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A review of environmental impacts and environmental applications of shredded scrap tires

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ABSTRACT: Scrap tires shredded into small pieces (called "chips") alone or mixed with soil can have properties favorable to civil and environmental engineering applications. Although the reuse of scrap tires has become more common, questions regarding environmental suitability still persist, particularly the potential impact on ground and surface waters and aquatic life due to leaching. In contrast to this concern on contamination of the environment, the significant sorption capacity of tire material renders it a potential material for environmental protection and remediation when in contact with contaminated waters and leachate. This paper provides a review of the leaching characteristics of scrap tire chips as well as their sorption capacity that can be used in environmental applications based on the author's own research and the available literature.

1 INTRODUCTION

Scrap tires can be used in several ways either as whole or halved or shredded. They can be used alone as well as embedded or mixed with soils. Geotechnical applications of shredded tires include embankment fill, retaining wall and bridge abutment backfill, insulation layer to limit frost penetration, vibration damping layer, and drainage layer (Edil & Bosscher 1992; Humphrey 2003). Environmental applications of shredded tires include use as reactive drainage layer in landfills, septic tank leach field aggregate and nutrient barrier in golf courses and athletic fields (Lerner et al. 1993, Park et al. 1996, Edil et al. 2004, Aydilek et al. 2006, Lisi et al. 2004). Whole tires are used as retaining walls (Caltrans 1988), as a reinforcement layer in earthfill (O'Shaughnessy and Garga 2000a), in artificial reef construction (Candle and Prod 1983), and floating breakwater (Lee 1982). In these applications tire materials of varying sizes (from small chips to whole tires) will have contact with water in varying conditions (infiltrating, seeping, circulating, stagnant, etc.) resulting in interactions either releasing metals and organic chemicals or absorbing them depending on the chemical environment (i.e., pH and concentration of various chemicals in the contacting water). This paper presents a review of these tire-water chemical interactions based on the author's own research as well as the available literature.

2 TIRE COMPOSITION

Tires are principally composed of vulcanized rubber, rubberized fabric containing reinforcing textile cords, steel or fabric belts, and steelwire-reinforced rubber beads. The most commonly used tire rubber is styrene-butadiene copolymer (SBR) containing about 75% butadiene and 25% styrene by weight. Other elastomers such as natural rubber (cis-polyisoprene), synthetic cis-polyisoprene, and cis-polybutadiene are also used in tires in varying amounts. Carbon black is used to strengthen the rubber and to increase abrasion resistance. Extender oil, a mixture of aromatic hydrocarbons, serves to soften the rubber and improves workability. Sulfur, the vulcanizing agent, is used to cross-link the polymer chains within the rubber and to harden and prevent excessive deformation at elevated temperatures. The accelerator is typically an organosulfur compound that acts as catalyst for the vulcanization process and to enhance the physical properties of the rubber (Dodds et al. 1983). A typical composition of tire rubber is shown in Table 1.

Table 1. Rubber compounding composition (Dodds et al. 1983)

Component	Weight Percent
SBR	62.1
Carbon black	31.0
Extender oil	1.9
Zinc oxide	1.9
Stearic acid	1.2
Sulfur	1.1
Accelerator	0.7

3 POTENTIAL ENVIRONMENTAL IMPACTS

Although use of scrap tires above groundwater table is widely accepted, use of tires under the groundwater table or directly in surface water bodies is still not permitted in some states due to concerns regarding potential for groundwater contamination. A better understanding of the interaction between scrap tires and aqueous environments is essential for the further development of innovative uses for scrap tires. To comprehensively study the toxicity of tire chips, an extensive literature review of the leaching characteristics of tires and tire chips was performed.

A significant body of literature describes research with shredded automobile tires and their environmental suitability when used in civil engineering applications. The research consists of laboratory and field studies on the leaching behavior of tire chips. The following is a review of laboratory and field studies dealing with environmental suitability of tire chips. Since tires contain ingredients such as carbon black, vulcanizing agents, metallic reinforcement, antioxidants, pigments, accelerators, etc. (Miller and Chadik 1993) in addition to petroleum products that might be collected during use, laboratory and field leaching studies have addressed organic and inorganic compounds.

3.1 *Leach Testing of Tire Chips*

Batch tests are typically used to determine the leaching characteristics of any by-product, such as tire chips. The mass of tire chips, the volume of the container i.e., solid-liquid ratio), and chemistry of the extraction liquid vary from one study to another. The majority of studies dealing with the leachability of tire chips were performed under stagnant conditions with a fixed volume of liquid. This testing setup is not realistic since in the field the tire chips leach into a flowing groundwater and there is potential for dispersion and adsorption. The methods of analysis of these leachates usually consist of gas chromatography for organics and spectrometry for inorganics.

The Toxicity Characteristic Leaching Procedure (TCLP) is a popular test used to determine if a waste material or a by-product is hazardous. The volume of the container is 500 to 600 mL with zero head space. Liquids of pH of 4.93 and 2.88 are recommended for use in these tests, and time allowed for leaching is 16 hrs. The minimum amount of solids placed in the extractor is 100 g for the non-volatile analysis and 25 g for volatile organics. The EP-Toxicity test was developed before the TCLP and is used for the same purpose. The EP-Toxicity test specifies a pH of 5 for the liquid, a time period of 24 hrs, and no minimum size of container. Rubber Manufacturers Association (RMA) (1990) compared leaching results from tire chips using both tests and found no significant difference between the two tests.

Another batch leaching test is Water Leach Test (WLT) (*Standard Test Method for Shake Extraction of Solid Waste with Water* - ASTM D 3987) typically used for non-hazardous materials to assess the leaching potential. In this test, the solid material (70 g) is crushed to pass a US No. 4 Standard sieve (4.8 mm) and combined with 1400 ml of ASTM Type II deionized water in a 2-L sealed container. This mixture is agitated continuously in a tumbler for 18 hr. The mixture is allowed to settle and then the leachate is sampled and subjected to chemical analysis.

Converting leachate concentrations and the concentrations of different standards from the mass of compound per volume of liquid to the mass of compound per mass of tire chips helps to compare the findings of many studies. Such a comparison is presented in Table 2 and 3 (Tatlisoz *et al.* 1996). Table 2 provides the conversion of several regulatory limits, i.e., TCLP, U.S. EPA recommended Maximum Concentration Levels (MCLs), and Wisconsin's Groundwater Preventive Action Limits (PALs).

Table 2. Conversion of regulatory concentration limits

Compound	Concentration limits based on tire chip mass		
	TCLP[1] [mg/kg]	US EPA's MCLs[2] [mg/kg]	WI PALs[2] [mg/kg]
As	25.9	0.06	6.15×10^{-3}
Ba	518.0	2.27	0.25
Cd	5.18	6.15×10^{-3}	1.23×10^{-3}
Cr	25.9	0.15	6.15×10^{-3}
Pb	25.9	0.025	6.15×10^{-3}
Fe		0.37	0.18
Mn		0.06	0.03
Zn		6.15	3.1
Se	5.18	0.055	1.23×10^{-3}
Hg	1.03	3.7×10^{-3}	2.5×10^{-3}
NO_2^-/NO_3^-		1.23	2.46
Toluene	33.79	2.46	84.3×10^{-3}
Carbon disulfide	332.64		
Phenol	332.64		1.23×10^{-3}
Benzene	0.36	6.15×10^{-3}	0.08×10^{-3}

[1] TCLP are converted to mass of compound per kg of tire chips assuming that 100 g of tire chips with a specific gravity of 1.22 is used. (volume of extractor = 600 mL; mass of solid = 100 g for inorganics and 25 g for volatile organics)

[2] U.S. EPA MCLs and Wisconsin PALs of 1.22 (1 mg/L = 1.22 mg/kg of tire chips)

Table 3 provides the conversions of concentrations from several batch tests reported in the literature. Zinc, iron, barium, manganese, selenium, lead, chromium, and cadmium were found at concentrations higher than the U.S. EPA's MCLs and Wisconsin's PALs in most studies. Zinc and iron (two compounds typically with the highest concentrations) are not classified as hazardous materials in TCLP limits. Concentration of arsenic exceeded Wisconsin PALs, but not MCLs (Miller & Chadik 1993) while arsenic was not detected in the Rubber Manufacturers Association (1990) study. Even though several inorganic and organic compounds have been detected in shredded tire leachates, concentrations were generally well below TCLP limits and were not significantly higher than recommended MCLs and Wisconsin PALs, regardless of differences in the test conditions. It is important to note that in many studies the extraction liquid or test setup was designed for worst case conditions that do not necessarily exist in the environment that tire chips are used. For example, laboratory tests performed with fixed volume of liquid or tire chips exposed to aggressive extractions do not simulate conditions likely to exist in most tire chips applications. Thus, in the field studies, lower concentrations are likely to exist.

For a more realistic assessment of leaching under flow-through conditions and to understand the temporal characteristics of leachate concentrations, Column Leaching Test (CLT) can be conducted. Specimens for the CLTs are prepared as for the WLTs and placed in the CLT cell in a density state similar to that expected in the field conditions and water flow is initiated at a hydraulic gradient or flow rate as expected in the field. Typically, ASTM Type II water can be used as the influent liquid. The ionic strength of this solution is comparable to that in natural waters percolating through the pavement base layer. A 0.1 M LiBr solution prepared with LiBr

Table 3. Compounds leached from tire chips

	Reported concentrations based on tire chip mass				
Compound	Grefe[1] (1988) [mg/kg]	RMA[1] (1990) [mg/kg]	TCTC[2] (1990) [mg/kg]	Miller & Chadik[3] (1993) [mg/kg]	Park et al.[4] (2003) [mg/kg]
As		-		0.02	
Ba	0.55	0.1	1.08		0.37
Cd		-	0.27		
Cr		0.008	0.51		0.019
Pb	0.075	0.003	0.92		0.14
Fe	1.15		1081		
Mn	1.5				
Zn	3.15		50.3	5.02	1.13
Se			0.44		0.05
Hg		7.2×10^{-5}			
NO_2^- /NO_3^-	1.85				
Toluene		0.034		0.28	
Carbon disulfide		0.012			
Phenol		0.01			
Benzene		-		0.63	

[1] The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study. (RMA=Rubber Manufacturers Association)

[2] Conducted by Twin City Testing Corporation (TCTC)

[3] Concentrations for compounds are taken from approximately 16 hour readings which are usually the highest concentrations achieved during the test. The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study.

[4] Concentrations for compounds are the final concentration reached in 800 days. The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study.

salts (99.9% purity) can be used to trace breakthrough. Leachate (effluent) from the CLTs is collected in airtight sampling bags made of Teflon. Leachate is collected periodically, filtered, acidified, and stored using the same protocol employed for the WLTs for chemical analysis.

J & L Testing Co. (1989) performed column tests on tire chips with the liquid flowing at a rate of 5.8 cm/day. The container was 20.3 cm in diameter and had a length of 121.9 cm. Kim (1995) used steel containers having diameters of 61 cm and lengths of 91.4 cm. When comparing the results of these tests, the concentrations should also be normalized with respect to the weight of tire chips. O'Shaughnessy and Garga (2000b) performed column tests on tire chips embedded in sand and clay. The former indicated increase in effluent certain metal elements (aluminum, iron, zinc, and manganese) which in some cases exceeded their respective drinking water standards. All target elements were below detection limits or background levels for tire chips embedded in clay.

3.2 *Factors affecting tire chips leachate*

The main factors affecting the characteristics of leachates from tire chips include the aquatic environment in which the tire chips are exposed, the age of the tires, the size of the tires, and the time of exposure of the tire to the liquid. Understanding the relationships between these factors and the chemical characteristics of tire chips leachate is crucial to any leaching study.

The aquatic environment is typically described by the pH of the extraction liquid. Twin City Testing Corporation (1990) used extraction liquids having pH of 3.5, 5.0, 7.0, and 8.0. This study showed that higher metal concentrations were obtained in the leachate when the pH was 3.5. Higher hydrocarbons concentration was observed when the pH was 8.0. Miller & Chadik (1993) performed leaching tests with liquids having pHs of 5.4, 7.0, and 8.6 and reported that there was no strong correlation between pH and leachate characteristics.

Twin City Testing Corporation (1990) and Rubber Manufacturing Association (1990) performed leach tests on new and old tire chips. They reported that both new and old tire chips leached organic and inorganic compounds, but at concentrations lower than the TCLP limits to classify as hazardous material. Twin City Testing Corporation (TCTC) (1990) reported that newer tire chips leached slightly higher concentrations of polycyclic aromatic hydrocarbons (PAHs).

3.3 *Tire chips and groundwater quality*

3.3.1 *Inorganic compounds*

Several laboratory leaching studies used worst case conditions (acidic or alkaline) when assessing the leachability of tires and tire chips. In civil engineering construction, however, the tire chips are typically used as fill material and these extreme conditions are not likely to appear. The leaching process is typically caused by the infiltration of rain water or when tire chips are in contact with groundwater. Using solutions that better represent the chemistry of rainwater and/or groundwater is of interest.

To further study the leaching characteristics of tire chips in various aquatic environments, a laboratory study consisting of batch tests was designed to simulate various environmental conditions, such as aquifers and wetlands (Gunter et al. 1999). The tire chips used in the laboratory investigation were mechanically processed from steel-belted automobile tires. The particle size of the tire chips ranged approximately from 2 to 10 cm (longest dimension). Six 184-liter stainless steel tanks were used. Three different waters were used: groundwater, marsh water, and deionized water. Groundwater was taken from a 90-m deep supply well and the pH of the groundwater was 6.7 to 7.4. Groundwater at this location is sampled quarterly and tested for the presence of organic and inorganic contaminants of concern. Lead and iron are the only compounds in the groundwater from the well that have exceeded the Wisconsin PAL in one sampling event of this well. The marsh water was collected from a marsh. Marsh water was collected since tire chips are used as light-weight fill on soft materials such as marsh deposits. This water was then passed through a #200 sieve to filter out soil and plant remains. Deionized water does not have dissolved chemicals; therefore, it represents a reference state for the other two aquatic environments.

Three different stagnant waters were simulated. Three tanks contained tire chips (about 100 kg) and water, whereas the other three tanks contained only water as control. The tanks were filled with tire chips and/or water to the top to eliminate any headspace and then were sealed. Initial samples of the water were analyzed for volatile organic compounds (VOCs) using a purge and trap method (EPA method 8021) and a headspace scan (gas chromatogram/mass spectrometer method). The tanks remained stagnant until sampling began and continued periodically for the next 12 months. Samples were collected using a hypodermic needle inserted through a sampling port that was located at mid-height of the tanks.

Table 4 shows the concentration of the inorganic parameters analyzed in the first sampling event. None of the inorganic parameters exceeded the Wisconsin PALs (PALs are lower limits than drinking water standards) in any of the water environments. Subsequent sampling events (not shown) confirmed this finding. Hardness of the groundwater increased with time and the tanks with tire chips contained oil and grease at the end of the monitoring period.

Twin City Testing Corporation (1990) performed a field study to determine how groundwater characteristics changed when exposed to tires and tire chips. The study consisted of comparing ground water samples collected beneath a tire stockpile to background concentrations of a typical groundwater samples. This study indicated that the average zinc concentrations increased from 0.1 to 0.87 mg/L, iron concentrations from 5.8 to 298 mg/L, and the magnesium concentrations from 6.2 to 383 mg/L. The arsenic, barium, cadmium, chromium, and lead concentrations for only the groundwater sample collected underneath the tire stockpile exceeded the Minnesota recommended allowable limits. Soil samples were also collected from the area and the concentrations of arsenic, barium, calcium, and selenium were higher than those for the background samples. In contrast, aluminum, iron, magnesium, and zinc were found in lower concentrations when analyzing the soil sample.

In one of the earliest embankment fill application of shredded tires, Edil & Bosscher (1992) installed two lysimeters beneath the areas containing tire chips to collect the leachate. The pH was found to be stable around 7.5. Leaching of zinc, manganese, and iron was observed. However, these may have leached from the surrounding soil as there was a history of high manganese concentrations in the areas around the test fill. The Wisconsin groundwater PALs was exceeded in the leachate for several metals. However, it was concluded that the possibility of tire chips affecting groundwater quality was highly unlikely (Bosscher et al 1993).

Table 4. Summary of Inorganic parameters analyzed in the last sampling (12 months later)

Compound	Unit	PAL	Tank 1 (GW)	Tank 2 (GW + T)		Tank 3 (MW)	Tank 4 (MW + T)		Tank 5 (DI)	Tank 6 (DI + T)	
				Total	From Tires		Total	From Tires		Total	From Tires
As	µg/L	5	1			<1			<1		
Ba	µg/L	400	42	120	78	15	220	205	<1	120	119
Ca	µg/L			42000	42000				<100		
Cd	µg/L	0.5				<0.08					
Cr	µg/L	10	<2	<2			<2		<2	<2	0
Co	µg/L										
Cu	µg/L	130		<8	<8				13		
Fe	µg/L	150	<20	15000	14980	1200	71000	69800	20	18000	17980
Pb	µg/L	1.5	1	2	1	2	1	1		20	20
Mg	µg/L			37000	37000				<30		
Mn	µg/L	25	6	770	764	110	3200	3090	3	1400	1397
Mo	µg/L										
Ni	µg/L	20									
Se	µg/L	10	2			<1			<1		
Na	µg/L			11000	11000				<700		
Zn	µg/L	2500	750	<19	731	32	<19	13	30	42	12
TOC	mg/Kg		<0.5	220	220	5.6	270	264.4	<0.5	150	150

Humphrey& Katz (2000) describes the results of a five year field study on the effects of tire chips placed above the water table on the groundwater quality. The tire chips were placed beneath a secondary highway and the leachate was collected using geomembrane-lined basins located below the tire chips. One control section (constructed with typical granular materials) was also constructed adjacent to the tire chips sections. Samples of leachate were collected on a quarterly basis for constituent testing. Filtered and unfiltered samples were analyzed for barium, cadmium, chromium, lead, and selenium. Humphrey & Katz (2000) reported that there was no evidence that the presence of tire chips altered the concentrations of these substances from their naturally occurring background levels. In additions they reported that there was no evidence that the tire chips have increased the concentration levels of aluminum, zinc, chloride, or sulfate, which are secondary drinking water standards. Humphrey & Katz (2000) added that under some conditions, iron, and manganese levels might exceed secondary standards. In another study, O'Shaughnessy & Garga (2000b) reported that field monitoring of leachate from a prototype test embankment constructed with cut (one side wall removed) and whole tires above the groundwater table showed insignificant adverse effect on groundwater quality over a period of 2 years.

In a subsequent study, Humphrey & Katz (2001) constructed a field trial to evaluate the water quality effects of tire shreds placed below the water table. The study consisted of three sites, each with 1.4 metric tons of tire shreds buried in a trench below the water table. The tire shreds were made from a mixture of steel and glass belted tires and had a maximum size of about 75 mm. The soil types at the sites were marine clay, glacial till, and peat. At each site, one water sampling well was located upgradient to obtain the background water quality, one well was located in the tire shred filled trench, and two to four wells were located 0.6 m to 3 m downgradient of the trench. Samples were taken over a four-year period and analyzed for a range of metals, volatile organics, and semivolatile organics. Their results showed that tire shreds had a negligible effect on the concentration of metals with primary (health based) drinking water standards. For metals with secondary (aesthetic based) drinking water standards, samples from the tire shred filled trench had elevated levels of iron, manganese, and zinc. However, the concentrations of these metals decreased to near background levels for samples taken downgradient of the tire shred filled trench. Tire shreds placed below the water table appear to have a negligible off-site effect on water quality.

These investigations address the initial leachate concentrations but evaluating potential impacts on ground water quality caused by leaching of heavy metals from the tire chips is an important step in applying this technology. It can be done on a site-specific basis. WiscLEACH, a Windows-based computer application developed for assessing potential ground water impacts associated with use of recycled materials such as scrap tires in roadway construction provides a means of making such an evaluation (Li et al. 2006). The application is designed to be easy to use and to function rapidly so that a designer or regulator can quickly conduct a series of simulations without training in numerical modeling. WiscLEACH is freeware that is available at www.uwgeosoft.org. The conceptual model consists of a recycled material layer in a typical highway structure as shown in Figure 1. As water percolates down through the profile, heavy metals leach from this layer and then migrate downward through the subgrade soils until they reach the ground water table (GWT). Flow in the recycled material layer and subgrade is assumed to occur only in the vertical direction and transport is assumed to follow the advection-dispersion-reaction equation (ADRE) with instantaneous and reversible sorption and a linear isotherm. Bin-Shafique et al. (2006) show that this assumption is valid for such systems and typical subgrades. Metals that reach the GWT are transported horizontally and vertically, although the flow of ground water is assumed to occur predominantly in the horizontal direction. Transport in ground water is also assumed to follow the ADRE with instantaneous and reversible sorption and a linear isotherm. In both layers, chemical and biological reactions that may consume or transform metals are assumed to be absent. The recycled material and all soils in the profile are assumed to be homogenous and isotropic.

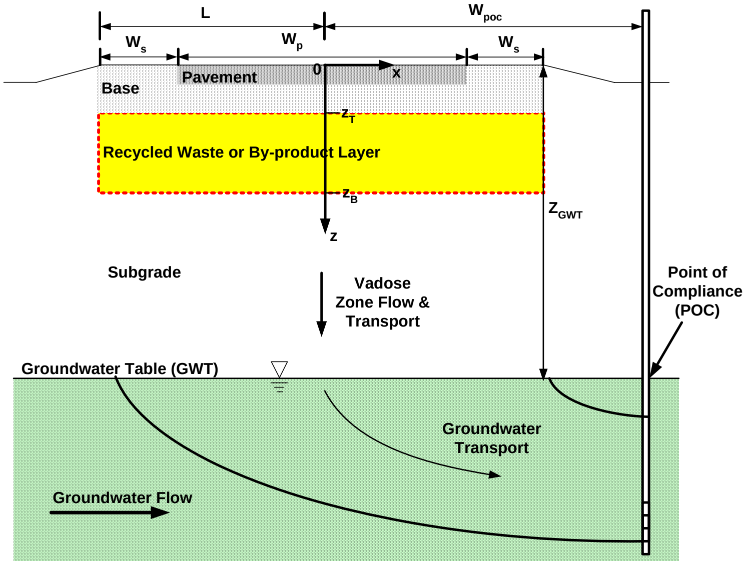

Figure 1 Conceptual model in WiscLEACH for predicting impacts to the vadose zone and groundwater caused by leaching from a pavement structure with a recycled waste or by-product layer

An example problem has shown that maximum concentrations typically occur near the ground water table and the peak ground water concentration decreases as the depth to ground water increases (Li et al. 2006). Parametric studies also showed that the variables having the greatest influence on maximum concentrations in ground water are depth to the ground water table, thickness and width of the recycled material layer, hydraulic conductivity of the recycled material layer and the aquifer, and the initial metals concentration in the recycled material layer.

3.3.2 *Organic compounds*

A study conducted by Twin City Testing Corporation (1990) indicated that under alkaline conditions, the concentration of polycyclic aromatic hydrocarbons (PAHs) in tire chip leachate exceeded drinking water standards. Miller & Chadik (1993) suggested that these compounds may leach from carbon black, petroleum residues, and recipe extenders associated with the manufacturing of tires. Rubber Manufacturers Association (1990) reported that VOCs such as toluene, carbon disulfide, and methyl ethyl ketone might leach from tire chips. In addition, benzene was detected in tire chip leachates, and that only phenol was detected as a semi-volatile compounds. This study added that the concentrations of these organic compounds are below TCLP limits. Bosscher et al (1993) used biological and chemical oxygen demand (BOD, COD) as indicators of organic compounds in leachates from tire chips and reported decreasing BOD and COD in their leachates. Miller & Chadik (1993) prepared 27 aquatic solutions in the laboratory at different pH levels and varying ionic strengths. Tire chips of various sizes were then submerged in these aquatic solutions and the liquids periodically analyzed. Miller & Chadik (1993) reported that organic compounds such as aromatic compound of gasoline, carboxylic acids, and aniline were leached from tire chips. Two of their solutions used were similar to groundwater. The leachates obtained using these liquids had benzene concentrations as high as 0.0115 mg/L, and toluene concentrations of 0.0112 mg/L. Humphrey & Katz (2001) found trace concentrations of a few organic compounds in the tire shred filled trenches in their study of tire shreds placed below the groundwater table, but concentrations were below method detection limits for virtually all the samples taken from the downgradient wells.

In the tank batch tests described above the organic chemicals were also analyzed. Table 5 shows the results for organics in the first sampling event. The steel tank that contained groundwater and tire chips (Tank 2) initially had concentrations above the Wisconsin PALs for benzene and trichloroethylene (TCE). This tank also exceeded the Wisconsin drinking water standard, which is 10 times higher than PAL, in methyl isobutyl ketone (MBIK). This compound is also known as hexanone, 2-methyl-4-pentanone. MIBK is a compound derived from the tire-manufacturing process. There were no organic compounds detected in Tank 1, the control tank that was filled with groundwater from the same source as Tank 2. In the second sampling for VOCs there were no contaminants found that exceeded any PAL. Initially, the steel tank that contained marsh water and tires chips (Tank 4) had a high concentration of MIBK. It exceeded the Wisconsin PAL. The control tank for marsh water (Tank 3) showed trace levels of toluene but nothing above the Wisconsin PALs. In the second testing for VOCs, neither Tank 3 nor 4 had detectable amounts of any organic compounds. Initially, the tank that contained deionized water and tire chips (Tank 6) exceeded the Wisconsin PAL in TCE. It also showed a small amount of toluene. MIBK was detected in high concentration. The control tank contained no detectable VOCs. In the second testing for VOCs, benzene was detected in a concentration above that of the PAL in Tank 6. Tank 5, the control tank was not sampled but was expected to be below the standard limits.

The overall conclusion of these studies is that tire shreds may increase levels of certain metals (e.g., iron and manganese) and some organic compounds; however, as concluded by Humphrey & Swett (2006) in a detailed literature review report, there appears to be limited effect on drinking water quality of groundwater from leachate derived from tires for a range of applications involving tires or tire shreds, so human health concerns are minimal.

3.4 *Tires and aquatic life*

B.A.R. Environmental Inc. (1992) reports that new and older tires are both toxic to rainbow trout, and therefore indicating that the toxicity is caused by materials associated with the manufacturing of tires and not by other materials accumulated during the life of tires. In addition they reported that the toxicity concentrations were slightly higher in older tires. The effects of tire size on the chemical characteristics were addressed by the Rubber Manufacturers Association

(1990) study and Miller & Chadik (1993). Both studies show that, in general, the leachates obtained from ground and whole tires are comparable.

B.A.R. Environmental Inc. (1992) tested the toxicity of leachates generated from tires at 5, 10, 20, and 40 days of exposure. This study showed that toxicity concentrations reached a peak at 5 days and did not change then after. Miller & Chadik (1993) reported that benzene concentrations were highest at the beginning of the test and decreased exponentially with time, and that toluene concentrations were lowest at the start of the test but increased gradually with time. They also reported that the concentration of zinc increased with time for 63 days and then decreased thereafter. Edil & Bosscher (1992) also observed time-dependent composition of their leachate collected from field lysimeters underneath their shredded tire embankment. They attributed this change to the change in construction activities such as roadway dust treatment with calcium chloride and the asphalt paving operation performed on the roadway.

Table 5. Summary of Organic Compound Analysis for Laboratory Tests

Volatile Organic Compounds	Units	WI PALs	Tank 1 (GW)	Tank 2 (GW + Tire)	Tank 3 (MW)	Tank 4 (MW + Tire)	Tank 5 (DI)	Tank 6 (DI + Tire)
Acetone	mg/L	0.1479	ND	ND	ND	0.1149	ND	0.0014
Benzene	mg/L	0.0004	ND	0.0015	ND	ND	ND	ND
Ethylbenzene	mg/L	0.1035	ND	ND	ND	ND	ND	ND
Methyl ethyl ketone	mg/L	0.0666	ND	0.0147	ND	0.01724	ND	ND
Methyl isobutyl ketone (MIBK)	mg/L	0.0370	ND	1.1513	ND	0.9577	ND	1.0407
Toluene	mg/L	0.0509	ND	ND	0.0019	ND	ND	0.0012
Trichloroethylene	mg/L	0.0001	ND	0.0008	ND	ND	ND	0.0008

Abernethy (1994) reported tire leachate obtained by immersing an automobile tire in 300 L of water caused mortality in trout and other species. Abernethy (1996) also reported that tires placed in a tank of flowing water were non-lethal to trout. Hartwell et al (2000) showed that toxicity decreased with increasing salinity and concluded that tire shreds are probably a greater threat to freshwater habitats than brakish or marine habitats. Sheehan et al. (2006) conducted aquatic toxicity tests on leachate samples collected from the below groundwater disposal study sites of Humphrey & Katz (2001). They found elevated levels of iron, manganese, and several other chemicals but no adverse effect to test organisms from the leachate of the tire chips placed above the groundwater table. However, leachate from the tire chips placed below the groundwater resulted in significant reduction to both survival and reproduction of a test organism. However, they expected these effects to decrease downstream from the tire chips. Sheehan et al. (2006) recommend a buffer zone of 3 to 11 m between the tire chips fill and the surface water to avoid impact on aquatic life.

Laboratory aquatic toxicity studies and field leachate samples indicate that tire shred leachate impacts test organisms. The implication of these tests is now confirmed. Tires placed in open water such as reef construction have proven to be a huge ecological blunder. Little sea life has formed on the tires. Some tires have broken loose from their bundles and scouring the ocean floor and washing up on beaches. Similar problems have been reported at tire reefs worldwide and expensive removal activities are underway as reported by The New York Times on February 18, 2007. However, the impact of leachate from tire shreds placed below the groundwater on the surface waters may be limited by allowing an appropriate separation zone between the tires and the surface water. More field evidence is needed.

4 ENVIRONMENTAL APPLICATIONS

The process of manufacturing tires combines raw materials into a special form that yields unique properties such as strength, resiliency, and high absorbency of chemicals (Edil & Bosscher

1994). These unique properties of tires can be exploited in a beneficial manner if scrap tires are used as a construction material. Scrap tires used in civil engineering applications have ten times better drainage than well graded soil, eight times better insulation than gravel, and 33 to 55% weight of soil (Rubber Manufacturers Association 2002). Tire chips and tire chips-sand mixture have high permeability and retain it even under high vertical loads (Edil et al. 1992). These properties make shredded tire chips a good lightweight substitute for aggregate in general construction.

Park et al. (1996) found that the tire chips have relatively high VOC sorption capacities based on batch isotherm tests on scrap tire chips. This suggests yet another innovative environmental application in which shredded tire chips could be used to eliminate VOCs from contaminated water or leachate thus alleviating the contamination problem. Kim et al. (1997) conducted a series of batch isotherm test with ground tire powder to investigate the effect of environmental conditions such as presence of other organic materials, ionic strength and pH of the solution, particle size of tire powder, and temperature. Since this study used only ground tire rubber not tire chips, it was possible to identify which part of tire chips played a major role in adsorbing organic compound. They found that organic compounds sorbed primarily onto tire rubber polymeric materials and partially other materials in tire rubber such as carbon black. Styrene butadiene rubber (SBR) is one of the major components of tires Table 1). Non polar organic compounds such as benzene, toluene, trichloroethylene, and tetrachloroethylene, are attracted by non polar materials such as SBR. Park et al. (1996) found that tire chips have 1.4 to 5.6% of the sorption capacity of granular activated carbon on a volume basis. In addition, Park et al. (1996) found that of the organic compounds sorbed in tire chips, only 3.5 to 7.9% were desorbed. Twin City Testing Corporation (1990) also indicated that the average concentrations of zinc, iron, and manganese increased in the groundwater samples under a tire stockpile but at the same time the concentration of petroleum hydrocarbons decreased from 11.8 to < 0.5 mg/L compared to background groundwater samples indicating the potential of tires to absorb these compounds. Therefore, another application for scrap tires is to use them as a sorptive medium taking advantage of their sorptive quality to chemicals.

One such application is to use tire chips as a reactive drainage medium in landfills, i.e., in leachate collection layer. A wide range of VOCs have been detected in leachates from municipal solid waste and hazardous waste landfills (Plumb & Pitchford 1985; Gibbons et al. 1992; Klett et al. 2005). Research has also shown that diffusive transport (contaminant migration driven by the difference in concentration between the upper and lower sides of the liner) is often the dominant mode of contaminant transport in well-built liner systems (e.g., Edil et al. 1996, Kim et al. 2001, Foose et al. 2002), and that transport of VOCs generally is more critical than transport of inorganic compounds (e.g., toxic heavy metals), even though VOCs are often found at lower concentrations in leachates (Foose et al. 2002). VOCs generally are more critical for two reasons. First, VOCs are not as much retarded in clay liner and generally toxic at lower concentrations than many inorganic compounds. Second, geomembrane do little to inhibit the transport of VOCs in modern composite liner systems, because VOCs diffuse readily through geomembrane polymers (Park and Nibras 1993). A recent study showed that there is not a significant difference in concentration of VOCs in pan lysimeters placed under the liners in Wisconsin landfills at both compacted clay and composite (compacted clay plus geomembrane) lined sites (Klett et al. 2005). Furthermore, in many cases the VOC concentrations in the lysimeters exceeded the Wisconsin PALs. Therefore, the effectiveness of modern landfill liner systems to minimize migration of VOCs is a concern.

Based on batch isotherm tests on tire chips in contact with various organic compounds, Park et al. (1996) proposed equations to determine the thickness of the tire chip layer needed to remove a given amount of organic compounds and the mass of tire chips required. When the leachate generation rate in a landfill is 1,500 m^3/ha·yr and the porosity is 0.4, the required tire layer thicknesses for 90% organic compound removal over various design lives are shown in Figure 2. The mass density of tire chips used in the calculation was 1.22 g/cm^3. If the design life of a landfill is 30 years, then the tire layer thickness required for 90% removal of benzene, trichloroethylene (TCE), *m*-xylene, and pentachlorophenol are approximately 50, 28, 15, and 1 cm, respectively. Polar organic compounds, such as methylene chloride and chloroform, that require large quantities of tire chips, tend to be more biodegradable in landfills. For general landfill application, the tire chip layer thickness of 30 to 45 cm is recommended. Since the rate of organic compound sorption is a function of the diffusion coefficient and not the surface area (Kim et al. 1997), tire chip size does not play a significant role. Therefore, the tire chip size ranging from 5 to 30 cm is recommended for use as a substitute for landfill leachate collection media. As a rule of thumb, a 1-ha landfill requires approximately 300,000 tires to fill 30 cm of a leachate collection layer. The hydraulic conductivity of tire chips is very high when they are not compressed under load and not mixed with soil (Edil et al. 1992). In tests for use of tire shreds in leachate collection layer, hydraulic conductivity decreased with increasing vertical pressure from 0.87 (no load) to 0.13 cm/s (at 478 kPa vertical stress) under 300 mm head (about a hydraulic gradient of 1) and higher values (down to 0.19 cm/s) under the lower hydraulic head of 150 mm (about a hydraulic gradient of 0.5). Having different hydraulic conductivities at different heads is not unusual because of large pore sizes the flow is more turbulent than laminar. The flow rate divided by the square root of hydraulic head was nearly constant at the two heads giving support to the observation that a more of a turbulent flow rather than laminar flow existed.

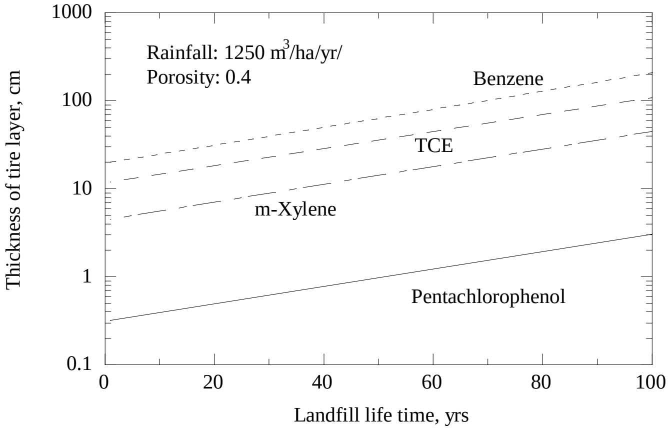

Figure 2. Estimated tire layer thickness required for 90% removal over landfill life based on batch isotherm tests

Although there are many advantages to using recycled tires in civil and environmental applications, concerns have been raised about their self-combustion potential and environmental suitability. However, guidelines have been developed to deal with this issue. It is recommended that the thickness of a tire shred layer be limited to 3 meters and that relatively large shreds with a minimum of rubber fines be used along with limiting the flow of air and water into the interior of tire-shred fills (ASTM D6270-98). Thus, it is possible to use tire chips alone and especially in mixture with granular soils (such mixtures are not known to self combust) as a sorptive drainage material taking advantage of their high permeability and high absorbency of chemicals without the fear of self-combustion.

4.1 *Large-scale laboratory tests*

Edil et al (2004) conducted large-scale laboratory tests simulating a clay liner with a tire-chips drainage layer over it to quantify the effect of tire chips in reducing the transport of VOCs through compacted clay liners. Tanks with diameters of 0.6 m were used in these tests. This experimental apparatus has been described in detail by Edil et al. (1994) and Kim et al. (2001). The influent and the effluent were supplied and collected using Teflon bags, which allow control of hydraulic heads. This system permits the water to flow evenly across the entire soil layer. All parts used were made of stainless steel and brass and tubing was made of Teflon. Tire chips (2 to 10 kg) were placed over the compacted clay in the upper influent reservoir. After the hydraulic conductivities of clay specimens stabilized, the upper reservoir and the influent bag fluid is replaced with the VOC containing solution. For the tank tests, methylene chloride, toluene, and trichloroethylene were the selected VOCs. The initial target concentration of each VOC was 16 mg/L.

The concentrations of toluene in the upper influent reservoir are shown in Figure 3. The organic compound concentrations in Tank 4 (T4), which did not contain tire chips, were relatively constant and higher than those in the three other tanks, which contained tire chips, because the sorption of organic compounds onto tire chips is much greater and faster than the mass transfer of organic compounds through a clay layer. However, in the tanks with tire chips (Tanks 1, 2, & 3), concentrations in the upper reservoirs decreased in a few days. Since no breakthrough of any of the VOCs was observed in the lower effluent reservoir of the tanks with tire chips (due to the sorption of VOCs by tire chips), the clay liner layers were cored to obtain the concentration-depth profiles. The cores were sectioned to obtain the concentration-depth data. The concentration-depth profile was obtained by analyzing the pore water of each section of the core. Figure 4 shows the concentration-depth profile for toluene. Toluene was not detected in any sectioned clay specimens of the tanks with 10-kg tire chips (T1 and T2) as well as in the upper compartment.

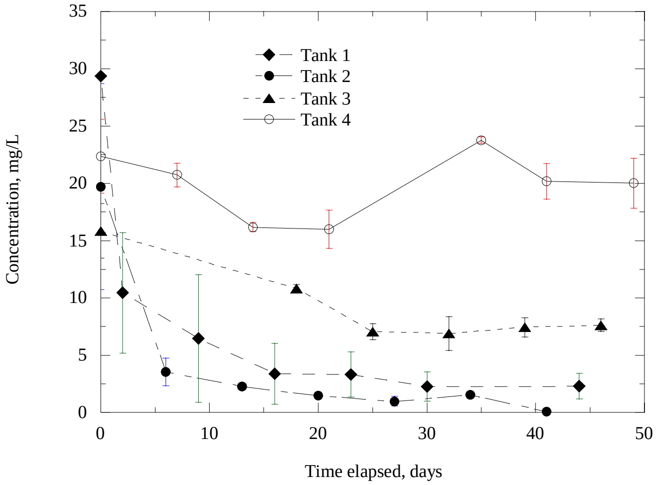

Figure 3. Toluene concentration in the upper reservoir in tank tests.

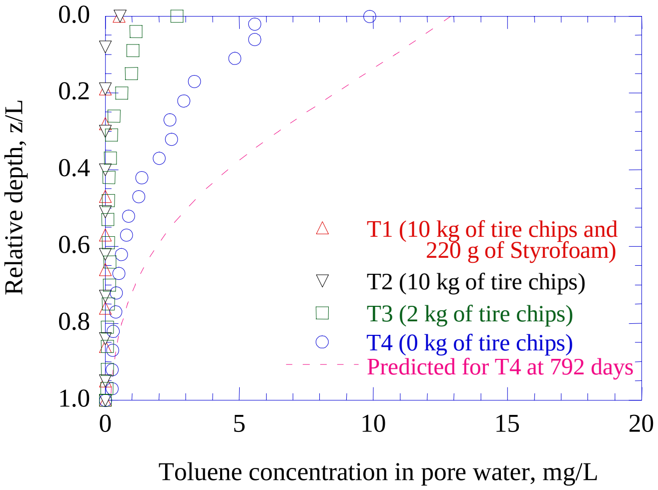

Figure 4. Toluene concentration-depth profile in tank tests

4.2 *Field Tests*

To demonstrate the effectiveness of tire chips as a sorptive layer, two geomembrane lined collection cells were constructed in a landfill. Each basin was 7.32 m long by 7.32 m wide. Detailed schematics can be found in Park et al. (2003). A drainage layer was placed directly on top of the geomembrane. One of the test cells contained gravel (30-cm thick) and the other contained tire chips (30-cm thick). The gravel was the same gravel that was used in the drainage layer of the landfill. Municipal refuse was placed to a height of 4.57 m over the test cells and covered with wood chips. Pipes were installed down-slope side of the collection cells in order to drain the leachate periodically. The base of the collection cells was sloped 4% to drain the leachate to the leachate collection pipe. The leachate collection pipe was constructed from a high density polyethylene (HDPE) pipe section welded with a boot to the HDPE liner using extrusion welding. A steel pipe with a valve was fitted and sealed to the HDPE pipe.

The leachate production volumes were estimated to be 3.9 and 5.2% over a 2-year period in gravel- and tire chip-containing cells, respectively. There was no indication of any retardation of leachate drainage due to use of tire chips instead of gravel in the drainage layer under 4.57-m of refuse and over 2 years. Leachate samples generated by rainfall and taken 1 and 6 months after construction showed a wide variety of metals and large amounts of oil and grease (i.e., 25,000 mg/L in gravel cell and 7,000 mg/L in tire chips cell). These two leachate samples were analyzed for VOCs following the EPA Method 8021. Methyl isobutyl ketone (MIBK) was detected only in the cell samples from the tire chip-containing cell, but not in those from the gravel-containing cell, indicating that tire chips might leach MIBK. In leaching tests performed on the shredded tires, MIBK was not reported (Gunter et al., 1999), indicating that the tire chips used in the collection cells might have been exposed to MIBK, or refuse containing MIBK might have been landfilled over the tire chip-containing cell. On the other hand, toluene was only detected in collection cell samples from the gravel-containing cell. The concentration increased from 1.4 to 32 μg/L, implying that toluene existed in the refuse and leached out. Since tire chips could sorb toluene (Park et al., 1996), collection cell samples from the tire chip-containing cell did not contain toluene. It can be said that the gravel-containing and tire chip-containing cells had different water quality that closely reflected the properties of tire chips and gravel.

The test cells were spiked with gasoline. First the leachate was drained entirely from the cells. Then, ten holes were dug in the refuse, five on each of the test cells. Approximately 3.79 L of gasoline was poured in each hole and the holes were covered with wood chips. A sample of leachate was taken from the drainage pipes two weeks later. In the gravel-containing cell, the leachate exceeded the U.S. EPA’s MCLs in all of the BETX compounds while in the tire chip-containing cell, the leachate did not exceed the MCLs in its concentration of benzene. This supports the evidence from past laboratory batch isotherm tests in which tire chips were found to have beneficial sorption properties (Park et al., 1996). The leachate was sampled again on about one month after spiking. Results similar to the previous sampling were obtained further supporting the previous findings by Park et al. (1996) and provide evidence that tire chips have favorable sorptive characteristics. The gravel-containing cell exceeded the MCLs in benzene, toluene, and xylenes. The tire chip-containing cell did not exceed the MCLs, and had a much lower concentration than in the gravel-containing cell. It may not be possible to sorb all VOCs in leachate with tire chips. However, the concentration of VOCs in leachate will be lowered significantly with tire chips so that potential VOC migration from landfills will be minimized.

Another study conducted by Aydilek et al. (2006) to investigate the performance of tire chips as leachate collection material in municipal solid waste landfills indicated that the leachate flow rates and total leachate volumes generated by the two field test cells are comparable indicating no flow retardation of leachate drainage due to use of tire chips instead of gravel as the leachate collection layer material. The field temperatures inside the tire chips were between 28 and 61°C, which is comparable to the temperatures observed in solid waste landfills. Moreover, these temperatures were well below the approximate threshold temperature for potential combustion of tire chips. The leachate collected from the tire-chip layer had lower inorganic compound, dissolved metal and VOC concentrations than those collected from the gravel layer. Furthermore, the concentrations of the inorganics and VOCs of samples collected from the tire-chip cell were below the U.S. EPA’s MCLs.

4.3 *Mitigating nutrient leaching*

Sand-based root zones, typically used for golf course putting green and athletic field construction, lack sufficient cation exchange capacity to restrict nitrogen and phosphorus migration through the root zone and into sub-surface drainage systems. The adsorptive properties of tire rubber for retaining nitrogen and phosphorus were studied by Lisi et al. (2004) for application as a distinct sub-surface drainage or intermediate layer in golf course putting greens. A statistically significant reduction in the concentration of nitrate in leachate was achieved by replacing traditional pea gravel with equally sized granulated tires for the drainage layer media, although the mechanism of nitrate mitigation remains unclear. The results indicate that using granulated tires as a drainage layer or fill material beneath sand-based root zones does not compromise the function of the profile or quality of the vegetation while creating an environmentally beneficial and value-added option for scrap tire reuse.

5 SUMMARY

Scrap tires shredded into small pieces (called "chips") alone or mixed with soil can have properties favorable to civil and environmental engineering applications. Although the reuse of scrap tires, either as whole tires but most commonly as tire chips (alone or mixed) has become more common, questions regarding environmental suitability still persist, particularly the potential impact on ground and surface waters and aquatic life due to leaching. This review indicates that a significant body of research has evolved over the last 25 years. Although the levels of certain metals (e.g., iron and manganese) increase, the impact of tire leachate on drinking water quality of groundwater is limited for a range of applications involving tires or tire shreds, so human health concerns are minimal. The compliance with the drinking water standards at a chosen point of compliance in the groundwater resulting from the initial increased tire leachate concentrations can be assessed through the advection-dispersion-reaction transport principles. Tires placed in surface water are shown to be toxic to aquatic life and this practice should be abandoned. Tires placed in groundwater also generate leachate that is toxic to aquatic life but again, if there is enough separation zone from the surface water, the toxic effects may decrease by the time the leachate reaches the surface water.

In contrast to this concern on contamination of the environment, the significant sorption capacity of tire material renders it a potential material for environmental protection and remediation when in contact with contaminated waters and leachate. This allows use of tires as a reactive drainage medium in landfills in reducing the strength of the landfill leachate but most importantly sorbing highly toxic volatile organic compounds. Similarly, the sorptive properties of tire rubber for retaining nitrogen and phosphorus can be beneficial beneath sand-based root zones in golf courses and athletic fields.

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