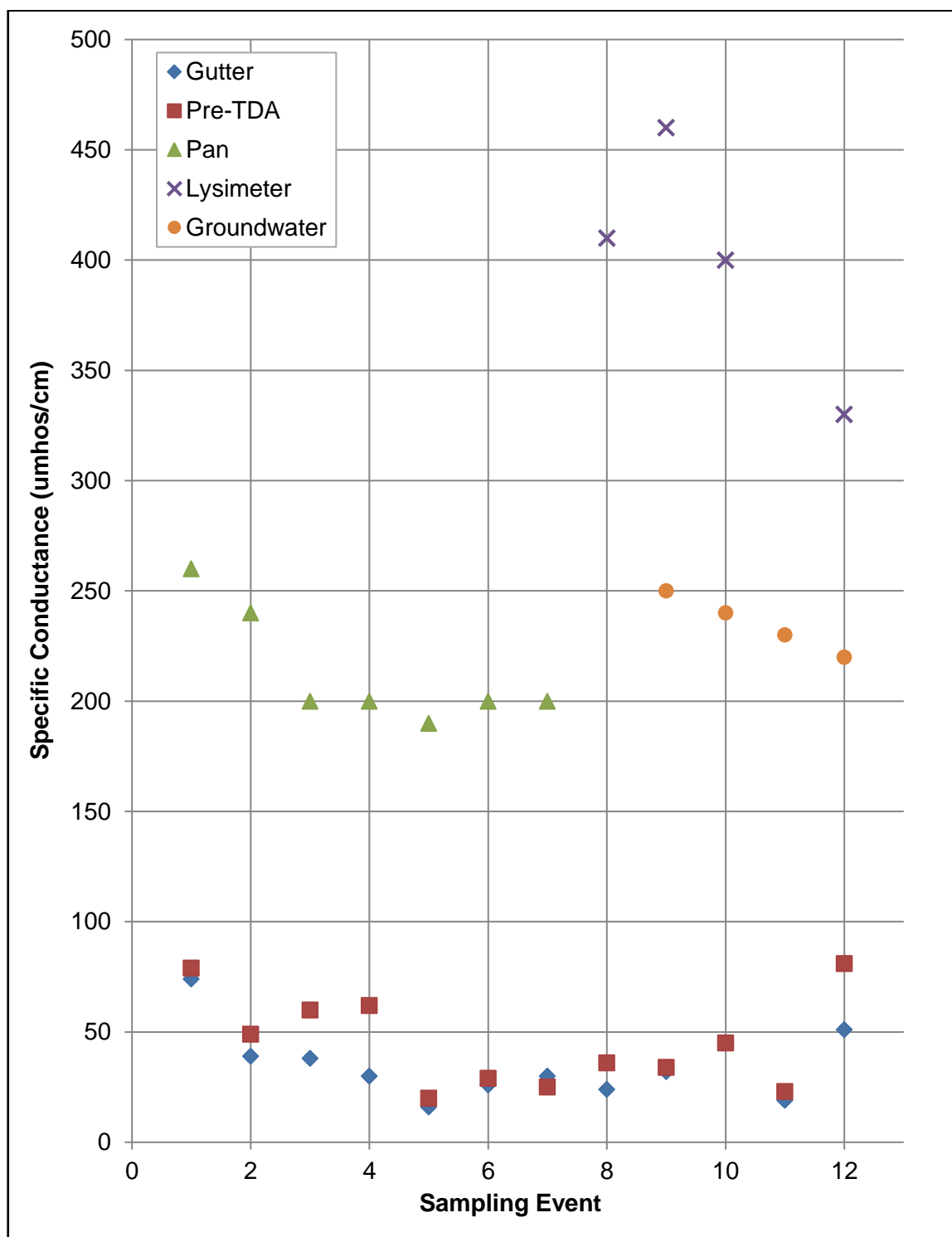


Figure 65. Specific conductance at sampling locations with all samples above the detection limit of 1.0 umhos/cm.

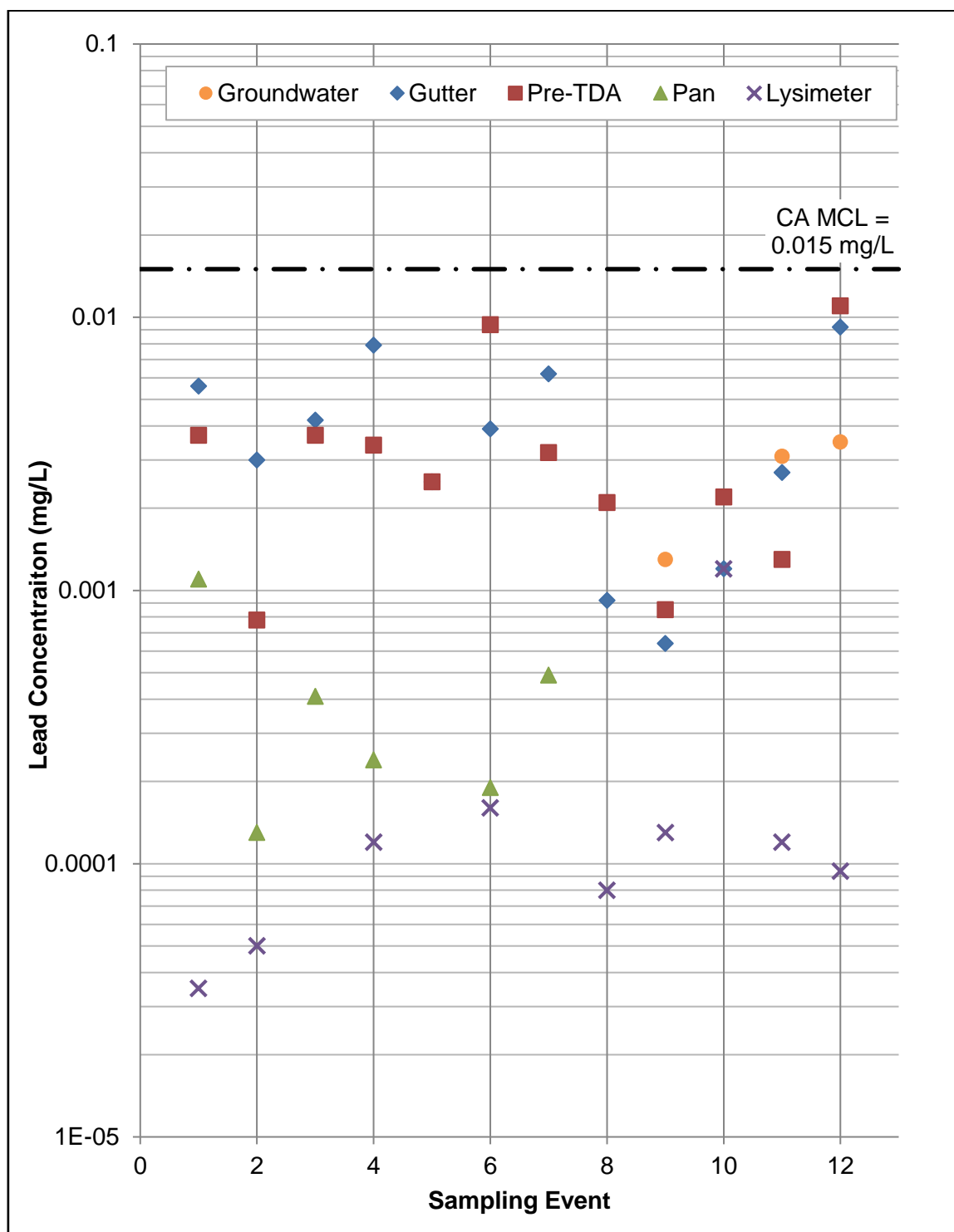


Figure 66. Lead concentrations at sampling locations with all samples above the detection limit of 0.00002 mg/L. (Note: logarithmic vertical scale).



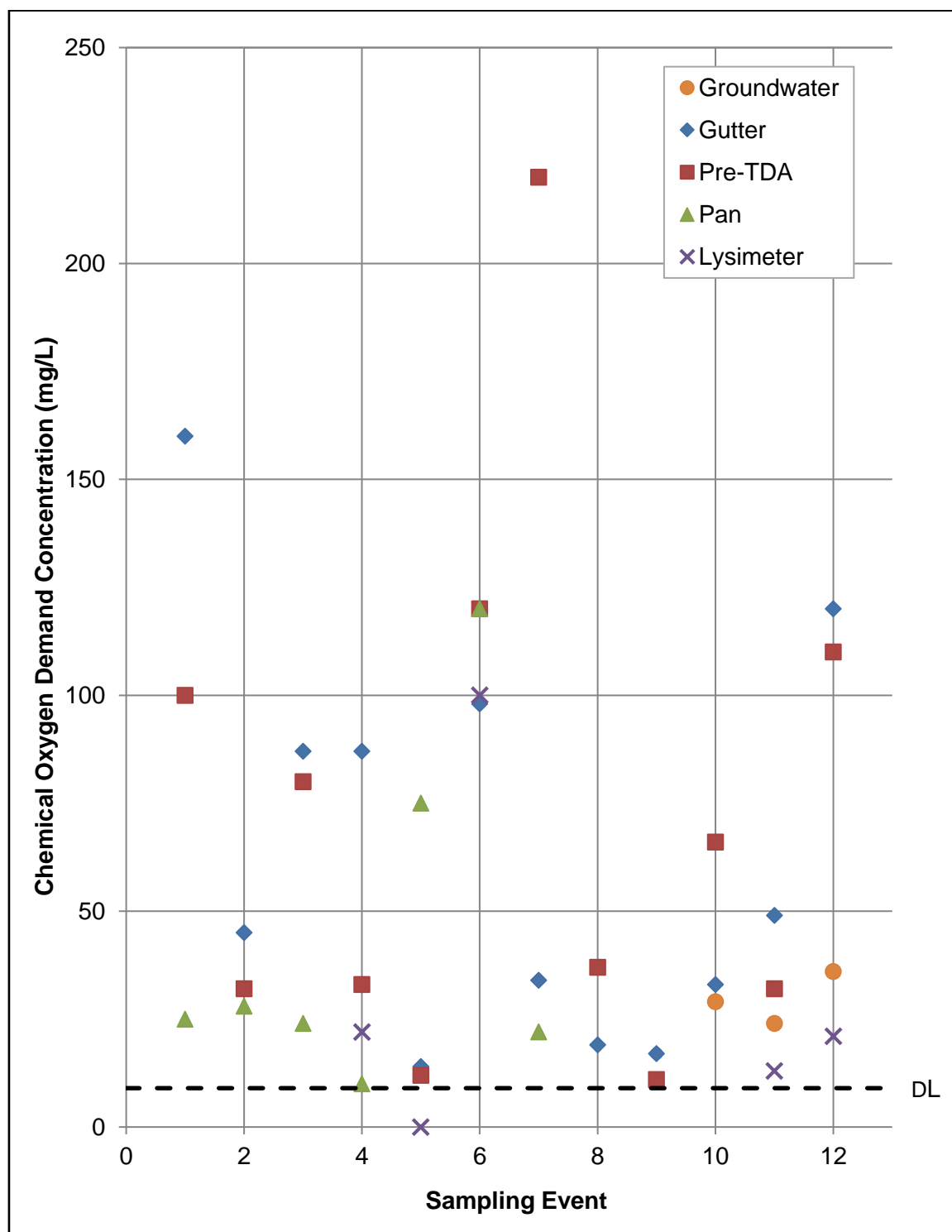


Figure 67. Chemical oxygen demand concentrations at sampling locations. Detection limit is 9 mg/L.

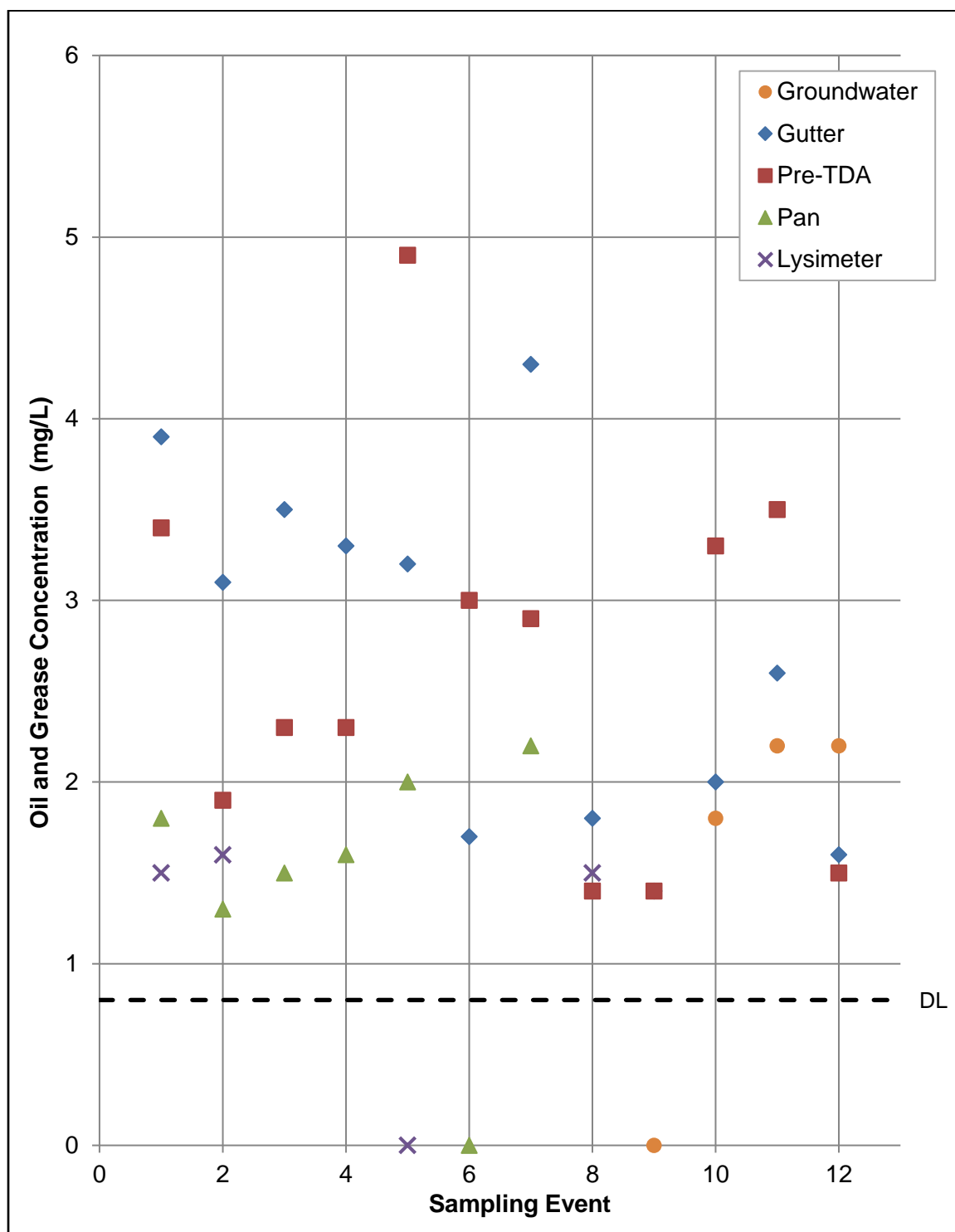


Figure 68. Oil and grease concentrations at sampling locations. Detection limit is 0.8 mg/L.

### *Oil and Grease*

With the exception of a single data point (Sampling Event 8 in the lysimeter), all oil and grease concentrations detected below the TDA system were less than those of the gutter and pre-TDA (Figure 68). Due to a lack of sample water volume available and results from previous events which suggested oil and grease is removed by the system, oil and grease was not analyzed for the last four sampling events in the lysimeter. Concentrations observed in the pan and lysimeter fall within the range detected in the groundwater. These results suggest that the TDA system reduces oil and grease concentration to a level comparable to that of the groundwater.

### *Nitrate*

With the exception of Sampling Event 5, all samples analyzed for nitrate were above the detection limit of 0.2 mg/L (Figure 69). Concentrations in the pan and lysimeter were typically higher than those observed in the gutter and pre-TDA. As with sulfate, prior testing has established that the TDA is not a source of nitrates, therefore the source of nitrates in the post-system samples is either from the sand and cobble layer above the TDA, the soil layer below the TDA or some other unknown source.

### *Acetone*

Acetone was only detected in the gutter and pre-TDA (Figure 71). No sample was above the detection limit of 0.9 mg/L for the pan, lysimeter, and groundwater. These results suggest that the TDA system can provide acetone removal for stormwater runoff.

*pH*

The pH of the pan was typically within the range detected in the gutter and pre-TDA (Figure 72). Results for the lysimeter are consistently higher than all other sampling locations. Although results from the laboratory experiment in this project did not definitively suggest that TDA increases the pH of its environment, other studies (e.g., Miller and Chadik, 1993) have reported the material may slightly increase pH for unknown reasons. All results below the TDA system fall within the Secondary MCL range of 6.5-8.5.

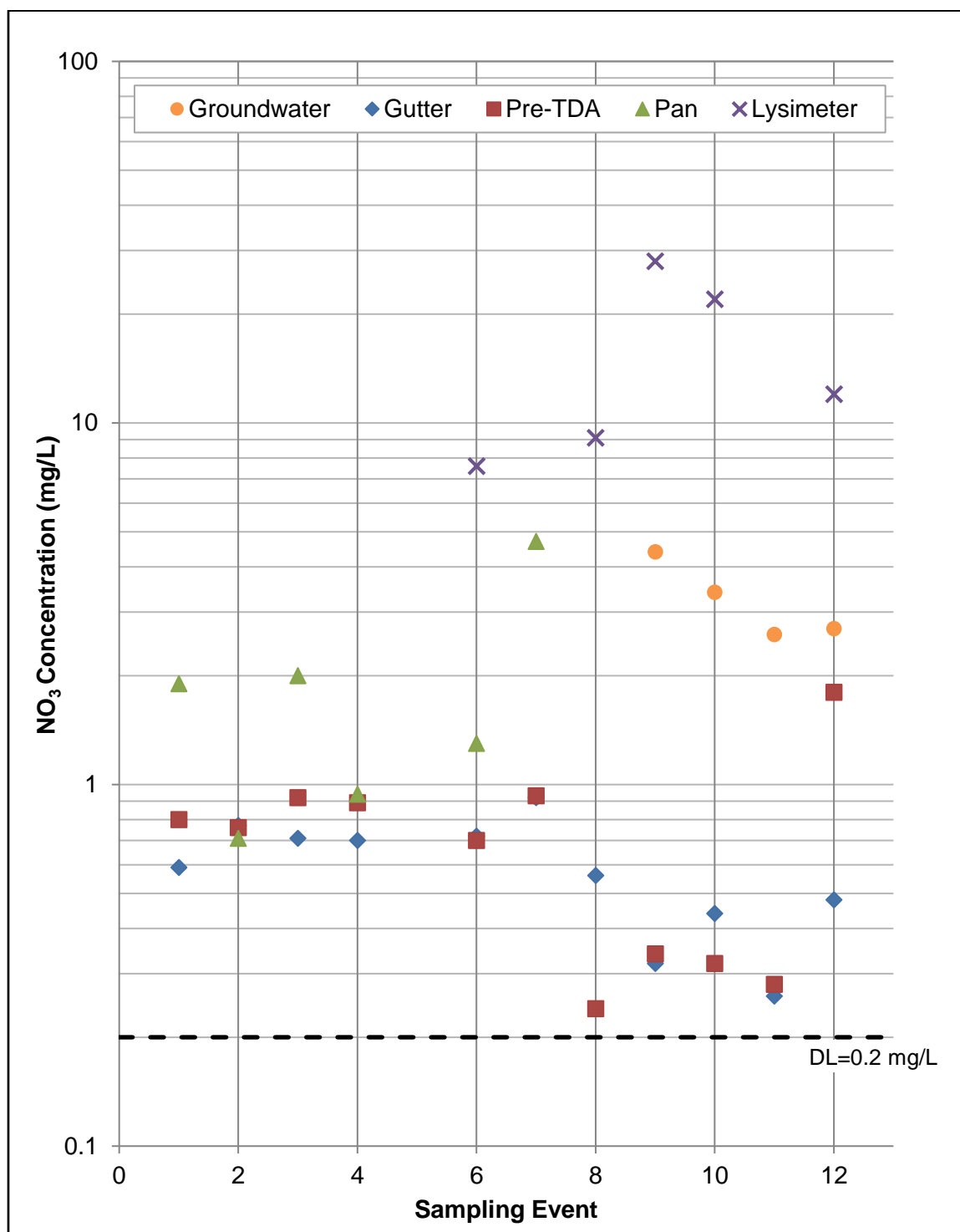


Figure 69. Nitrate concentration at sampling locations. All results for Sampling Event 5 were below the detection limit. (Note: logarithmic vertical scale).

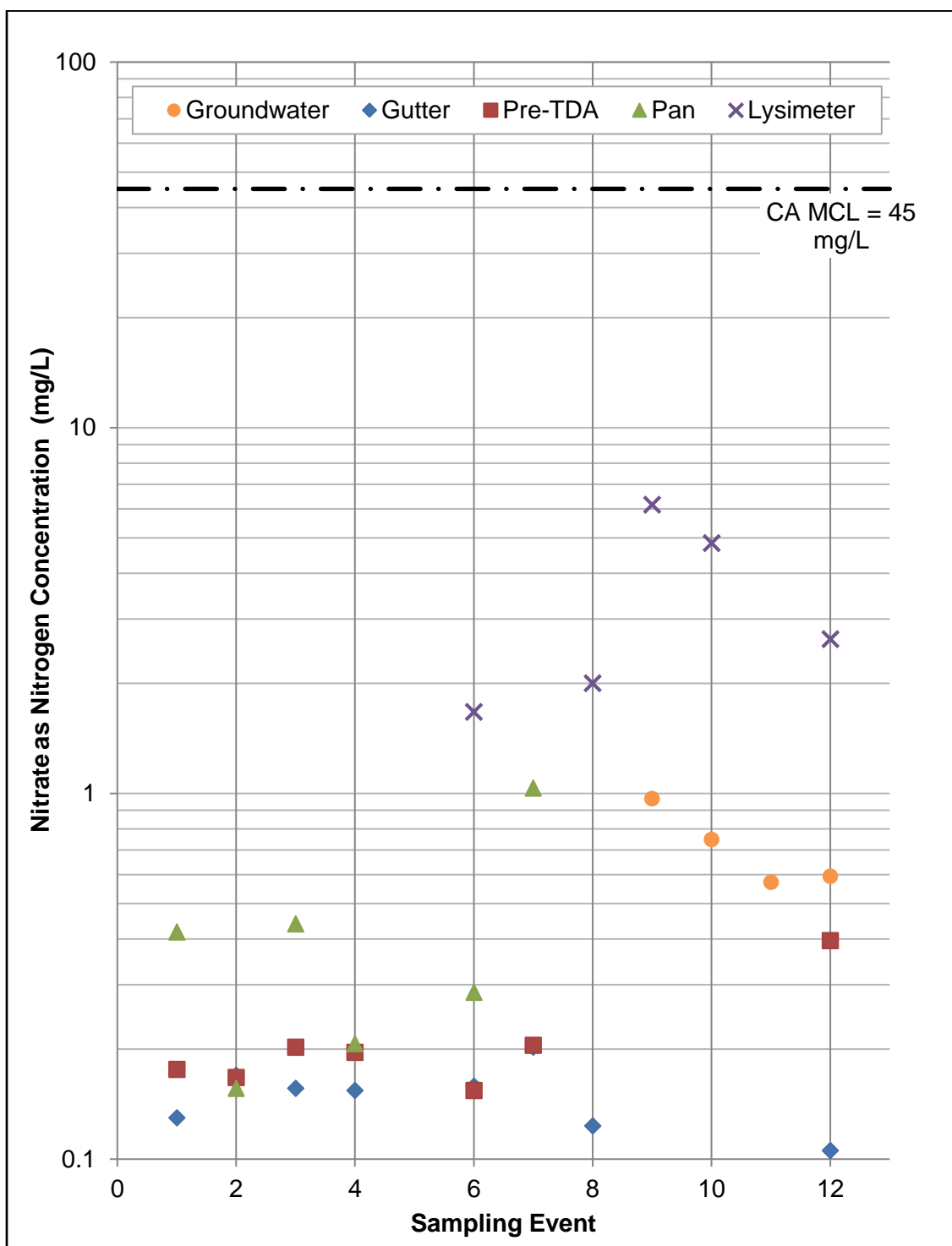


Figure 70. Nitrate as nitrogen concentrations at sampling locations compared to California MCL. (Note: logarithmic vertical scale).

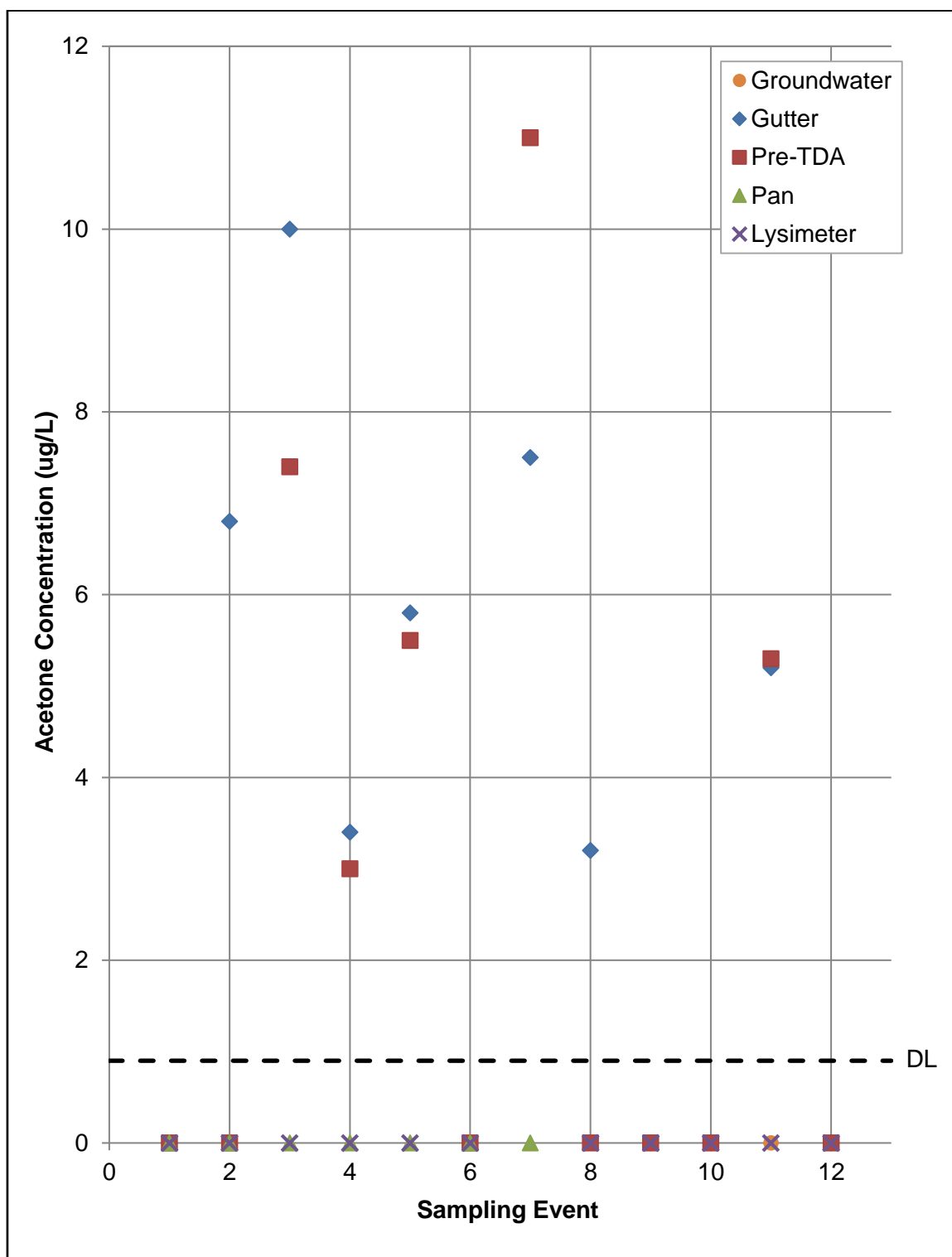


Figure 71. Acetone concentration at sampling locations.

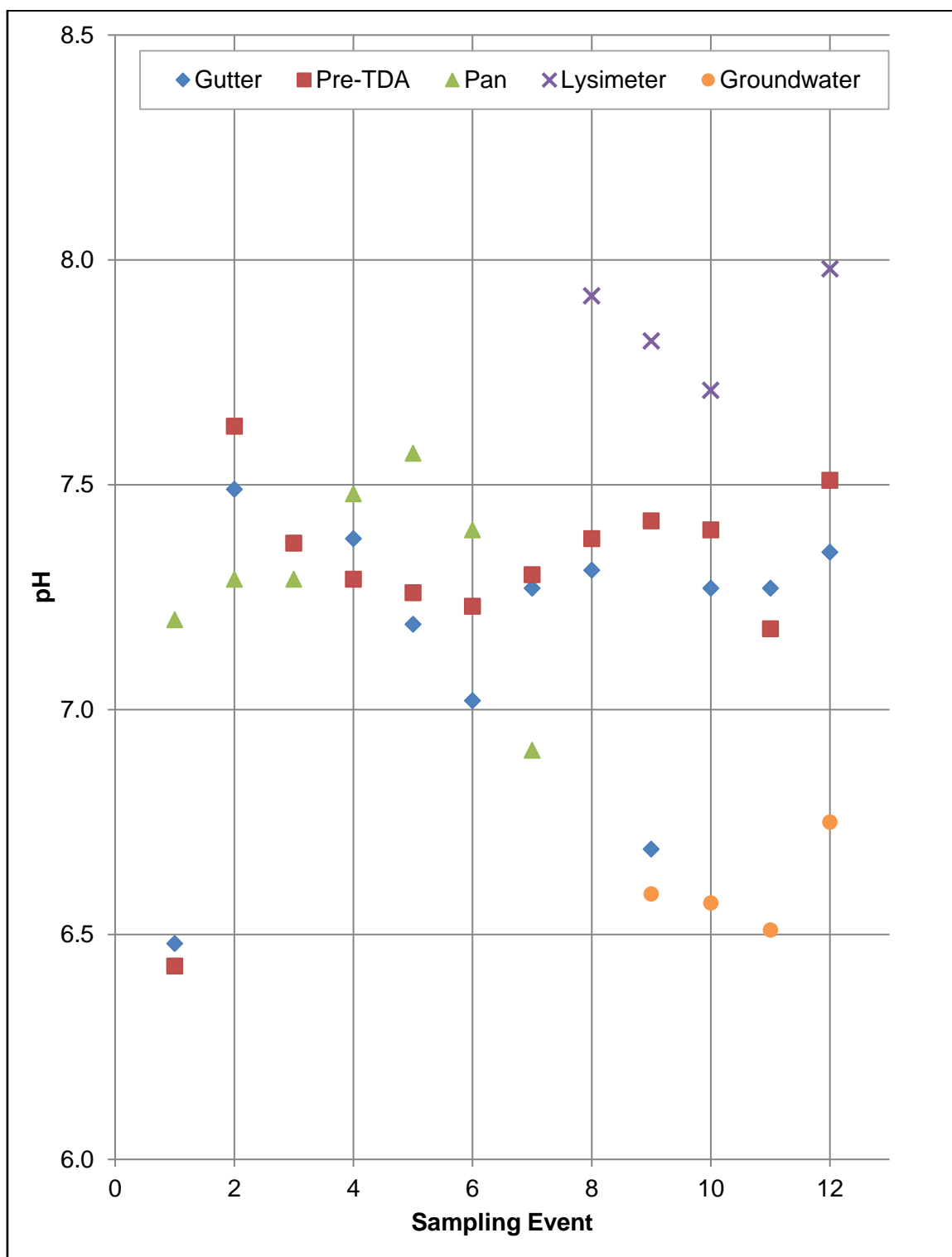


Figure 72. pH at sampling locations.



## **STUDY CONCLUSIONS**

### **Summary and Conclusions of Laboratory Results**

A fifteen-month batch experiment was conducted to investigate the behavior of TDA constituents that the available literature suggests may be of concern. This study focused on confirming the primary water quality constituents in TDA leachate identified in previous studies, quantifying the mass loss rate of the important inorganic constituents in the TDA leachate, and the effects wet/dry cycles resulting from seasonal meteorological or operating conditions have on the mass loss rate of these constituents. The mass loss rates were further used to characterize the behavior of the constituents over the lifetime of a TDA fill in typical civil engineering applications. The results from the laboratory experiment also characterize the concentrations of these constituents in the pore water of a submerged TDA fill.

A list of concluding remarks of the study is provided, but a few considerations should be addressed prior to interpreting the results. The concentrations of water quality constituents in the TDA leachate reported in this portion of the study invite a comparison to regulatory standards. However, these concentrations reflect a scenario that is not representative of many civil engineering applications. In typical applications, water would make a single pass through a TDA fill. In this study, the TDA remained in contact

with the same water for up to one month. Thus, the concentrations measured in this study are likely higher than would be observed in typical civil engineering applications.

To quantify concentrations into a more useful form, the mass of a constituent entering the water from the TDA per mass of TDA per day (specific loss rate) was determined. This quantity can be used to estimate the mass of the various TDA constituents that enter into the leachate during a specified time period. In addition, the expected concentration these constituents in the leachate from TDA can be estimated based on the amount of water that is expected to pass through a known amount of TDA in a fill. Further, the specific loss rate provides a standard form of laboratory results, unlike concentrations which vary depending on the mass of TDA and mass of water used.

Specific conclusions from the laboratory portion of the study are as follows:

- Cadmium and lead release from TDA is insignificant and concentrations of these metals in the leachate are not likely to exceed their respective California MCLs, as evidenced by the low concentrations observed in this study.
- Metals leach from TDA at the highest rate when constantly submerged, as indicated by the higher specific loss rates and cumulative specific losses of the always wet containers compared to the containers with intermediately wet TDA.

At the end of the fifteen-month experiment, manganese, zinc, and iron cumulative mass losses (per kg of tire) were 1.7, 1.6, and 2.6 times greater under the always wet operating condition compared to the average of the other operating conditions.

- The specific loss rate of metals from the TDA decreased over time, reaching very low values by the end of the experiment under all operating conditions.
- After approximately three months, the rate at which metals were released in intermittently wet containers slowed considerably and reached a relatively constant value after eight months.
- The dramatic decrease in the metals loss from the TDA in the always wet containers did not occur until approximately eight months of operation and reached a constant value by the end of the 15 month experiment.
- Variation in the length of a dry period ranging from one to seven days does not significantly affect the release rate of metals from TDA. The containers that were intermittently submerged for differing amounts of time exhibited similar specific rate losses over the course of the experiment.
- Iron and manganese will likely be released from a submerged TDA fill at low, detectable rates for the lifetime of typical civil engineering applications. During the 15 month experiment, the highest cumulative mass losses, observed in the always wet containers, amounted to approximately 3% of the exposed iron and 12% of the exposed manganese with 75% of the loss occurring in the first seven months.
- With few exceptions, TDA leachate does not appear to be a source of VOCs. The rate of loss of those VOCs that do originate from the TDA will likely decrease rapidly over the first year or two of exposure to water. Of the 68 VOCs analyzed in this experiment, only methyl isobutyl ketone and benzene appeared to come

from the TDA. For both compounds, specific loss rates were highest at the beginning of the experiment and declined rapidly over the first 18 weeks.

- TDA is not likely to alter the specific conductance or the concentration of nitrate, oil and grease, and sulfate in the leachate. For these water quality parameters, the source water values were typically within the range or greater than those observed in the TDA containers.
- A submerged TDA fill will likely initially decrease the dissolved oxygen concentration of the leachate water. However, as observed in this study, the minimum concentrations (approximately 3 mg/L) are sufficient for supporting oxidation reduction reactions. After 14 weeks, DO concentrations ranged from 6 to 10 mg/L.
- TDA will initially contribute to the TSS of the leachate, however the majority of the impact on the TSS concentration should occur within the first two years of use. Over the course of this study, a 90% decrease in the specific loss rate of TSS from the TDA was observed.
- TDA will likely contribute to a minor increase in the total phosphate concentration of the leachate for six months to one year. In this experiment, concentrations of phosphate in the leachate ranged from 0.06 mg/L to 0.24 mg/L for the first six months, after which all but one sample were below the detection limit of 0.06 mg/L.

- While no apparent trends were observed in this study, further study is required to determine if the pH and the concentration of COD in the leachate is changed by the TDA.
- After an extended dry period, an initial pulse of iron and manganese mass may occur. At the onset of exposure to water, higher specific loss rates for manganese and iron were observed in the containers that were dry for six months compared to containers that operated under the same intermittently wet condition but without a dry period. However, variations in the behavior of the replicate containers made it difficult to be certain that the long dry period was responsible for the higher specific rate losses. If an initial high loss rate does occur, the loss rate is not expected to exceed those observed at the beginning of a project.

### **Summary and Conclusions of Field Results**

A six cubic yard TDA fill was placed in a street rain garden to observe the performance of a TDA-soil stormwater treatment system. The concentration of select water quality constituents were determined for samples collected during storm events that occurred over the fifteen-month observation period. The concentration of the soil water samples collected below the TDA fill (lysimeter and pan) were compared to the stormwater constituents prior to the TDA fill (gutter and pre-TDA), and to the concentration of the constituents in groundwater up gradient from the TDA during the wet and dry season. The results from the sampling locations below the TDA fill reflect the effects of both the TDA and approximately one foot of soil. Water level

measurements indicate that the TDA fill was typically only submerged during rain events. The majority of these events resulted in water level depths above the TDA fill. The rapid decline in water levels after a rain event suggests that the fill is essentially rinsed during a rain event and drains quickly after precipitation stops.

Concluding remarks associated with the field portion of this study are provided below. These remarks focus on the constituents identified to originate in the TDA based on the laboratory portion of this study. Reference to drinking water standards is provided as a point of comparison, and not to indicate that the standard is applicable in this setting. In addition, TDA leachate would likely pass through more than one foot of soil before reaching a potential location where low levels of TDA constituents may be of concern.

- A TDA-soil system removes iron from stormwater runoff. For all 12 sampling events, the iron concentration in the pan and lysimeter were below that of the gutter and pre-TDA. All iron concentrations below the TDA fill were much lower than the concentrations detected in the groundwater during a storm event, and with the exception of a single sampling event, lower than the dry season background concentration of 0.69 mg/L. Only two iron concentrations in the pan exceeded the Secondary MCL (0.3 mg/L) while all gutter and pre-TDA concentrations were above this regulatory standard.
- A TDA-soil system likely removes manganese from stormwater runoff. The highest concentrations observed in the pan and lysimeter occurred in the first two sampling events. The concentration of manganese in all subsequent samples from these locations was less than those of the gutter and pre-TDA with the exception

of a single data point. Concentrations in the pan and lysimeter were all within or below those of the groundwater and all but two data points from the first two sampling events were below the Secondary MCL (0.05 mg/L).

- A TDA-soil system removes zinc from stormwater runoff. With the exception of a single sampling event, the concentration of zinc in all samples taken below the TDA system was less than those of the sampling locations before the TDA system. The concentration of zinc in samples from below the TDA system was approximately two orders of magnitude less than the Secondary MCL of 5 mg/L.
- A TDA-soil system does not elevate cadmium levels above that of stormwater runoff. After the first two sampling events, the cadmium concentration was above the detection limit for approximately half of the gutter and pre-TDA samples, yet below the detection limit for all samples below the TDA system. The cadmium concentrations in the samples taken below the TDA system were above the detection limit for the first two sample events, but were still two orders of magnitude less than the Secondary MCL (0.005 mg/L).
- A TDA-soil system will likely provide methyl isobutyl ketone removal from stormwater runoff. Methyl isobutyl ketone was detected in the gutter or pre-TDA for 11 of the 12 sampling events, but only once in the lysimeter (at a lower concentration than that of the gutter and pre-TDA).
- Benzene is not likely to be released from a TDA-soil system. Any benzene that may have leached from the surface of the TDA was removed by the soil below the fill since benzene was not detected in any lysimeter or pan sample.

- A TDA-soil system will likely provide phosphate removal from stormwater runoff. Of the nine sampling events with data available for comparison, all concentrations of total phosphate in the pan and lysimeter were less than those of the gutter and pre-TDA.
- A TDA-soil system removes lead. With the exception of a single sampling event in which concentrations before and after the system were comparable, concentrations were typically more than an order of magnitude lower after the system compared to concentrations before system. Further, the system removed lead to levels lower than those observed in the groundwater.
- A TDA-soil system removes oil and grease. With the exception of a single data point, all oil and grease concentrations below the system were less than those detected before the system. The system removed oil and grease to levels comparable to that of the groundwater.
- A TDA-soil system removes acetone. Acetone was detected before the system for 7 of the 12 events, and was not detected in a single sample below the system.

### **Final Conclusions and Recommendations**

California generates more than 40 million scrap tires each year. The reuse of scrap automotive tires provides an alternative to the current disposal methods. One possible reuse option for waste tires is tire-derived aggregate (TDA) in civil engineering applications. TDA is a light-weight fill material that has desirable engineering properties,



providing an alternative to typical fill material, such as rock aggregate. For many of its intended civil engineering applications, TDA comes into contact with water and may leach organic and inorganic compounds that could degrade the quality of nearby ground and surface waters. This study investigated the use of TDA as a media of a stormwater treatment system, which would be periodically submerged during the wet season. The study determined compounds in TDA leachate that could impair receiving water quality, the rate at which the compounds leach from the TDA, and how that rate changes over time. The study also determined the performance of TDA media stormwater treatment basin that receives runoff from an urban street. Based on the results from 15 months of laboratory and field data, the following conclusions can be made.

- Water quality constituents leaching from TDA include iron, manganese, zinc, benzene, MIBK, phosphate, and TSS.
- The highest leaching rate occurs when the TDA is always submerged.
- Leaching rate of all constituents decreased dramatically over time, with at least 50 percent of the mass lost during the 15 month observation period occurring during the first 3 months.
- Benzene and MIBK appears to “rinse” off relatively quickly, and is likely from compounds adsorbed onto the surface while the tire was in use.
- Material contributing to TSS is from rubber crumb, exposed tire cording fabric, broken pieces of exposed steel wire, and oxidized metal from the wire.
- Phosphate appears related to particulate matter in the leachate, and the changes in the rate of loss mirror that of TSS.

- The rubber and exposed wire are the source of the zinc, while the wire is the primary source of the iron and manganese.
- Based on an estimate of the mass of exposed wire, the rate of mass loss, and the accumulated mass lost during the experiment, concentrations of iron, zinc and manganese are likely to be detectable in the leachate for the entire life of any engineered fill of TDA.
- With the exception of iron and manganese, the concentrations of detected constituents in a batch container even during the period of highest leaching rate are below or near MCL standards. Although iron and manganese typically exceeded their respective standards, concentrations near the end of the 15-month study were near or below their respective secondary MCLs. The conditions of the laboratory experiment result in concentrations higher than would be expected in an actual field application, suggesting the risk of significant impairment of receiving water quality from a TDA fill is very low.
- TDA is an excellent choice as a media in a stormwater treatment and infiltration basin. There is no evidence any nutrient, metal, or VOC leached from the TDA poses any risk of receiving water quality impairment in this application. The concentration of detected constituents measured one foot below a TDA fill were lower than those of the influent runoff and in most cases, below the background groundwater concentrations.

Based on the results from this study, it is clear that TDA fills that are seasonally or always saturated are very unlikely to compromise the quality of the surrounding water. The number of potentially harmful compounds leaching from the TDA is limited, and the rate of leaching is sufficiently low that the concentrations of these compounds in the surrounding waters remain manageable. Sufficient dilution and soil adsorption processes further reduce the potential impacts that these compounds might have on any receiving water. The loss rate of the primary constituents in the leachate, iron, manganese and zinc, could be reduced if necessary by enforcing more stringent standards on the amount of exposed wire that is acceptable in the TDA.

This study, along with previous research has demonstrated that TDA also can serve as an attached growth media for water treatment, such as in stormwater retention and infiltration systems. It is recommended that additional field applications of TDA fills that are saturated be pursued. Monitoring data from these applications should provide regulatory bodies additional confidence that this practice is a responsible use of a recycled product, reduces the demand for gravel mining, and provides for a number of beneficial applications including the opportunity for stormwater treatment.

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## Appendix A TESTED CONSTITUENTS

Table 31. Alpha Laboratories' detection limit (DL), reporting limit (RL), and method name for all analyzed constituents.

Constituent	DL	RL	Units	Method Name
1,1,1,2-Tetrachloroethane	0.40	0.50	ug/L	EPA 8260B
1,1,1-Trichloroethane	0.40	0.50	ug/L	EPA 8260B
1,1,2,2-Tetrachloroethane	0.30	0.50	ug/L	EPA 8260B
1,1,2-Trichloroethane	0.40	0.50	ug/L	EPA 8260B
1,1-Dichloroethane	0.50	0.50	ug/L	EPA 8260B
1,1-Dichloroethene	0.30	0.50	ug/L	EPA 8260B
1,1-Dichloropropene	0.40	0.50	ug/L	EPA 8260B
1,2,3-Trichlorobenzene	0.50	0.50	ug/L	EPA 8260B
1,2,3-Trichloropropane	0.40	0.50	ug/L	EPA 8260B
1,2,4-Trichlorobenzene	0.20	0.50	ug/L	EPA 8260B
1,2,4-Trimethylbenzene	0.40	0.50	ug/L	EPA 8260B
1,2-Dibromo-3-chloropropane	0.60	2.0	ug/L	EPA 8260B
1,2-Dibromoethane (EDB)	0.40	0.50	ug/L	EPA 8260B
1,2-Dichlorobenzene	0.40	0.50	ug/L	EPA 8260B
1,2-Dichloroethane	0.40	0.50	ug/L	EPA 8260B
1,2-Dichloropropane	0.40	0.50	ug/L	EPA 8260B
1,3,5-Trimethylbenzene	0.30	0.50	ug/L	EPA 8260B
1,3-Dichlorobenzene	0.40	0.50	ug/L	EPA 8260B
1,3-Dichloropropane	0.40	0.50	ug/L	EPA 8260B
1,4-Dichlorobenzene	0.30	0.50	ug/L	EPA 8260B
2,2-Dichloropropane	0.50	0.50	ug/L	EPA 8260B
2-Chlorotoluene	0.40	0.50	ug/L	EPA 8260B
2-Hexanone	4.0	5.0	ug/L	EPA 8260B
4-Chlorotoluene	0.30	0.50	ug/L	EPA 8260B
Acetone	0.90	5.0	ug/L	EPA 8260B
Ammonia as NH3	0.20	0.50	mg/L	SM4500NH3C
Benzene	0.30	0.30	ug/L	EPA 8260B
Bromobenzene	0.40	0.50	ug/L	EPA 8260B
Bromochloromethane	0.40	0.50	ug/L	EPA 8260B
Bromodichloromethane	0.40	0.50	ug/L	EPA 8260B
Bromoform	0.30	0.50	ug/L	EPA 8260B

<b>Constituent</b>	<b>DL</b>	<b>RL</b>	<b>Units</b>	<b>Method Name</b>
Bromomethane	0.40	0.50	ug/L	EPA 8260B
Cadmium	8.0E-05	0.0010	mg/L	EPA 200.8
Carbon disulfide	0.40	5.0	ug/L	EPA 8260B
Carbon tetrachloride	0.40	0.50	ug/L	EPA 8260B
Chemical Oxygen Demand	9.0	50	mg/L	SM5220D
Chlorobenzene	0.30	0.50	ug/L	EPA 8260B
Chloroethane	0.40	0.50	ug/L	EPA 8260B
Chloroform	0.40	0.50	ug/L	EPA 8260B
Chloromethane	0.40	0.50	ug/L	EPA 8260B
cis-1,2-Dichloroethene	0.40	0.50	ug/L	EPA 8260B
cis-1,3-Dichloropropene	0.40	0.50	ug/L	EPA 8260B
Dibromochloromethane	0.40	0.50	ug/L	EPA 8260B
Dibromomethane	0.40	0.50	ug/L	EPA 8260B
Dichlorodifluoromethane	0.40	0.50	ug/L	EPA 8260B
Ethylbenzene	0.40	0.50	ug/L	EPA 8260B
Hexachlorobutadiene	0.50	0.50	ug/L	EPA 8260B
Iron	0.020	0.10	mg/L	EPA 200.7
Isopropylbenzene	0.40	0.50	ug/L	EPA 8260B
Lead	8.0E-05	0.0050	mg/L	EPA 200.8
m,p-Xylene	0.50	0.50	ug/L	EPA 8260B
Manganese	4.0E-04	0.020	mg/L	EPA 200.7
Methyl ethyl ketone	0.70	1.0	ug/L	EPA 8260B
Methyl isobutyl ketone	0.60	1.0	ug/L	EPA 8260B
Methyl tert-butyl ether	0.50	0.50	ug/L	EPA 8260B
Methylene chloride	0.50	0.50	ug/L	EPA 8260B
Naphthalene	0.50	0.50	ug/L	EPA 8260B
n-Butylbenzene	0.40	0.50	ug/L	EPA 8260B
Nitrate as NO <sub>3</sub>	0.20	1.0	mg/L	EPA 300.0
n-Propylbenzene	0.40	0.50	ug/L	EPA 8260B
Oil & Grease (HEM)	1.4	5.0	mg/L	EPA 1664A
o-Xylene	0.40	0.50	ug/L	EPA 8260B
Phosphate, Total	0.060	0.10	mg/L	SM4500-P E
p-Isopropyltoluene	0.40	0.50	ug/L	EPA 8260B
sec-Butylbenzene	0.40	0.50	ug/L	EPA 8260B
Specific Conductance (EC)	1.0	20	umhos/cm	SM2510B
Styrene	0.40	0.50	ug/L	EPA 8260B
Sulfate as SO <sub>4</sub>	0.090	0.50	mg/L	EPA 300.0

<b>Constituent</b>	<b>DL</b>	<b>RL</b>	<b>Units</b>	<b>Method Name</b>
tert-Butylbenzene	0.30	0.50	ug/L	EPA 8260B
Tetrachloroethene	0.40	0.50	ug/L	EPA 8260B
Toluene	0.30	0.30	ug/L	EPA 8260B
Total Suspended Solids	1.0	1.0	mg/L	SM2540D
trans-1,2-Dichloroethene	0.40	0.50	ug/L	EPA 8260B
trans-1,3-Dichloropropene	0.40	0.50	ug/L	EPA 8260B
Trichloroethene	0.40	0.50	ug/L	EPA 8260B
Trichlorofluoromethane	0.50	0.50	ug/L	EPA 8260B
Trichlorotrifluoroethane	0.50	0.50	ug/L	EPA 8260B
Vinyl acetate	0.80	1.0	ug/L	EPA 8260B
Vinyl chloride	0.40	0.50	ug/L	EPA 8260B
Xylenes (total)	0.50	0.50	ug/L	EPA 8260B
Zinc	0.0020	0.050	mg/L	EPA 200.8

## Appendix B   LABORATORY WATER VOLUMES

Table 32. Volume of water (L) for all containers for each data collection.

<b>Week No.</b>	<b>C1</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>	<b>C7</b>	<b>C8</b>	<b>C9</b>	<b>C10</b>
2	47.1	48.7	56.1	56.5	54.9	54.1	59.5	54.2	51.0	52.9
4	33.8	38.9	41.3	42.3	45.3	44.5	43.0	41.2	45.3	44.4
6	31.7	36.4	46.6	42.1	44.3	43.5	40.7	41.5	41.5	45.3
8	30.5	36.2	32.6	44.0	42.2	40.8	38.9	43.0	38.8	44.2
11	30.0	36.7	38.1	42.7	42.0	41.5	35.1	38.5	44.5	42.6
14	32.2	34.4	36.7	41.9	36.5	34.3	38.3	37.2	37.6	39.4
18	36.2	36.1	41.8	41.4	45.0	43.5	39.5	40.7	42.7	41.3
22	32.6	36.1	38.9	45.5	44.5	41.2	40.7	38.5	39.3	34.3
26	38.2	37.2	41.7	39.8	48.1	41.3	39.0	38.1	40.2	35.5
30	38.8	35.1	36.2	40.8	37.4	37.4	44.9	40.1	-	-
34	41.7	39.1	38.7	41.0	40.9	36.3	41.9	39.9	-	-
38	42.0	34.2	54.3	35.3	36.0	37.7	36.8	38.5	-	-
42	39.0	43.6	43.8	42.8	43.9	48.2	49.9	42.7	-	-
46	38.0	31.4	42.4	35.6	40.1	41.5	42.6	39.0	-	-
50	35.3	34.8	41.8	34.5	39.4	34.9	36.7	36.1	-	-
54	34.0	35.1	41.7	37.6	45.4	37.4	38.6	43.8	-	-
58	36.6	32.2	36.4	35.8	37.9	34.9	37.9	36.8	40.0	45.5
62	36.5	35.4	39.4	42.9	44.5	37.5	40.2	41.9	39.6	39.8
66	36.5	33.8	35.0	36.1	41.3	38.9	35.2	36.8	40.7	38.3

(-) = sample not analyzed for indicated week

**Appendix C RAW DATA FOR ACID BATH**

Table 33. Masses (grams) of TDA batches used to determine the percent (by mass) of oxidizable steel.

<b>Sample Description</b>	<b>Initial Mass (g)</b>	<b>Final Mass (g)</b>
Pieces with no wire* (Run 1)	68.61	69.69
Pieces with no wire* (Run 2)	581.83	590.15
Acid bath (Run 1)	4396.70	4298.04
Acid bath (Run 2)	4543.27	4593.04

\*The pieces with no visible wire protruding from TDA were used to determine the change in mass from soaking TDA in an acid bath.

### Appendix D ORIGINAL LABORATORY CONCENTRATIONS

Table 34. Iron concentration (mg/L) for Source (S) and Containers (C1-C10).

Week No.	S	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
2	0.000	4.6	7.7	3.3	2.7	3.1	2.3	2.0	1.9	5.1	3.8
4	0.021	12	10	4.5	3.9	3.3	4.0	4.9	3.9	4.6	3.9
6	0.027	11	10	3.6	3.6	3.9	3.5	3.5	4.0	3.7	3.3
8	0.061	4.9	9.8	3.6	2.7	3.6	2.4	3.5	4.0	3.2	2.3
11	0.029	7.5	26	3.6	2.5	2.2	1.8	4.4	3.4	2.2	4.3
14	-	10	7.3	2.4	4.2	1.5	3.2	2.0	2.5	2.1	2.0
18	ND	16	3.3	1.3	1.7	2.0	2.3	3.9	2.6	3.5	1.8
22	ND	20	3.1	1.0	0.74	1.3	1.9	3.2	1.4	2.6	2.5
26	0.085	11	6.4	1.7	0.63	1.2	1.8	3.5	4.0	3.8	1.8
30	0.033	17	4.3	1.8	0.61	1.5	7.2	1.6	4.9	-	-
34	0.024	7.0	9.3	4.1	1.4	4.1	4.2	2.7	2.8	-	-
38	0.099	3.0	4.4	2.7	0.75	1.7	1.4	2.3	2.7	-	-
42	0.099	3.7	4.5	1.3	0.86	1.6	1.1	2.2	2.5	-	-
46	ND	3.7	3.6	2.7	0.79	1.4	0.76	1.5	2.0	-	-
50	ND	1.7	3.0	1.6	0.68	0.63	1.2	1.9	1.3	-	-
54	0.022	2.1	2.8	1.9	0.52	0.59	2.8	2.8	1.0	-	-
58	0.062	1.5	2.4	0.93	0.37	0.64	1.7	1.6	1.2	2.4	1.0
62	0.065	3.9	3.0	0.53	0.21	1.4	1.1	0.7	0.47	1.2	0.36
66	ND	4.1	2.7	0.49	0.36	0.7	0.59	0.56	0.53	0.61	0.5

Table 35. Zinc concentration (mg/L) for Source (S) and Containers (C1-C10).

Week No.	S	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
2	0.016	0.570	0.600	0.500	0.380	0.370	0.370	0.430	0.420	0.520	0.500
4	0.009	0.470	0.300	0.260	0.370	0.180	0.240	0.230	0.270	0.240	0.230
6	0.013	0.410	0.260	0.210	0.260	0.150	0.180	0.180	0.180	0.190	0.190
8	0.019	0.180	0.200	0.170	0.160	0.120	0.110	0.110	0.120	0.110	0.110
11	0.024	0.220	0.710	0.150	0.150	0.072	0.077	0.130	0.100	0.072	0.190
14	-	0.340	0.140	0.120	0.220	0.057	0.110	0.055	0.086	0.068	0.085
18	0.015	0.420	0.080	0.074	0.110	0.063	0.079	0.100	0.072	0.110	0.078
22	0.016	0.630	0.080	0.054	0.060	0.045	0.081	0.110	0.065	0.062	0.110
26	0.013	0.230	0.088	0.067	0.043	0.033	0.058	0.088	0.100	0.130	0.088
30	0.028	0.440	0.071	0.084	0.053	0.048	0.210	0.058	0.160	-	-
34	0.017	0.140	0.130	0.18	0.069	0.110	0.120	0.072	0.071	-	-
38	0.017	0.064	0.061	0.110	0.063	0.054	0.045	0.059	0.120	-	-
42	0.020	0.073	0.061	0.065	0.048	0.057	0.032	0.059	0.080	-	-
46	0.010	0.092	0.064	0.150	0.054	0.047	0.031	0.045	0.067	-	-
50	0.018	0.040	0.061	0.088	0.047	0.026	0.049	0.072	0.042	-	-
54	0.008	0.055	0.049	0.10	0.040	0.019	0.091	0.078	0.032	-	-
58	0.022	0.038	0.035	0.052	0.035	0.021	0.070	0.054	0.042	0.086	0.052
62	0.014	0.110	0.063	0.049	0.037	0.570	0.070	0.032	0.029	0.060	0.036
66	0.018	0.110	0.051	0.043	0.038	0.085	0.036	0.024	0.055	0.053	0.031



Table 36. Cadmium concentration (mg/L) for Source (S) and Containers (C1-C10).

[illegible]

Table 37. Original manganese concentration for Source and Containers (mg/L).

Week No.	S	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
2	0.0010	0.26	0.230	0.170	0.16	0.18	0.18	0.170	0.170	0.200	0.200
4	0.0020	0.22	0.260	0.210	0.17	0.19	0.21	0.180	0.160	0.190	0.190
6	0.0019	0.27	0.280	0.170	0.16	0.20	0.18	0.180	0.180	0.160	0.140
8	0.0027	0.2	0.270	0.150	0.12	0.20	0.17	0.160	0.170	0.150	0.047
11	0.0021	0.22	0.350	0.150	0.14	0.16	0.12	0.170	0.160	0.120	0.072
14	-	0.22	0.120	0.140	0.14	0.16	0.06	0.140	0.100	0.034	0.036
18	0.0010	0.22	0.068	0.037	0.11	0.13	0.03	0.096	0.032	0.051	0.036
22	0.0013	0.34	0.084	0.032	0.03	0.11	0.03	0.059	0.024	0.054	0.051
26	0.0034	0.18	0.091	0.05	0.04	0.06	0.04	0.064	0.060	0.077	0.036
30	0.0022	0.29	0.055	0.046	0.04	0.03	0.10	0.031	0.078	-	-
34	ND	0.31	0.094	0.086	0.06	0.07	0.09	0.055	0.055	-	-
38	0.0022	0.08	0.053	0.059	0.06	0.05	0.03	0.055	0.068	-	-
42	0.0018	0.07	0.049	0.051	0.05	0.04	0.03	0.058	0.055	-	-
46	ND	0.06	0.054	0.086	0.05	0.04	0.02	0.063	0.038	-	-
50	ND	0.03	0.087	0.043	0.06	0.03	0.03	0.082	0.030	-	-
54	0.0020	0.05	0.094	0.051	0.05	0.04	0.07	0.078	0.026	-	-
58	0.0046	0.04	0.066	0.029	0.02	0.02	0.04	0.043	0.035	0.072	0.036
62	0.0005	0.12	0.078	0.021	0.07	0.05	0.03	0.047	0.014	0.046	0.020
66	ND	0.14	0.065	0.02	0.01	0.03	0.02	0.030	0.023	0.039	0.021

Table 38. pH for Source (S) and Containers (C1-C10).

Week No.	S	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
2	-	7.0	6.7	7.1	7.0	7.0	7.0	7.1	7.0	7.0	7.0
4	6.9	6.1	6.7	7.0	-	7.1	-	7.2	-	7.1	-
6	7.1	7.2	7.1	7.0	7.1	7.2	7.1	7.3	7.2	7.2	7.2
8	6.0	6.9	7.2	7.1	7.2	7.0	7.1	7.3	7.4	7.0	7.3
11	-	7.8	7.7	7.6	7.7	7.8	7.8	7.8	7.9	7.8	7.8
14	7.4	7.9	8.0	8.2	8.1	8.1	8.1	8.0	8.0	8.0	8.0
18	7.7	7.7	7.7	8.1	8.0	8.2	7.9	7.8	7.8	7.9	7.8
22	7.9	7.6	7.7	7.9	8.0	8.0	7.8	7.8	7.8	7.8	7.8
26	7.7	7.7	7.7	7.9	7.8	7.9	7.8	7.9	7.9	7.8	7.9
30	7.8	8.1	8.0	8.1	8.2	8.2	8.2	8.2	8.2	-	-
34	8.0	7.8	7.8	7.8	7.8	7.9	7.9	7.9	7.9	-	-
38	7.8	7.5	7.4	-	7.4	7.4	7.5	7.6	7.5	-	-
42	7.2	7.7	7.5	8.0	8.0	7.5	7.5	7.7	7.5	-	-
46	7.5	8.3	8.2	8.2	8.2	8.3	8.3	8.3	8.3	-	-
50	8.0	7.6	7.5	7.2	7.5	7.6	7.6	7.5	7.8	-	-
54	6.9	7.6	7.5	7.2	7.5	7.6	7.6	7.5	7.8	-	-
58	6.9	7.7	7.6	7.9	7.9	7.9	7.9	7.8	7.8	7.8	7.7
62	7.7	8.1	8.1	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2
66	8.2	7.9	7.8	7.8	7.7	7.8	7.8	7.9	7.9	7.9	7.9

Table 39. Dissolved oxygen (mg/L) for Containers (C1-C10).

Week No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
5	5.52	3.85	4.35	5.85	-	-	-	-	5.84	5.42
8	6.34	4.34	6.18	5.99	5.22	4.71	5.62	4.93	6.09	5.99
9	5.13	3.66	5.54	5.25	4.35	4.27	-	-	5.20	5.25
10	3.74	2.92	3.75	3.65	3.52	3.10	3.42	2.91	3.85	3.84
11	4.67	4.11	4.59	4.98	4.4	4.22	-	-	5.37	5.46
12	6.60	5.88	6.78	6.53	6.49	3.36	6.52	6.38	7.28	7.38
13	6.86	6.25	6.86	6.73	6.72	6.29	-	-	7.60	7.79
14	4.29	4.01	4.46	4.44	5.15	4.22	4.41	4.07	4.63	5.05
16	6.49	6.28	7.11	6.83	7.49	6.30	6.84	6.55	6.78	7.67
17	5.85	5.48	6.36	6.23	7.41	5.66	-	-	6.41	6.94
18	8.11	6.64	7.87	8.51	8.43	7.07	7.03	6.59	8.22	7.85
21	8.11	7.17	8.06	9.13	8.31	7.45	-	-	8.29	8.61
23	6.93	7.51	9.43	8.84	9.07	8.03	-	-	8.29	8.90
26	7.02	6.21	6.67	7.27	7.92	6.62	7.21	6.31	-	-
27	7.38	6.87	7.82	8.11	7.22	6.73	-	-	-	-
28	7.71	-	8.46	8.54	8.16	7.83	8.22	7.83	-	-
29	7.99	7.98	8.84	8.70	7.67	7.93	-	-	-	-
30	8.91	7.38	8.29	8.42	7.44	7.21	8.21	7.89	-	-
31	8.84	7.44	8.08	8.31	7.44	7.58	-	-	-	-
33	8.51	7.86	8.44	8.65	7.51	8.02	-	-	-	-
34	9.07	8.42	9.28	8.82	8.13	7.91	7.88	8.03	-	-
36	8.72	7.52	8.27	8.02	7.69	8.03	9.45	7.41	-	-
37	8.80	7.35	8.20	7.97	7.48	8.24	-	-	-	-
38	8.33	8.64	7.72	8.68	8.50	8.34	8.10	7.28	-	-
39	8.33	8.17	7.79	8.37	8.47	8.58	-	-	-	-
40	8.31	8.23	7.76	7.86	7.99	8.14	7.97	7.32	-	-
41	8.41	8.45	7.99	7.67	8.08	8.38	-	-	-	-
42	8.40	8.40	8.20	7.90	8.10	8.90	8.10	7.90	-	-
43	7.30	7.30	7.70	7.80	6.20	8.60	-	-	-	-
44	7.90	7.90	8.30	8.50	8.20	8.70	8.30	8.20	-	-
45	8.00	7.50	7.10	8.00	7.90	8.60	-	-	-	-
49	6.57	5.81	6.36	7.12	6.78	7.09	-	-	-	-
50	7.62	6.27	6.57	7.07	7.04	7.04	6.73	6.89	-	-
51	6.92	5.76	6.59	6.77	6.73	7.03	-	-	-	-

<b>Week No.</b>	<b>C1</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C6</b>	<b>C7</b>	<b>C8</b>	<b>C9</b>	<b>C10</b>
52	7.02	5.93	6.76	7.12	6.58	6.16	6.38	6.16	-	-
53	7.77	6.77	7.26	7.23	6.87	6.46	-	-	-	-
54	7.21	7.04	7.24	7.37	6.64	6.86	6.45	6.90	5.97	6.54
55	6.77	6.72	6.48	6.42	6.69	7.53	-	-	5.61	6.48
56	6.93	6.83	7.17	7.01	6.46	7.03	6.67	6.87	5.98	6.89
57	7.29	7.16	7.43	7.48	7.17	7.62	-	-	6.20	7.21
58	7.38	6.91	7.64	7.87	6.80	6.98	6.98	7.39	7.11	8.01
59	7.96	6.97	7.83	7.99	6.52	7.01	-	-	7.67	7.78
60	8.13	6.88	7.67	7.48	6.29	6.67	6.71	7.24	7.47	7.72
61	8.64	7.46	7.72	7.94	6.68	6.88	-	-	7.92	8.10
62	7.81	7.27	8.23	7.93	7.68	6.95	7.66	7.42	8.26	8.78
63	8.18	7.50	7.92	8.07	7.83	7.16	-	-	8.26	8.18
64	9.14	8.56	9.41	8.99	8.81	8.15	8.34	8.38	9.14	9.22
65	9.63	9.39	10.29	10.03	9.69	9.63	-	-	9.82	10.26

For further original laboratory results, the reader is referred to Finney and Maeda (2016).

## Appendix E ORIGINAL FIELD CONCENTRATIONS

Table 40. Acetone (ug/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	ND	ND	ND	ND	-
2	6.8	ND	ND	ND	-
3	10	7.4	ND	ND	-
4	3.4	3.0	ND	ND	-
5	5.8	5.5	ND	ND	-
6	ND	ND	ND	ND	-
7	7.5	11	ND	-	-
8	3.2	ND	-	ND	-
9	ND	ND	-	ND	ND
10	ND	ND	-	ND	ND
11	5.2	5.3	-	ND	ND
12	ND	ND	-	ND	ND

Table 41. Ammonia (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.68	0.68	ND	-	-
2	ND	ND	ND	-	-
3	0.26	0.30	0.26	-	-
4	ND	ND	ND	ND	-
5	ND	ND	ND	ND	-
6	ND	ND	ND	ND	-
7	ND	0.21	ND	-	-
8	ND	ND	-	-	-
9	ND	ND	-	-	ND
10	ND	ND	-	-	ND
11	ND	ND	-	ND	ND
12	0.30	ND	-	ND	ND

Table 42. Cadmium (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.000140	0.000080	0.000062	0.000030	-
2	0.000048	ND	ND	0.000048	-
3	0.000110	0.000110	ND	-	-
4	0.000120	ND	ND	ND	-
5	ND	ND	ND	ND	-
6	ND	0.000130	ND	ND	-
7	0.000200	0.000086	ND	-	-
8	0.000031	ND	-	ND	-
9	ND	ND	-	ND	ND
10	ND	ND	-	ND	0.000087
11	ND	ND	-	ND	0.000230
12	0.000180	0.000110	-	ND	0.000280

Table 43. Chemical Oxygen Demand (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	160	100	25	-	-
2	45	32	28	-	-
3	87	80	24	-	-
4	87	33	10	22	-
5	14	12	75	ND	-
6	98	120	120	100	-
7	34	220	22	-	-
8	19	37	-	-	-
9	17	11	-	-	17
10	33	66	-	-	29
11	49	32	-	13	24
12	120	110	-	21	36

Table 44. Iron (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	3.60	2.40	1.50	0.033	-
2	1.60	0.55	0.19	0.044	-
3	2.70	2.30	0.27	-	-
4	4.50	2.40	0.23	0.026	-
5	1.70	1.00	0.18	0.054	-
6	2.60	6.10	0.16	0.050	-
7	3.80	1.90	0.76	-	-
8	0.63	1.50	-	0.036	-
9	0.38	0.49	-	0.082	1.7
10	0.77	1.20	-	0.053	3.4
11	1.30	0.56	-	ND	3.6
12	4.50	4.70	-	ND	4.8

Table 45. Lead (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.0056	0.0037	0.0011	0.00004	-
2	0.0030	0.0008	0.0001	0.00005	-
3	0.0042	0.0037	0.0004	-	-
4	0.0079	0.0034	0.0002	0.00012	-
5	0.0025	0.0025	-	-	-
6	0.0039	0.0094	0.0002	0.00016	-
7	0.0062	0.0032	0.0005	-	-
8	0.0009	0.0021	-	0.00008	-
9	0.0006	0.0009	-	0.00013	0.0013
10	0.0012	0.0022	-	0.00120	0.0022
11	0.0027	0.0013	-	0.00012	0.0031
12	0.0092	0.0110	-	0.00009	0.0035



Table 46. Manganese (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.120	0.093	0.150	0.014	-
2	0.033	0.011	0.040	0.074	-
3	0.062	0.049	0.012	-	-
4	0.096	0.056	0.007	0.041	-
5	0.044	0.029	0.006	0.037	-
6	0.055	0.14	0.008	0.004	-
7	0.099	0.046	0.018	-	-
8	0.018	0.042	-	0.011	-
9	0.012	0.020	-	0.005	0.062
10	0.016	0.026	-	0.005	0.160
11	0.031	0.014	-	ND	0.065
12	0.093	0.095	-	0.002	0.110

Table 47. Methyl isobutyl ketone (ug/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	ND	ND	ND	ND	-
2	1.4	ND	ND	ND	-
3	2.8	3.0	ND	1.2	-
4	1.6	1.2	ND	ND	-
5	2.8	2.6	ND	ND	-
6	3.4	3.6	ND	ND	-
7	3.0	2.7	ND	-	-
8	1.6	1.3	-	ND	-
9	0.9	ND	-	ND	ND
10	0.9	1.1	-	ND	ND
11	1.3	1.4	-	ND	ND
12	4.3	3.6	-	ND	ND

Table 48. Nitrate as NO<sub>3</sub> (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.59	0.80	1.90	-	-
2	0.77	0.76	0.71	-	-
3	0.71	0.92	2.00	-	-
4	0.70	0.89	0.94	-	-
5	ND	ND	ND	-	-
6	0.72	0.70	1.30	7.6	-
7	0.92	0.93	4.70	-	-
8	0.56	0.24	-	9.1	-
9	0.32	0.34	-	28.0	4.4
10	0.44	0.32	-	22.0	3.4
11	0.26	0.28	-	-	2.6
12	0.48	1.80	-	12.0	2.7

Table 49. pH.

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	6.48	6.43	7.20	-	-
2	7.49	7.63	7.29	-	-
3	7.37	7.37	7.29	-	-
4	7.38	7.29	7.48	-	-
5	7.19	7.26	7.57	-	-
6	7.02	7.23	7.40	-	-
7	7.27	7.30	6.91	-	-
8	7.31	7.38	-	7.92	-
9	6.69	7.42	-	7.82	6.59
10	7.27	7.40	-	7.71	6.57
11	7.27	7.18	-	-	6.51
12	7.35	7.51	-	7.98	6.75

Table 50. Total phosphate (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	1.50	1.10	0.36	-	-
2	0.40	0.28	0.14	-	-
3	0.43	0.69	0.17	-	-
4	0.52	0.41	0.15	0.17	-
5	0.29	0.28	0.14	0.17	-
6	0.73	0.77	0.19	0.14	-
7	0.53	0.45	0.26	-	-
8	0.27	0.36	-	-	-
9	0.27	0.27	-	-	0.49
10	0.21	0.30	-	-	0.42
11	0.27	0.25	-	0.15	0.44
12	0.72	0.58	-	0.16	0.56

Table 51. Specific conductance (umhos/cm).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	74	79	260	-	-
2	39	49	240	-	-
3	38	60	200	-	-
4	30	62	200	-	-
5	16	20	190	-	-
6	26	29	200	-	-
7	30	25	200	-	-
8	24	36	-	410	-
9	32	34	-	460	250
10	45	45	-	400	240
11	19	23	-	-	230
12	51	81	-	330	220

Table 52. Sulfate as SO<sub>4</sub> (mg/L)

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	2.20	5.6	22	-	-
2	1.40	1.3	19	-	-
3	1.30	2.0	12	-	-
4	1.20	3.2	10	-	-
5	0.60	0.64	9.4	-	-
6	1.30	0.93	10	-	-
7	0.94	1.0	10	-	-
8	0.63	0.75	-	25	-
9	0.85	0.74	-	29	14
10	1.30	1.3	-	23	13
11	0.42	0.49	-	-	12
12	1.80	3.2	-	15	12

Table 53. Tetrachloroethane (ug/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	ND	ND	ND	ND	-
2	ND	ND	ND	ND	-
3	ND	ND	0.95	ND	-
4	ND	ND	ND	ND	-
5	ND	ND	0.92	ND	-
6	ND	ND	1.1	ND	-
7	ND	ND	2.4	-	-
8	ND	ND	-	ND	-
9	ND	ND	-	ND	29
10	ND	ND	-	ND	33
11	ND	ND	-	29	30
12	ND	ND	-	ND	29

Table 54. Total suspended solids (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	240	39	37	-	-
2	54	13	5.1	-	-
3	78	61	12	-	-
4	110	120	10	-	-
5	41	40	16	-	-
6	100	190	24	-	-
7	58	68	16	-	-
8	12	28	-	2.7	-
9	14	12	-	4.2	30
10	14	44	-	1.1	51
11	31	23	-	-	49
12	84	57	-	2.0	63

Table 55. Zinc (mg/L).

Sampling Event	Gutter	Pre-TDA	Pan	Lysimeter	Groundwater
1	0.190	0.096	0.025	0.013	-
2	0.059	0.030	0.010	0.007	-
3	0.130	0.089	0.014	-	-
4	0.140	0.063	0.010	0.021	-
5	0.052	0.053	0.007	0.026	-
6	0.160	0.140	0.007	0.005	-
7	0.160	0.087	0.014	-	-
8	0.028	0.038	-	0.018	-
9	0.031	0.023	-	0.083	0.032
10	0.038	0.048	-	0.020	0.035
11	0.160	0.041	-	0.023	0.150
12	0.150	0.130	-	0.004	0.039