

# **Contractor's Report to the Board**

## *Evaluation of Health Effects of Recycled Waste Tires in Playground and Track Products*

*Produced under contract by:*



*January 2007*



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**Additional Resources: The CIWMB suggests that in order to make an informed decision as to whether rubberized products for your playground and track are best for your needs, you should review the ASTM standard F1292, "Standard Specification for Impact Attenuation of Surfacing Materials within the Use Zone of Playground Equipment," and the Handbook for Public Playground Safety, U.S. Consumer Product Safety Commission, Pub. No. 325, and ask your playground/track contractor and/or manufacturer about any safety concerns you may have.**

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# Executive Summary

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In response to the California Integrated Waste Management Board's (CIWMB) need to better understand the potential health risks to children using outdoor playground and track surfaces constructed from recycled waste tires, the Office of Environmental Health Hazard Assessment (OEHHA) conducted the following studies.

- The playground surfaces were evaluated for the release of chemicals that could cause toxicity in children following ingestion or dermal contact. Three routes of child exposure to chemicals in the rubber were considered: 1) ingestion of loose rubber tire shreds (acute exposure), 2) ingestion via hand-to-surface contact followed by hand-to-mouth contact (chronic exposure), and 3) skin sensitization via dermal contact (acute exposure).
- Playground surfaces constructed from recycled tires were tested for their ability to attenuate fall-related impacts.
- The potential of these rubberized surfaces to impact the local environment, including the local ecology, was also addressed through a discussion of the published literature.

## **Evaluation of toxicity due to ingestion of tire shreds based on the existing literature**

OEHHA found 46 studies in the scientific literature that measured the release of chemicals by recycled tires in laboratory settings and in field studies where recycled tires were used in civil engineering applications: 49 chemicals were identified. Using the highest published levels of chemicals released by recycled tires, the likelihood for noncancer health effects was calculated for a one-time ingestion of ten grams of tire shreds by a typical three-year-old child; only exposure to zinc exceeded its health-based screening value (i.e., value promulgated by a regulatory agency such as OEHHA or U.S. EPA). Overall, we consider it unlikely that a one-time ingestion of tire shreds would produce adverse health effects. Seven of the chemicals leaching from tire shreds in published studies were carcinogens, yielding a  $1.2 \times 10^{-7}$  (1.2 in ten million) increased cancer risk for the one-time ingestion described above. This risk is well below the *di minimis* level of  $1 \times 10^{-6}$  (one in one million), generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006).

## **Evaluation of toxicity due to ingestion of tire shreds based on gastric digestion simulation**

OEHHA conducted a gastric digestion experiment in which 22 chemicals were found to be released by tire shreds incubated for 21 hours at 37°C in a solution mimicking the gastric environment. OEHHA then compared the levels of released chemicals to their health-based screening values, assuming a young child ingested ten grams of tire shreds; all exposures were at or below the screening values suggesting a low risk of noncancer acute health effects. Five of the chemicals released by tire shreds in the gastric digestion experiment were carcinogens. If the released chemicals were ingested as a onetime event and averaged over a lifetime, the cancer risk would be  $3.7 \times 10^{-8}$  (3.7 in one hundred million). This risk is considerably below the *di minimis* risk level of  $1 \times 10^{-6}$  (one in one million), generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006). The assumption that the risk from a onetime exposure is equivalent to the risk from the same dose spread over a lifetime is uncertain, and may overestimate or underestimate the true risk.

## **Evaluation of toxicity due to chronic hand-to-surface-to-mouth activity**

OEHHA performed wipe sampling of in-use playground surfaces containing recycled tire rubber; one metal (zinc) and four PAHs were measured at levels that were at least three times background. Assuming ingestion of the above five chemicals via chronic hand-to-mouth contact, exposures were below the corresponding chronic screening values, suggesting a low risk of

adverse noncancer health effects. From among the five chemicals identified by wipe sampling, the PAH chrysene is a carcinogen. Assuming playground use from 1 through 12 years of age, an increased cancer risk of  $2.9 \times 10^{-6}$  (2.9 in one million) was calculated due to the chronic ingestion of chrysene. This risk is slightly higher than the *de minimis* risk level of  $1 \times 10^{-6}$  (one in one million), generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006). Calculation of the  $2.9 \times 10^{-6}$  (2.9 in one million) value does not account for many uncertainties, some of which would decrease the risk while others would increase the risk.

### **Testing for skin sensitization by playground surfaces made of recycled tires**

Since children commonly contact these rubberized surfaces with their hands and other body parts, and since natural rubber contains the proven skin sensitizer latex, OEHHA contracted a laboratory to perform skin sensitization testing of tire-derived surfacing. Skin sensitization testing in the guinea pig was performed by Product Safety Laboratories (Dayton, NJ) with tire-derived playground surfacing as well as with the synthetic rubber EPDM; no sensitization was observed, suggesting that these surfaces would not cause skin sensitization in children, nor would they be expected to elicit skin reactions in children already sensitized to latex.

### **Evaluating the potential for damage to the local environment and ecology**

Following a fire in a playground surface made of chipped tires at the Yulupa Elementary School in Sonoma County, soil samples from under the playground contained levels of metals, VOCs, PAHs, dioxins and furans that were at or below background, suggesting a low risk to the local ecology. Also following the Yulupa fire, the air above the burn site was judged by U.S. EPA to pose no health risks to clean-up workers, and the soil/rubber mixture removed from the site was judged not to be hazardous waste, and could therefore be deposited in a designated class III waste facility.

Groundwater in contact with tire shreds contained elevated levels of many chemicals; however, those levels rapidly approached background a few feet outside of the tire trench. Additional published studies indicate that concentrated leachate produced in the laboratory from tire shreds, crumb rubber or whole tires was toxic in 19/31 studies to a variety of organisms including bacteria, algae, aquatic invertebrates, fish, frogs and plants; however, it is unlikely that the use of shredded tires in outdoor applications such as playground surfaces would result in the leaching during rain events of high enough concentrations of chemicals to cause such effects. Further, shredded tires used in applications above the ground water table, as is the case for playground surfaces, produced no toxicity in sentinel species.

### **Evaluation of potential injury from falls on playground surfaces made of recycled tires**

Using an accelerometer to test impact attenuation by California playground surfaces made of recycled tires, OEHHA staff visited 32 rubberized playground surfaces, to determine if the state mandated (CCR sections 65700-65750) standard for head impact (Head Impact Criterion or HIC) of  $\leq 1000$  was being met. Only 31 percent of rubberized playground surfaces passed the HIC standard. This is compared to 100 percent for surfaces made of wood chips, although only five surfaces of wood chips were tested. As the fall heights of playground structures increased, the underlying rubberized playground surface was more likely to fail the HIC standard; however, even at fall heights of 9-12 feet, some rubberized surfaces passed the standard. HIC values were not affected by the age of the rubberized surface, either during the first 2-3 months following installation or during the first two years. HIC values of rubberized surfaces increased with increasing surface temperature; in one playground the HIC value measured at dawn increased almost 20 percent when measured again in the afternoon during the heat of the day. These data point out the importance of testing the impact attenuation of rubberized playground surfaces to ensure that they meet the safety standards already in place.

Unfortunately, our survey found a 69 percent failure rate for rubberized California playground surfaces using attenuation standards. Theoretically, failure and potential injuries could be prevented with better installation practices by contractors who had placed rubberized material too thin. Further, if the purchaser of the product would have sought certification of impact attenuation standards at the completion of the project, each playground's HIC value should have been assured. This represents a missed opportunity for prevention of playground fall injuries, which are estimated to be in the thousands and which include serious trauma such as brain injury.

# Chapter 1: Introduction

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Waste tires are being used increasingly as a primary component of children's playground surfaces and running tracks. In addition to the benefits of recycling, playground surfaces made from recycled tires have the potential to reduce child injury due to falls in the playground. CIWMB provides grant funds to schools and city recreation departments to construct outdoor playgrounds and tracks using recycled waste tires. To be thorough and diligent, and to assure no inadvertent adverse health consequences, CIWMB asked OEHHA to evaluate outdoor playground and track surfaces made of recycled tires for potential toxicity from chemical exposure and for injury from falls.

Recycled tires in playground surfaces take one of three forms:

1. As uncompressed tire shreds or crumb comprising a rakeable surface,
2. As rubber tire shreds that are poured-in-place along with a binder, hardening into a permanent surface,
3. As tiles molded in the factory from tire shreds and binder, which are then transported to the playground and locked or glued into place, forming a permanent surface.

Track applications use the method described in #2 above.

## **Studying the toxicology of recycled tires used in playground surfaces**

The first part of this study addresses the toxicologic safety of rubber playground and track surfaces made of recycled tires. We examined whether such surfaces release toxicants capable of adversely affecting either children's health or the health of the local ecology. These issues are addressed in three ways:

1. Through a review of the literature covering what is known to be released by recycled tires in laboratory studies and in civil engineering projects that utilized tire shreds (e.g., roadways, parking lots, leachate fields).
2. By conducting studies to identify chemicals released by tire shreds in a laboratory setting and at actual rubber surfaces in use at selected playgrounds and a track within California.
3. By conducting a skin sensitization study of pieces of recycled tire rubber used in playground surfacing.

Once we identified the chemical substances to which a child could be exposed, we estimated exposure potential and compared those values to toxicologic reference values. This approach enabled us to quantify the risks to children's health. We took a similar approach in evaluating potential environmental risks from playground recycled tire leachate.

## **Studying impact attenuation and the prevention of fall injury by playground surfaces made of recycled tires**

The second part of this study evaluates whether playground surfaces made of recycled tires are an effective means for reducing serious head injury due to falls. The US CDC (2005) estimates that it cost 1.2 billion dollars to treat playground-related injuries in the United States in 1995. If 10 percent of these injuries occurred in California, then approximately 120 million dollars were spent in this state. Since approximately 80 percent of these injuries resulted from falls (Tinsworth and McDonald, 2001), then reducing the injury rate from falls by only 10 percent has the potential to save almost 10 million dollars in California. An accompanying reduction in injury severity would save even more.

While preliminary laboratory data suggest that crumb rubber should be effective at reducing the incidence of injury to children that fall, the three types of rubber surfaces have never been intercompared for injury reduction, and only sparse data exist regarding the efficacy of rubber surfaces relative to more traditional impact-absorbing surfaces such as sand or wood chips. While standards for head impact attenuation by playground surfaces have been written into California law (CCR sections 65700-65750), the compliance rate has not been systematically monitored.

Thus, measurement of the compliance rate for playground surfaces made of recycled tire rubber was an important part of this study. In effect, we have measured parameters of impact attenuation by in use playground surfaces to determine whether these surfaces, as they are currently being installed in California, can be expected to protect children from serious head injury due to falls. This approach was chosen in consultation with members of the Injury Surveillance and Epidemiology Section of the California Department of Health Services, and the Department of Epidemiology in the UCLA School of Public Health. Those discussions failed to identify a set of injury data collected from playgrounds before and after installation of a rubberized surface, or any information on insurance savings that could be directly linked to decreased playground injuries. Thus, we found it necessary to generate our own set of data covering the impact attenuating properties of California playground surfaces, from which estimates of fall injury risk could be made.

# Chapter 2: Survey of CIWMB playground grantees 2001–2003: playground surface types and locations

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**Background:** Municipalities and school districts receiving CIWMB grants for installation of playground surfaces made of recycled tires were surveyed by telephone. The CIWMB allocated 90 playground surface grants in the 2000-2001 cycle and 59 grants in the 2001-2002 cycle. Contact persons were asked to provide information on the type of surface installed (pour-in-place, tiles or rakeable shreds/crumb), the composition of the surface and the name of the manufacturer/installer. Approximately one third of the grantees who were contacted provided this information. Below are the data on surface type and composition.

**Nomenclature:** The synthetic rubber called styrene-butadiene rubber is a major component of tires. Thus, the abbreviation SBR is often used as a designation for the shredded tire component of these surfaces. For pour-in-place surfaces, the SBR is mixed with a binder and poured at the playground site, where it hardens into a uniform surface. At this point, granules of synthetic rubber called ethylene propylene diene monomer (EPDM) are often mixed with a binder and poured into the playground to serve as a top layer. When this process is performed at a factory using molds, tiles of SBR with top layers of EPDM result. These tiles are put in the playground and locked in place, also forming a uniform surface. Both pour-in-place surfaces and surfaces of tiles can be constructed using SBR only. Lastly, shredded SBR can be used much like wood chips or gravel by simply transporting it to the playground site where it is raked into place.

## Playground materials survey results

- **Pour-in-place SBR only:** no grantees installed surfaces of this material
- **Pour-in-place SBR with a pour-in-place top layer of EPDM:** 44 playground surfaces in Antioch, Bear Mountain, Belvedere, Cathedral City, Commerce, Conejo, Culver City, Downey, Duarte, El Cerrito, Eureka, Fair Oaks, Greater Vallejo Recreation District, Imperial, Kern County, King City, Lodi, Long Beach, Modesto, Monterey, Morongo Valley Community Service District, Napa, Pacheco, Pacifica Community Charter School (L.A. Unified School District), Paramount, Pico Rivera, Poway, Reef Sunset Unified, San Clemente, San Diego, San Francisco, San Luis Obispo, Santa Barbara, Saugas, Silverado-Modjeska, Sunrise, Union City, Wilsona School District
- **SBR tiles:** 2 playground surfaces in Gridley and Smith River
- **SBR tiles with top layer of EPDM:** 2 playgrounds in Long Beach and Bell
- **Rakeable rubber shreds:** 3 playgrounds in Horicon Elementary School District, Morongo Valley Community Service District and Salinas

**Comment:** Since the great majority of grantees (44/51) installed a pour-in-place surface consisting of a base layer of recycled SBR covered by an EPDM top layer, OEHHA focused its testing on both EPDM and SBR playground materials. These products were used to analyze the chemicals released by in-use playground surfaces and for conducting the skin sensitization test.

# Chapter 3: Substances released by recycled tires: values from the published literature

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## Introduction

Table 1 lists the published studies that identified metals, compounds and particulates released by tires in laboratory and field settings. In some cases, whole tires were used, but more often tire shreds, chips or crumb was tested. The studies are approximately evenly distributed between field and laboratory studies. Field studies involved the use of tire pieces in road beds, road embankments, leachate fields, a parking lot, and as a component of turf. In addition, an application with whole tires in water was that of reef construction. No study was located identifying substances released by recycled tires in playground surfaces, although a single study tested for ecotoxicity by the water-soluble extracts from playground tire crumb (Birkholz et al., 2003). Therefore, until our gastric digestion and wipe sampling studies, the data shown here were the only information available for making predictions about the behavior of tire pieces in playground surfaces. Using these surrogate data to assess risks from rubberized playground and track surfaces introduces a variety of uncertainties due to the following:

1. Waste tire processing for playground and track surfaces includes a step to remove the metal belts and metal beads, and the rubber end product is generally washed, while the shredded tires used in these published studies still contained the metallic components, and the end product was not necessarily washed; therefore, the shredded tires used in these published studies represent a potentially greater source of leaching chemicals compared to the tire shreds and crumb rubber used in playground surfaces,
2. Most playground and track surfaces made of the recycled tire rubber also use a chemical binder such as polyurethane to hold the rubber pieces in place, while the shredded tires used in these published studies did not include a binder; therefore, chemicals leaching from the binder cannot be identified from these published studies,
3. Playground and track surfaces are continually exposed to changing climatic conditions including sunlight, precipitation, and variations in temperature, as well as to volatile chemicals in the ambient atmosphere,
4. The laboratory studies collected from the literature generally consisted of day, week, or month-long incubations of tire shreds in aqueous solutions in closed tanks or other reaction vessels; these laboratory conditions do not replicate the predicted routes of child exposure to recycled tire rubber in playground surfaces, such as through hand-to-surface-to-mouth contact or ingestion of tire shreds.

**Table 1. Substances released by whole tires or tire chips/shreds in laboratory and field studies**

<b>Authors</b>	<b>Type of study</b>	<b>VOCs</b>	<b>sVOCs</b>	<b>Metals</b>	<b>Other</b>
Al-Tabbaa and Aravinthan, 1998	Lab			Cu, Ni	
Anthony et al., 1995	Tire shred leachate in lab	Nitro compounds, hydrophilic compounds	Morpholino-thio-benzothiazole	Iron, manganese, nickel, zinc	
Anthony and Latawiec, 1993	Whole tire leachates in lab	An olefinic hydrocarbon, an alkoxy ether/alcohol, series of nitro-aliphatic ethers	Morpholino-thio-benzothiazole		
BAS Inc., 1993	MSDS for crumb rubber				Fine particles
Boniak et al., 2001	Tire crumb in field test			Zn	
Chien et al., 2003	Tire shredding factory-particulates in air		Amines, aniline, quinoline, amides, benzothiazole all in particulates		Respirable particulates
Edil et al., 2003	Tire chip leachate in field	Methyl isobutyl ketone			
Exponent, 2003	Tire shred leachate in field	Acetone, 1,1-dichloroethane, cis-1,2-dichloroethene, chloroethane, benzene, trichloroethene, toluene	Aniline, N-Nitrosodimethylamine, N-Nitrosodiphenylamine	Manganese, iron	
Florida Community College, 1999	Leachate from crumb rubber in the field and soil measurements	Toluene		Fe, Zn, Ba, Na, Cr, Pb, Cu, Sb	
Florida Dept. of Envir. Protect., 1999	Lab study conducted by the Virginia DOT			Cd, Cr, Pb, Al, Cu, Fe, Ni, Zn	

<b>Authors</b>	<b>Type of study</b>	<b>VOCs</b>	<b>sVOCs</b>	<b>Metals</b>	<b>Other</b>
Florida Dept. of Envir. Protect., 1999	Field study conducted in Idaho			Zn	
Fukuzaki et al., 1986	Field				5-24 ng/m <sup>3</sup> tire dust
Gaultieri et al., 2005	Lab			Zn	
Gunter et al., undated	Tire chip leachate in lab	Acetone, benzene, trichloroethylene, methyl ethyl ketone, methyl isobutyl ketone		Iron, lead, manganese	
Hartwell et al., 1998	Tire shred leachate in lab	Naphthalene, 2 Methyl naphthalene	Morpholiniothio-benzothiazole, bis(2-ethylhexyl)phthalate	Al, Ba, Cd, Cr, Co, Cu, Mn, Ni, Zn, Fe	
Hildemann et al., 1991	Field + lab				Fine particulate organic C (105 µg/m <sup>2</sup> /day)
Horner, 1996	Tire chip leachate in lab and soil near tire dump			Cadmium, zinc, lead	
Humphrey, 1999	Tire chip leachate in field	None detected	None detected	Barium, iron, manganese, zinc	Chloride, sulfate
Humphrey and Katz, 2000	Tire shred leachate in field	1,1-dichloroethane, 4-methyl-2-pentanone (MIBK)	2-(4-morpholinyl)-benzothiazole	Iron, manganese	
Humphrey and Katz, 2001	Tire shred leachate in field	1,1-dichloroethane, 4-methyl-2-pentanone (MIBK), acetone, benzene, cis-1,2-dichloroethene	Aniline, m+p cresol	Iron, manganese, zinc	

<b>Authors</b>	<b>Type of study</b>	<b>VOCs</b>	<b>sVOCs</b>	<b>Metals</b>	<b>Other</b>
Johnson et al., 2002	Tire chip leachate in lab			Zinc	
Kim et al., 1990	Suspended particulate matter in urban air				Tire tread particles
Kumata et al., 1996	Street dust, river sediment, air		2-(4-morpholinyl)benzothiazole		
Kumata et al., 2002	Highway runoff, river sediment		2-(4-morpholinyl)-benzothiazole, N-cyclohexyl-2-benzothiazolamine		
Liu et al., 1998	Tire shred leachate in field			Iron, manganese	Latex allergens
Miguel et al., 1996	Air samples and guardrail swipes near freeway				Particulates with latex allergens
Miller and Chadik, 1993	Tire shred leachate in field and laboratory	Methyl isobutyl ketone, 1,3,5-trimethylbenzene, benzene	aniline	Arsenic, zinc	
Minn. DOT, 1995	Tire chip leachate in lab	Isophorone, 2,6-dinitrotoluene		Mercury, zinc	
Minn. Pollution Control Agency, 1990	Tire chip leachate in lab	Total petroleum hydrocarbons, PAHs		Aluminum, barium, cadmium, chromium, iron, selenium, zinc, lead	

<b>Authors</b>	<b>Type of study</b>	<b>VOCs</b>	<b>sVOCs</b>	<b>Metals</b>	<b>Other</b>
Nelson et al., 1994	Whole tire and tire plug leachates in lab			Zinc copper, cadmium lead	
Ontario Ministry of Environment and Energy, 1994	Lab		Benzothiazole, 4-(phenylamino)-phenol, 2-(4-morpholinyl)benzothiazole, 24 other organic compounds at lower levels	Zn	
O'Shaughnessy and Garga, 2000	Lab		Benzothiazole, 2(3H)-benzothiazolone, (1,1-diethylethyl)-2-methoxyphenol, 4-(2-benzothiazolythio)-morpholine	Al, Fe, Mn, Zn	
Park et al., 2003	Tire shred leachate in lab			Zinc, barium and lead in precipitates	
Pierce and Blackwell, 2003	Lab	VOCs absorbed by ground tire rubber added to slurry cutoff wall backfill material			
Radian Corp., 1989	Tire chip leachate in lab	Phenol		Barium, chromium, lead, mercury, selenium	
Reddy and Quinn, 1997	Field + lab		Benzothiazole, 2-hydroxybenzothiazole, 2-(4-morpholinyl)-benzothiazole		
Rogge et al., 1993	Tire dust generated in lab	Alkanes, PAHs	alkanoic acids, natural resins, benzothiazole		

<b>Authors</b>	<b>Type of study</b>	<b>VOCs</b>	<b>sVOCs</b>	<b>Metals</b>	<b>Other</b>
Schauer et al., 2002	Field				Fine particulate organic C (1 µg /m <sup>3</sup> ) [total part.=2µg]
Scrap Tire Management Council, 1991	Tire chip leachate in lab	Methyl ethyl ketone, toluene	phenol	Barium, chromium, lead, mercury	Carbon disulfide
Sengupta and Miller, 1999	Tire shred leachate in lab			Iron, aluminum, zinc, copper	Chloride
Shieh, 2001	Tire chip leachate in lab	Methyl ethyl ketone, toluene	Phenol	Arsenic, lead	Carbon disulfide
Spies et al., 1987	SF bay sediment		Benzthiazole, 2-(4-morpholinyl)-benzthiazole		
Stephensen et al., 2003	Lab	PAHs, aromatic nitrogen compounds			
Tatlisož et al., 1996	Field and lab	Benzene, toluene	Phenol	As, Ba, Cd, Cr, Pb, Fe, Mn, Se, Hg, Zn	
Williams et al., 1995	Air near freeway				Rubber particles with latex allergens
Yoon et al., 2005	Tire shred leachate in the field			As, Ba, Cd, Cr, Se	

VOC = volatile organic compound; sVOC = semi-volatile organic compound

## Substances released by tires

Tables 2 through 5 show the concentrations of substances released by recycled tires (or “in use” tires in the case of airborne particulates) for the studies listed in Table 1. The substances released comprise four groups consisting of 15 metals (Table 2), 20 volatile organic compounds (VOCs, Table 3), 14 semi-volatile organic compounds (sVOCs, Table 4), and particulates in air resulting from tire wear (Table 5). Where possible, the data are reported as amount of chemical released per gram of tire. This facilitated the use of these data to predict how much of each chemical would be released were a child to intentionally ingest a specific amount of tire shreds.

## Metals

From among the 15 metals listed in Table 2, zinc (21 instances) and iron (sixteen instances) were detected most frequently and at the highest levels. Iron is a component of the steel belts and beads, while zinc oxide is used as an activator in the vulcanization process (CIWMB, 1996). Manganese was the next most frequently detected (ten instances). Like iron, it probably originated from the steel belts and beads. Today, the production of crumb rubber from tires typically includes a step to remove 99 percent of the steel belting and bead material. This would be expected to greatly reduce the release of iron and manganese from the recycled tire material. Barium was the next most commonly detected metal (nine instances), possibly as a result of its use to catalyze the synthesis of polybutadiene rubber (Halasa et al., 2003).

Lead was also identified in eight instances, possibly due to its former use as an activator of the vulcanization process, in the form of lead oxide (CIWMB, 1996). Chromium detection in seven instances may have resulted from its use in steel production. If this is the case, removal of the steel wire from recycled tires should also markedly reduce the release of this metal. Unfortunately, none of the studies determined whether the chromium was in the +6 or +3 oxidation state, since the former ion is highly carcinogenic (by inhalation) while the latter is not. The remaining nine metals (cadmium, copper, aluminum, antimony, mercury, nickel, arsenic, selenium, cobalt) were detected in five or fewer instances.

While the presence of metals at levels above background is noteworthy, the toxicologic significance depends upon the concentrations and magnitude of exposure. As shown in Table 2, both zinc and iron were detected in tire chip leachate at levels indicating that milligram amounts of these metals were released per gram of tire. These studies were conducted in the laboratory under controlled conditions. Similar laboratory studies indicate that microgram amounts of manganese, aluminum, barium and copper were released per gram of tire, while only nanogram amounts of lead, cadmium, chromium, nickel, arsenic, selenium and cobalt were released (Table 2).

To assess the toxicologic significance of these findings, these levels will first be used to estimate child exposure by the oral route. Exposures will then be compared to corresponding oral reference toxicity values, such as a public health goal (PHG), reference concentration (RfC), minimal risk level (MRL), or reference exposure level (REL). These values have been developed by various authoritative bodies including OEHHA, U.S. EPA, the Centers for Disease Control (CDC), and the Agency for Toxic Substances and Disease Registry (ATSDR). The calculations will determine whether exposures are likely to cause adverse health effects.

## VOCs

Tire shreds released lower concentrations of volatile organic compounds (VOCs) than metals (Table 3). A total of 20 compounds were identified, including three classes of compounds (polycyclic aromatic hydrocarbons, aromatic nitrogen-containing, total petroleum hydrocarbons). Other than the unidentified ether compound whose level was estimated in the laboratory study by Anthony and Latawiec (1993), the highest values were for the solvent methyl isobutyl ketone (1,151 ng released per gram of tire; Gunter et al., undated) and for naphthalene (1,100 ng released per gram of tire; Hartwell et al., 1998). The presence of methyl isobutyl ketone may be the result of its use in the production of rubber antioxidants (U.S. EPA, 2003b), while naphthalene may originate from carbon black.

Seven compounds or groups of compounds were released in ng amounts per gram of tire: acetone, toluene, benzene, total petroleum hydrocarbons, polycyclic aromatic hydrocarbons, methyl ethyl ketone and 2-methyl naphthalene. All these compounds except for the last may result from the use of petroleum oils (the source of carbon black) and coal tar fractions in tire production, which serve as softeners and extenders (Sullivan et al., 1992). These findings were from studies performed in the laboratory, where the volatile organic compounds were released into aqueous solutions.

A clue towards how these volatile compounds might behave when tire shreds are used in playground surfaces, and the compounds are released directly into the air, may be provided by the study of Chang et al. (1999). In that study of rubberized athletic tracks, the emission of volatile organic compounds decreased with time, so that after about two years the levels at breathing heights were near background. Unfortunately, since recycled tire rubber was most likely not used in the construction of these tracks, it is problematic to use these data to draw firm conclusions about the release of VOCs from playground surfaces made of recycled tires. Chapter 8 presents wipe sampling data from a running track containing recycled tires as well as a discussion of the safety benefits of such a surface.

## sVOCs

A total of 14 sVOCs are listed in Table 4. This includes five different benzothiazoles, three of which were released at  $\mu\text{g}$  amounts per gram of tire. These benzothiazole contaminants have been proposed as environmental markers for tire-derived material (Kumata et al., 2002). Benzothiazoles are used in tire production to accelerate the vulcanization process (Kumata et al., 2002), as antioxidants (Spies et al., 1987), and to help bond the metal wire and metal belts to the tire rubber (CIWMB, 1996). Aniline, phenol, 4-(phenylamino)-phenol, phenoxazine, and 2(3H)-benzothiazolone were released in ng amounts per gram of tire. Aniline is added to tires to inhibit rubber degradation (CIWMB, 1996).

Detection of phenol (and cresol) may be due to the use of petroleum oils and/or coal tar fractions as softeners and extenders in tire production. In addition, treatment of the steel cords and fabrics comprising the belts with phenol/formaldehyde improves their adhesion to the rubber (Sullivan et al., 1992). Lastly, two nitrosoamines (diphenyl and dimethyl) were detected in the same study; this could be the result of their use to inhibit both the vulcanization process during tire production, and the decomposition of rubber in the finished product (CIWMB, 1996).

## **Particulates**

Particles of tire-derived rubber have been measured in the air in a number of studies (Table 5). Three studies measured from 1-7  $\mu\text{g}/\text{m}^3$  in ambient air (Kim et al., 1990; Miguel et al., 1996; Schauer et al., 2002). This demonstrates that any measurements of rubber particulates above a rubber playground surface must take into account the ambient, background level. Two of the studies in Table 5 (Williams et al, 1995; Miguel et al., 1996) identified latex as a component of the airborne particulate matter. Such airborne particles containing latex allergens have been suggested as potential inducers of both latex sensitization and asthma (Miguel et al., 1996; Williams et al., 1995).

**Table 2. Concentrations of metals leaching from tire shreds used in various civil engineering applications in the field or leaching in lab studies**

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
Aluminum (Al)	Lab leachate study (Minn Poll Cntrl Agency, 1990)	2,000 ng released (per g tire)
	Lab leachate study (Hartwell et al., 1998)	1200 ng released (per g of tire)
	Lab study (Florida Dept. Environ. Protection, 1999)	420 ng released (per g of tire)
	Lab leachate study (Sengupta and Miller, 1999)	790 ppb in leachate
	Lab leachate study (O'Shaughnessy and Garga, 2000)	550 ppb in leachate
Antimony	Field leachate study (FCC at Jacksonville, 1999)	489 ppb in soil
Arsenic (As)	Lab leachate studies (Miller and Chadik, 1993)	130 ng released (per g tire)
	Field leachate study (Yoon et al., 2005)	19 ppb in leachate
Barium (Ba)	Lab leachate study (Minn Poll Cntrl Agency, 1990)	1,000 ng released (per g tire)
	Lab leachate study (Scrap Tire Man Cncl, 1991)	590 ppb in leachate
	Lab leachate studies (Tatlisoiz et al., 1996)	100 to 1000 ng released (per g tire)
	Lab leachate study (Hartwell et al., 1998)	1700 ng released (per g of tire)
	Field leachate study (Humphrey, 1999)	21 ppb in leachate
	Field leachate study (FCC at Jacksonville, 1999)	1,230 ppb in surface water
	Field leachate study (FCC at Jacksonville, 1999)	10,000 ppb in soil
	Lab leachate study (Park et al., 2003)	340 ng released (per g of tire)
	Field leachate study (Yoon et al., 2005)	113 ppb in leachate
Cadmium (Cd)	Lab leachate study (Minn Poll Cntr Agency, 1990)	270 ng released (per g of tire)
	Lab leachate study (Hartwell et al., 1998)	270 ng released (per g of tire)

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
	Lab study (Florida Dept. Environ. Protection, 1999)	4 ng released (per g of tire)
	Field leachate study (Yoon et al., 2005)	1.1 ppb in leachate
Chromium (Cr) with oxidation state (Cr <sup>+3</sup> or Cr <sup>+6</sup> ) not determined	Lab leachate study (Minn Poll Cntrl Agency, 1990)	500 ng released (per g tire)
	Lab leachate study (Scrap Tire Man Cncl, 1991)	48 ppb in leachate
	Lab leachate studies (Tatlisoz et al., 1996)	8 to 500 ng released (per g of tire)
	Lab leachate study (Hartwell et al., 1998)	100 ng released (per g of tire)
	Field leachate study (FCC at Jacksonville, 1999)	2 ppb in surface water
	Field leachate study (FCC at Jacksonville, 1999)	4 ppb in ground water
	Lab study (Florida Dept. Environ. Protection, 1999)	8 ng released (per g of tire)
	Field leachate study (Yoon et al., 2005)	55 ppb in leachate
Cobalt (Co)	Lab leachate study (Hartwell et al., 1998)	100 ng released (per g of tire)
Copper (Cu)	Lab leachate study (Al-Tabbaa and Aravinthan, 1998)	360 to 4880 ng released (per g of tire)
	Lab leachate study (Hartwell et al., 1998)	320 ng released (per g of tire)
	Field leaching study (FCC at Jacksonville, 1999)	2,300 ppb in leachate
	Lab study (Florida Dept. Environ. Protection, 1999)	235 ng released (per g of tire)
	Lab leachate study (Sengupta and Miller, 1999)	2,400 ppb in leachate
Iron (Fe)	Lab leachate study (Gunter et al., undated)	13,000 ng released (per g of tire)
	Lab leachate study (Minn. Poll. Cntr. Agency, 1990)	1,100,000 ng released (per g of tire)
	Lab leachate study (Anthony et al., 1995)	26,000 ng released (per g of tire)

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
	Lab leachate studies (Tatlisoiz et al., 1996)	1,150 to 1,100,000 ng released (per g tire)
	Field leachate study (Liu et al., 1998)	55,000 ppb in leachate
	Lab leachate study (Hartwell et al., 1998)	27,000 ng released (per g of tire)
	Lab study (Florida Dept. Environ. Protection, 1999)	341,000 ng released (per g of tire)
	Field leachate study (Humphrey et al., 1999)	30,000 ppb in leachate
	Field leachate study (FCC at Jacksonville, 1999)	1,500 ppb in ground water
	Field leachate study (FCC at Jacksonville, 1999)	210 ppb in surface water
	Field leachate study (FCC at Jacksonville, 1999)	960,000 ppb in soil
	Field leachate study (Humphrey 1999)	22,000 ppb in leachate
	Lab leachate study (Sengupta and Miller, 1999)	18,000 ppb in leachate
	Lab leachate study (O'Shaughnessy and Garga, 2000)	700 ppb in leachate
	Field leachate study (Humphrey et al., 2001)	33,000 ppb in leachate
	Field leachate study (Exponent, 2003)	80,000 ppb in leachate
Lead (Pb)	Lab leachate study (Gunter et al., undated)	12 ng released (per g of tire)
	Lab leachate study (Minn. Poll. Cntr. Agency, 1990)	920 ng released (per g of tire)
	Lab leachate study (Scrap Tire Man. Cncl., 1991)	30 ppb in leachate
	Lab leachate studies (Tatlisoiz et al., 1996)	3 to 920 ng released (per g tire)
	Field leachate study (FCC at Jacksonville, 1999)	6 ppb in surface water
	Lab study (Florida Dept. Environ. Protection, 1999)	56 ng released (per g tire)
	Field leachate study (FCC at Jacksonville, 1999)	13,300 ppb in soil

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
	Lab leachate study (Park et al., 2003)	120 ng released (per g of tire)
Manganese (Mn)	Lab leachate study (Gunter et al, undated)	1,040 ng released (per g tire)
	Lab leachate study (Anthony et al., 1995)	5800 ng released (per g tire)
	Lab leachate studies (Tatlisoiz et al., 1996)	1,500 ng released (per g of tire)
	Field leachate study (Liu et al., 1998)	3,000 ppb in leachate
	Lab leachate study (Hartwell et al., 1998)	5800 ng released (per g of tire)
	Field leachate study (Humphrey, 1999)	2,500 ppb in leachate
	Lab leachate study (O'Shaughnessy and Garga, 2000)	180 ppb in leachate
	Field leachate study (Humphrey and Katz, 2000)	22,000 ppb in leachate
	Field leachate study (Humphrey and Katz, 2001)	1,300 ppb in leachate
	Field leachate study (Exponent, 2003)	910 ppb in leachate
Mercury (Hg)	Lab leachate study (Scrap Tire Man Cncl, 1991)	0.4 ppb in leachate
	Lab leachate study (Minn Dept Trans, 1995)	0.4 ppb in leachate
	Lab leachate studies (Tatlisoiz et al., 1996)	0.07 ng released (per g tire)
Nickel (Ni)	Lab leachate study (Anthony et al., 1995)	80 ng released (per g of tire)
	Lab leachate study (Hartwell et al., 1998)	120 ng released (per g of tire)
	Lab leachate study (Al-Tabbaa and Aravinthan, 1998)	5-12 µg released (per g of tire)
	Lab study (Florida Dept. Environ. Protection, 1999)	113 ng released (per g of tire)
Selenium (Se) (elemental)	Lab leachate study (Minn Poll Cntrl Agency, 1990)	440 ng released (per g tire)
	Lab leachate studies (Tatlisoiz et al., 1996)	50 to 440 ng released (per g tire)

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
	Field leachate study (Yoon et al., 2005)	23 ppb in leachate
Zinc (Zn)	Lab leachate study (Minn. Poll Cntrl Agency, 1990)	50,000 ng released (per g tire)
	Lab leachate study (Scrap Tire Man. Council., 1991)	500 ppb in leachate
	Lab leachate study (Miller and Chadik, 1993)	3,200 ng released (per g of tire)
	Lab leachate study (Nelson et al., 1994)	4,200 ng released (per g tire)
	Lab leachate study (Ontario Ministry of Environment and Energy, 1994)	1,000 ng released (per g of tire)
	Lab leachate study (Minn. Dept. Trans., 1995)	2,950 ppb in leachate
	Lab leachate study (Horner, 1996)	2,320,000 ng released (per g tire)
	Lab leachate studies (Tatlisoiz et al., 1996)	1,130 to 50,000 ng released (per g tire)
	Lab leachate study (Hartwell et al., 1998)	68,000 ng released (per g of tire)
	Field leachate study (FCC at Jacksonville, 1999)	45,000 ppb in soil
	Field leachate study (Humphrey, 1999)	140 ppb in leachate
	Field leachate study (FCC at Jacksonville, 1999)	103 ppb in surface water
	Field study (Florida Dept. Environ. Protection, 1999)	618 ppb in leachate
	Lab study (Florida Dept. Environ. Protection, 1999)	30,000 ng released (per g of tire)
	Field leachate study (Humphrey and Katz, 2000)	26 ppb in leachate
	Lab leachate study (O'Shaughnessy and Garga, 2000)	590 ppb in leachate
	Field leaching study (Boniak et al., 2001)	310 ppb in soil
	Lab leachate study (Johnson et al., 2002)	2,950 ppb in leachate

<b>Metal</b>	<b>Study Type</b>	<b>Concentration</b>
	Lab leachate study (Park et al., 2003)	1100 ng released (per g of tire)
	Lab leachate study (Birkholz et al., 2003)	68,000 ng released (per g of tire)
	Lab leachate study (Gualtieri et al., 2005)	890,000 ng released (per g tire rubber)

**Table 3. Concentrations of Volatile Organic Compounds (VOCs) released from tire shreds in various field applications and laboratory studies, and in ambient air samples**

<b>Compound</b>	<b>Study Type</b>	<b>Concentration</b>
1,1-dichloroethane	Field leachate study (Humphrey and Katz, 2000)	Trace (<5 ppb) in leachate
2,6-dinitrotoluene	Lab leaching study (Minn Dept Trans, 1995)	45 ppb in leachate
2-Methyl naphthalene	Lab leaching study (Hartwell et al., 1998)	540 ng released (per g of tire)
1,3,5-trimethylbenzene	Field leaching study (Miller and Chadik, 1993)	4 ppb in leachate
Acetone	Lab leachate study (Gunter et al., undated)	115 ng released (per g of tire)
	Leachate in field (Humphrey and Katz, 2001)	28 ppb in leachate
	Leachate in field (Exponent, 2003)	27 ppb in leachate
Benzene	Lab leachate study (Gunter et al., undated)	0.9 ng released (per g of tire)
	Leaching study in lab (Miller and Chadik, 1993)	218 ng released (per g of tire)
	Field leachate study (Humphrey and Katz, 2001)	4 ppb in leachate
	Field leachate study (Exponent, 2003)	1.35 ppb in leachate
Chloroethane	Field leaching study (Exponent, 2003)	2 ppb in leachate
Cis-1,2-dichloroethene	Field leachate study (Humphrey and Katz, 2001)	24 ppb in leachate
Isophorone	Lab leaching study (Minn Dept Trans, 1995)	2 ppb in leachate

Compound	Study Type	Concentration
Methyl ethyl ketone	Lab leachate study (Gunter et al., undated)	17 ng released (per g of tire)
	Lab leachate study (Scrap Tire Manag Concl, 1991)	21 ppb in leachate
Methyl isobutyl ketone	Lab leachate study (Gunter et al., undated)	1151 ng released (per g of tire)
	Field leachate study (Miller and Chadik, 1993)	3 ppb in leachate
	Field leachate study (Humphrey and Katz, 2000)	Trace (<5 ppb) in leachate
	Field leachate study (Humphrey and Katz, 2001)	58 ppb in leachate
	Field leachate study (Edil et al., 2003)	69 ppb in leachate
Naphthalene	Lab leaching study (Hartwell et al., 1998)	1,100 ng released (per g of tire)
A nitro-aliphatic ether compound	Lab leaching study (Anthony and Latawiec, 1993)	5000 to 25000 ppb in leachate
n-pentatriacontane	Air sampling study (Schauer et al., 2002)	3 ng/m <sup>3</sup>
n-tetraatriacontane	Air sampling study (Schauer et al., 2002)	3 ng/m <sup>3</sup>
Polycyclic aromatic hydrocarbons (PAHs)	Lab leaching study (Minn Poll Cntr Agency, 1990)	140 ng released (per g of tire)
Toluene	Lab leaching study (Scrap Tire Man Cncl, 1991)	190 ppb in leachate
	Lab leaching studies (Tatlisoiz et al., 1996)	34 to 280 ng released (per g of tire)
	Field leaching study (FCC at Jacksonville, 1999)	63 ppb in soil
	Field leaching study (Exponent, 2003)	2.6 ppb in leachate
Total petroleum hydrocarbons	Lab leaching study (Minn Poll Cntr Agency, 1990)	140 ng released (per g of tire)
	Lab leaching study (Stephensen et al., 2003)	Up to 450 ng/g fish bile fluid
Trichloroethene	Field leaching study (Exponent, 2003)	0.8 ppb in leachate

<b>Compound</b>	<b>Study Type</b>	<b>Concentration</b>
Trichloroethylene	Lab leachate study (Gunter et al., undated)	0.8 ng released (per g of tire)
	Field leachate study (Humphrey and Katz, 2001)	6 ppb in leachate
	Field leachate study (Exponent, 2003)	2 ppb in leachate
	Field leachate study (Exponent, 2003)	16 ppb in leachate

**Table 4. Concentrations of Semi-Volatile Organic Compounds (sVOCs) released from tire shreds in various field applications and laboratory studies, and in some ambient environmental samples**

Compound	Study Type	Concentration
(1,1-diethylethyl)-2-methoxyphenol	Lab leachate study (O'Shaughnessy and Garga, 2000)	330 ppb in leachate
2(3H)-benzothiazolone	Lab leachate (Ontario Ministry of Environment and Energy, 1994)	170 ng released (per g of tire)
	Lab leachate study (O'Shaughnessy and Garga, 2000)	640 ppb in leachate
2-hydroxybenzothiazole	Lab leachate study (Reddy and Quinn, 1997)	36,000 ng released (per g crumb rubber)
	Urban runoff (Reddy and Quinn, 1997)	7.0 ppb in urban runoff
2-(4-morpholinyl)benzothiazole	S.F. bay sediment (Spies et al., 1987)	360 ppb in sediment
	Lab leachate (Ontario Ministry of Environment and Energy, 1994)	260 ng released (per g of tire)
	Background air sample (Kumata et al., 1996)	5.9 pg/m <sup>3</sup>
	Lab leachate study (Reddy and Quinn, 1997)	2,000 ng released (per g crumb rubber)
	Urban runoff (Reddy and Quinn, 1997)	0.28 ppb in runoff
	Lab leachate study (Hartwell et al., 1998)	Not quantifiable
	Lab leachate study (O'Shaughnessy and Garga, 2000)	340 ppb in leachate
	River sediment (Kumata et al., 2002)	9 ppb in sediment
	Highway runoff (Kumata et al., 2002)	0.417 ppb in runoff
4-(phenylamino)-phenol	Lab leachate (Ontario Ministry of Environment and Energy, 1994)	340 ng released (per g of tire)
aniline	Lab leachate study (Miller and Chadik, 1993)	742 ng released (per g tire)
	Lab leachate (Ontario Ministry of Environment and Energy,	129 ng released (per g tire)

Compound	Study Type	Concentration
	1994)	
	Field leachate study (Humphrey and Katz, 2001)	71 ppb in leachate
	Field leachate study (Exponent, 2003)	100 ppb in leachate
benzothiazole	Lab leachate (Ontario Ministry of Environment and Energy, 1994)	430 ng released (per g of tire)
	Urban runoff (Reddy and Quinn, 1997)	1.3 ppb in urban runoff
	Lab leachate study (Reddy and Quinn, 1997)	100,000 ng released (per g crumb rubber)
	Lab leachate study (O'Shaughnessy and Garga, 2000)	900 ppb in leachate
Bis(2-ethylhexyl)phthalate	Lab leachate study (Hartwell et al., 1998)	Not quantifiable
m + p cresol	Field leachate study (Humphrey and Katz, 2001)	39 ppb in leachate
N-cyclohexyl-2-benzothiazolamine	Highway runoff (Kumata et al., 2002)	0.508 ppb in runoff
	River sediment (Kumata et al., 2002)	17 ppb in sediment
N-nitrosodimethylamine	Field leachate study (Exponent, 2003)	7 ppb in leachate
N-nitrosodiphenylamine	Field leachate study (Exponent, 2003)	7 ppb in leachate
phenol	Lab leachate study (Scrap Tire Man Concl, 1991)	50 ppb in leachate
	Lab leachate study (Tatlisoz et al., 1996)	10 ng released (per g of tire)
phenoxazine	Lab leachate (Ontario Ministry of Environment and Energy, 1994)	220 ng released (per g of tire)

**Table 5. Concentrations of particulates in the air resulting from tire wear**

<b>Substance</b>	<b>Study Type</b>	<b>Concentration</b>
Rubber particulates (<10 microns) containing latex	Air sampling and guardrail swipes near freeway (Miguel et al., 1996)	1 µg/m <sup>3</sup>
Rubber particles (59%<10 microns) with latex	Air sampling near freeway (Williams et al., 1995)	3800-6900 particles/m <sup>3</sup>
Rubber particulates	Air sampling in urban area (Kim et al., 1990)	Up to 7 µg/m <sup>3</sup>
Fine particulate organic carbon due to tire wear	Emissions into air in urban area (Hildemann et al., 1991)	105 µg /m <sup>2</sup> of urban surface area/day
Fine particulate organic carbon from tires	Air sampling (Schauer et al., 2002)	1 µg/m <sup>3</sup>
Airborne dust from tire tread	Air sampling near busy urban road (Fukuzaki et al., 1986)	24 ng/m <sup>3</sup>

## **Chapter 4: Toxicity reference values for substances released by recycled tires**

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To determine if an environmental contaminant poses a threat to human health, its environmental concentration is used to estimate human exposure, which is then compared to reference toxicity values. Such reference values (i.e., RfD = reference dose, MRL = minimal risk level, PHG = public health goal, REL = reference exposure level) are often derived from data determined experimentally in studies with laboratory animals. Alternatively, human epidemiologic data can be used. This section lists the reference toxicity values for most of the substances identified in the previous section. The tables are arranged according to type of toxicant (metal, VOC, sVOC, particulate) and are for the oral route of exposure. Reference values were collected for acute (single), subchronic (up to 90 days) and chronic (one year or more) exposures. When available, OEHHA values were used. Information was also included regarding carcinogenicity and whether children represent a sensitive subgroup relative to the adult population.

**Table 6: Metals: Oral route: Toxicity Values**

<b>Aluminum</b> (noncarcinogenic, the data do not suggest an increased susceptibility of infants or children; OEHHA, 2001a; ATSDR, 1999a)
<b>Acute:</b> not acutely toxic in healthy adults based on widespread exposure via food, water and antacid tablets (OEHHA, 2001a)
<b>Subchronic:</b> minimal risk level (MRL) = 2.0 mg/kg-d based on a NOAEL of 62 mg/kg-day in mice fed for 6 weeks and exhibiting decreased activity (uncertainty factors of 3 for interspecies and 10 for intraspecies variability; ATSDR, 1999a)
<b>Chronic:</b> a public health goal (PHG) for aluminum in drinking water was developed using a chronic oral screening value of 0.018 mg/kg-d derived from a human study in which volunteers fed the metal for 20 days exhibited a significant increase in serum aluminum (NOAEL/LOAEL = 125 mg/d, UF = 10 for intrahuman variability and 10 for subchronic to chronic extrapolation; OEHHA, 2001a)
<b>Antimony</b> (no data were located on carcinogenicity by the oral route or whether children represent a sensitive subpopulation)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> An LOAEL of 0.43 mg/kg-day was based on minor clinical signs and a slight decrease in longevity in a chronic rat study, yielding a chronic screening level of 1.4 µg/kg-day (UFs of 3 for LOAEL to NOAEL extrapolation, and 100 for intra- and interspecies extrapolation) (OEHHA, 1997c)
<b>Arsenic</b> (considered a group A human carcinogen; IRIS, 1998a) (no evidence that the young are more sensitive than adults)
<b>Acute:</b> an acute Minimal Risk Level (MRL) of 5 µg/kg-d was developed based on a 2-3 week exposure in humans which produced nausea, vomiting, diarrhea, occult blood in feces and duodenal juice (UF = 10 for LOAEL to NOAEL extrapolation; ATSDR, 2000a)
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> a $1 \times 10^{-6}$ excess risk of lung and bladder cancer was calculated for a chronic oral intake by humans of $1.1 \times 10^{-4}$ µg/kg-d (OEHHA, 2004a)
<b>Barium</b> (Dog and rat pharmacokinetic studies (Taylor et al., 1962; Cuddihy and Griffith, 1974) suggest that gastrointestinal absorption of barium may be higher in young animals than in older animals; IRIS, 1999) (not carcinogenic; OEHHA, 2003b)

<b>Acute:</b> LD <sub>50</sub> in weanling and adult rats of 220 and 132 mg/kg, respectively (OEHHA, 2003b); fatal dose of barium carbonate suggested to be about 800 mg (OEHHA, 2003b)
<b>Subchronic:</b> NOAEL of 0.21 mg/kg-day in adult humans exposed for four weeks (OEHHA, 2003b)
<b>Chronic:</b> 0.07 mg/kg-day in adult humans based on the absence of cardiovascular effects (NOAEL = 0.21 mg/kg-day) and an uncertainty factor (human variability) of 3 (OEHHA, 2003b)
<b>Cadmium</b> (considered a potential human carcinogen by the oral route; OEHHA, 1999a) (following ingestion, absorption was higher in young rats and guinea pigs compared to adults, suggesting that young humans may also absorb more ingested cadmium than adults; ATSDR, 1999b)
<b>Acute:</b> a single dose of 25 mg/kg was lethal in a human suicide (ATSDR, 1999b); a single dose LD <sub>50</sub> of 29 mg/kg was measured in 2 week old rats (ATSDR, 1999b)
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> a Reference Exposure Level (REL) of 0.5 µg/kg-day was calculated based on proteinuria in an exposed human population (UFs = 10 for intraspecies variation; OEHHA, 2000a); an RfD of 0.5 µg/kg-day for cadmium intake in water was calculated based on the same critical study and UF listed above for the REL (IRIS, 1994a); Minimal Risk Level (MRL) = 0.21 µg/kg-day based on kidney effects in an exposed human population (UF = 10 for intraspecies variability; ATSDR, 1999b); a dose of 2.6 ng/kg-day yielded a <i>de minimis</i> excess lifetime cancer risk of 1x10 <sup>-6</sup> (OEHHA, 1999a)
<b>Chromium (hexavalent)</b> (no data to indicate children more susceptible; listed as a carcinogen by inhalation, OEHHA, 2004b)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> RfD = 3 µg/kg-day in rats based on the absence of toxicity at the highest dose tested (2.5 mg/kg-d) (uncertainty factors of 10 each for intraspecies and interspecies variability and 3 for subchronic to chronic extrapolation; IRIS, 1998b); the RDA for total chromium for a 1-3 year old child is 11 µg/day (USDA, 2006)
<b>Cobalt</b> (no data were located on carcinogenicity by the oral route or whether children represent a sensitive subpopulation)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> an MRL of 10 µg/kg-day was developed based on a 25 day study in which exposed humans exhibited polycythemia (UFs of 10 for LOAEL to NOAEL extrapolation and 10 for intrahuman variability) (ATSDR, 2004b)

<b>Chronic:</b> no screening level identified
<b>Copper</b> (infants and children may be more susceptible; OEHHA, 1997a) [Carcinogenicity classification -- D; not classified basis -- There are no human data, inadequate animal data from assays of copper compounds, and equivocal mutagenicity data (IRIS, 1991a)]
<b>Acute:</b> 5.3 mg (76 µg/kg) ingested by human adults caused gastrointestinal distress, headaches and dizziness (OEHHA, 1997a)
<b>Subchronic:</b> in adults a NOAEL of 0.0538 mg/kg-day (over two weeks) for gastrointestinal effects was divided by an UF = 3 (for human variability) to give an MRL (minimal risk level) of 0.02 mg/kg-day (ATSDR, 2002)
<b>Chronic</b> the RDA (recommended daily allowance) is 13 µg /kg-day (ATSDR, 2002) for an adult and 23 µg /kg-day for a 1-3 year old child weighing 15 kg (USDA, 2006).
<b>Iron</b>
<b>Acute:</b> 0.5 grams can be lethal if ingested by a child (Goyer, 1996; Spivey and Rader, 1988); acute ingestion of 20 mg/kg by adults was associated with gastrointestinal irritation (Institute of Medicine, 2002).
<b>Subchronic:</b> LOAEL = 70 mg/day (1 mg/kg/day in 70 kg adult) for 4 weeks of ingestion by adults resulting in GI effects, UL = LOAEL/1.5 (UF) = 45 mg/day (Institute of Medicine, 2002)
<b>Chronic:</b> Upper intake level = 40 mg/day for ingestion by infants and small children (Institute of Medicine, 2002); the RDA for a 1-3 year old child is 7 mg/day (USDA, 2006).
<b>Lead</b> (children may be most sensitive group, possibly due to greater absorption; OEHHA, 1997b) [B2; probable human carcinogen (IRIS, 1993a); determined to be carcinogenic by the oral route (OEHHA, 2004b)]
<b>Acute:</b> colic would be expected in a child following ingestion of approximately 80 µg /kg bodyweight (approximately 60 µg /dL blood level; ATSDR, 1999c) and dividing by UFs of 10 for intrahuman variability and 3 for LOAEL to NOAEL extrapolation gives an acute screening level = 2.7 µg /kg
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> intake of 29 µg/day by children associated with decreased IQ and other neurological effects, then, applying an UF = 3 results in a screening value of 10 µg/day or 0.67 µg /kg-day for a 15 kg child (OEHHA, 1997b); NSRL = 15 µg/day, MADL = 0.5 µg/day (OEHHA, 2004b); a dose of 0.18 µg/kg-day yielded an excess lifetime cancer risk of $1 \times 10^{-6}$ (OEHHA, 1997b)

<b>Manganese</b> (neonates may absorb and retain more manganese than adults)
<b>Acute:</b> acute LD <sub>50</sub> in rats = 200-300 mg/kg/day (ATSDR, 2000b)
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> RfD = 3 mg/day for non-food sources of manganese in adults (IRIS, 1996a); the RDA for a 1-3 year old child is 1.2 mg/day (USDA, 2006)
<b>Mercury (inorganic)</b> (not on Proposition 65 list as chemical known to the state to cause cancer; OEHHA, 2004b; listed as a Group C possible human carcinogen by the IRIS, 1995b) (suckling rats absorbed inorganic mercury from ingested food at a 30 to 40-fold higher rate than adults; ATSDR, 1999d)
<b>Acute:</b> Ingestion of 0.5 g can be lethal in humans, while LD <sub>50</sub> s in rats ranged from 30 to 77 mg/kg (OEHHA, 1999b)
<b>Subchronic:</b> a subchronic screening value of 1.6 µg/kg-d was based on decreased weight gain and increased kidney weights in rats (UFs = 10 for intrahuman variability and 10 for interspecies extrapolation; OEHHA, 1999b)
<b>Chronic:</b> a screening value of 0.16 µg/kg-d was calculated based on decreased weight gain and increased kidney weights in rats (UFs = 10 for intrahuman variability, 10 for interspecies extrapolation, 10 for subchronic to chronic extrapolation; OEHHA, 1999b)
<b>Molybdenum</b> (no data located on carcinogenicity or whether children represent a sensitive subpopulation)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> an RfD of 5 µg/kg-day was developed based on increased serum uric acid levels in a chronically exposed human population (a UF of 3 was applied for intrahuman variability and 10 for LOAEL to NOAEL extrapolation; IRIS, 1993c)
<b>Nickel (water soluble)</b> (not a known oral carcinogen) (no data were located indicating that the young are more susceptible than adults)
<b>Acute:</b> adult humans became sick (nausea, abdominal cramps, diarrhea, vomiting) after ingesting water contaminated with nickel at dose levels ranging from 7 to 36 mg nickel/kg (OEHHA, 2001b) and dividing by UFs of 10 for intrahuman variability and 3 for LOAEL to NOAEL extrapolation gives an acute screening level = 233 µg/kg
<b>Subchronic:</b> no screening level identified

<p><b>Chronic:</b> a chronic screening level of 1.12 µg/kg-d was calculated based on increased pup mortality in rat reproductive toxicity studies (UFs = 10 for intrahuman variability, 10 for interspecies extrapolation, 10 for potential carcinogenicity of soluble nickel by the oral route; OEHHA, 2001b); an RfD of 20 µg/kg-d was calculated based on decreased body and organ weights in rats fed nickel (UFs = 10 for intrahuman variability, 10 for interspecies extrapolation, 3 for inadequacies in the reproductive toxicity studies; IRIS, 1996b)</p>
<p><b>Selenium</b> (designated a class D carcinogen: not classifiable as to carcinogenicity in humans; IRIS, 1993b) (no data to indicate that children are more sensitive than adults; ATSDR, 2003a)</p>
<p><b>Acute:</b> no screening level identified</p>
<p><b>Subchronic:</b> use chronic REL</p>
<p><b>Chronic:</b> a chronic oral reference exposure level (REL) of 0.005 mg/kg-day was developed based on a human epidemiological study of lifetime exposures (3-fold UF for intrahuman variability; OEHHA, 2003a); the recommended daily allowance is 1.07 to 1.53 µg/kg-day for children (IRIS, 1993b)</p>
<p><b>Vanadium</b> (no data were located on carcinogenicity by the oral route or whether children represent a sensitive subpopulation)</p>
<p><b>Acute:</b> no screening level identified</p>
<p><b>Subchronic:</b> An intermediate MRL of 3 µg/kg-day was developed based on a 3 month study in the rat producing hemorrhagic foci in the renal system (UFs of 10 for interspecies and 10 for intrahuman variability) (ATSDR, 1992c)</p>
<p><b>Chronic:</b> an RfD of 9 µg/kg-day was developed based on decreased hair cystine in chronically exposed rats (an UF of 10 was applied for interspecies extrapolation and 10 for intrahuman variability; IRIS, 1996c).</p>
<p><b>Zinc</b> (no evidence to suggest children more sensitive than adults)</p>
<p><b>Acute:</b> LOAEL approx. 2-8 mg/kg based on gastrointestinal distress in adults after single-dose ingestion (ATSDR, 2003b)</p>
<p><b>Subchronic:</b> subchronic MRL = 0.3 mg/kg-day based on decreased erythrocyte SOD activity, hematocrit and serum ferritin in human females (composite UF = 3; ATSDR, 2003b)</p>
<p><b>Chronic:</b> RfD = 0.3 mg/kg-day based on same subchronic study cited above (IRIS, 1992); Recommended Dietary Allowance of 3 mg/day and a Tolerable Upper Intake Level of 7 mg/day in 1-3 year olds (The National Academies, 2001)</p>

**Table 7: VOCs: Oral route: Toxicity Values**

<b>1,1-Dichloroethane</b> (carcinogenic based on rodent studies, no evidence of enhanced sensitivity of infants or children; OEHHA, 2003c; ATSDR, 1990)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> lifetime oral consumption of 0.171 µg/kg-d yielded an excess individual cancer risk of 10 <sup>-6</sup> (OEHHA, 2003c); no significant risk level (NSRL) = 100 µg/day (yields an excess individual cancer risk of 10 <sup>-5</sup> for a 70 year exposure; OEHHA, 2004b)
<b>1,2-Dichloroethene</b> (no carcinogenicity studies were located, ATSDR, 1996; IRIS, 1995a; no evidence of increased sensitivity of infants or children, ATSDR, 1996)
<b>Acute:</b> minimal risk level (MRL) = 1.0 mg/kg-d based on decreased hematocrit and erythrocytes in female rats treated by single-dose oral gavage (NOAEL = 97 mg/kg-day, UFs of 10 for intraspecies and 10 for interspecies variability, ATSDR, 1996)
<b>Subchronic:</b> minimal risk levels (MRL) = 0.3 mg/kg-day based on decreased hematocrit in male rats dosed by gavage for 90 days with the cis isomer (NOAEL = 32 mg/kg-day, UFs 10 for intraspecies and 10 for interspecies variability, ATSDR, 1996); MRL = 0.2 mg/kg-day based on increased serum alkaline phosphatase and increased relative liver weight in male mice fed the trans isomer via the drinking water for 90 days (NOAEL = 17 mg/kg-day, UFs of 10 for intraspecies and 10 for interspecies variability, ATSDR, 1996)
<b>Chronic:</b> no screening level identified
<b>Acetone</b> (minimal evidence that young or pregnant rats more sensitive than nonpregnant adults; ATSDR, 1994) (data inadequate for assessment of human carcinogenic potential; IRIS, 2003c)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> Minimal Risk Level (MRL) = 2 mg/kg-day based on a 13 week study in rats identifying mild macrocytic anemia (UFs of 10 for intraspecies and 10 for interspecies extrapolation; ATSDR 1994)
<b>Chronic:</b> RfD = 0.9 mg/kg-day based on same subchronic rat drinking water study as above producing nephropathy (NOAEL = 900 mg/kg-day, UF = 10 for intraspecies, 10 <sup>1/2</sup> for interspecies, 10 <sup>1/2</sup> for subchronic to chronic extrapolation, 10 for data base deficiencies; IRIS, 2003c)
<b>Benzene</b> (classified as a human carcinogen; IRIS, 2000; OEHHA, 2001c; no data to indicate that infants or children are more susceptible than adults to the carcinogenic effects)

<b>Acute:</b> a single oral dose of 125 mg/kg is estimated to be lethal in humans (OEHHA, 2001c); as little as 50 mg/kg has caused death in humans (ATSDR, 2004)
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> a noncancer screening value of 9 µg/kg-day was based on hematological effects in workers exposed for up to 21 years (UF = 10 for intrahuman variability; OEHHA, 2001c); a <i>de minimis</i> excess individual cancer risk of 10 <sup>-6</sup> was associated with a lifetime exposure of 0.01 µg/kg-d (OEHHA, 2001c); a No Significant Risk Level (NSRL) of 7 µg/day for a cancer risk of 10 <sup>-5</sup> (equivalent to 0.01 µg/kg-d at a cancer risk level of 10 <sup>-6</sup> ; OEHHA, 2004b); MADL = 0.34 µg/kg-day (OEHHA, 2004b)
<b>Benzo[b]fluoranthene</b> (classified as a group B2 probable human carcinogen by IRIS, 1994d)
<b>Acute:</b> no data located
<b>Subchronic:</b> no data located
<b>Chronic:</b> a No Significant Risk Level (NSRL) of 0.096 µg/day (equivalent to 0.16 ng/kg-d at the 10 <sup>-6</sup> cancer risk level; OEHHA, 2004b)
<b>Chrysene</b> (classified as a group B2 probable human carcinogen by IRIS, 1994e)
<b>Acute:</b> no data located
<b>Subchronic:</b> no data located
<b>Chronic:</b> a No Significant Risk Level (NSRL) of 0.36 µg/day (equivalent to 0.58 ng/kg-d at the 10 <sup>-6</sup> cancer risk level; OEHHA, 2004b)
<b>Fluoranthene</b> (classified as a group D carcinogen [not classifiable as to human carcinogenicity] by IRIS, 1990b)
<b>Acute:</b> no data located
<b>Subchronic:</b> see chronic study below
<b>Chronic:</b> an oral RfD of 40 µg/kg-d was developed based on a 13 week subchronic study in which mice developed nephropathy, increased liver weights, hematological changes and clinical signs (UFs of 10 for intraspecies extrapolation, 10 for interspecies extrapolation, and 30 for both subchronic to chronic extrapolation and the absence of reproductive/developmental data and data from a second animal species; IRIS, 1990b)
<b>Methyl ethyl ketone</b> (data judged inadequate for determination of carcinogenicity in humans; IRIS, 2003a) (no data on whether the young are more susceptible)
<b>Acute:</b> mild renal tubular necrosis in rats after a single oral dose of 1080 mg (ATSDR, 1992a)
<b>Subchronic:</b> no screening level identified

<b>Chronic:</b> RfD of 0.6 mg/kg-day based on decreased rat pup weight in a repro study, UF = 1000 (10 for interspecies, 10 for intraspecies, 10 for deficiencies in data base) (IRIS, 2003a)
<b>Methyl Isobutyl Ketone</b> (listed as food additive by FDA)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> NOAEL = 250 mg/kg-day based on a variety of mild effects at 1000 mg/kg-day in rats gavaged for 13 weeks (IRIS, 2003b); applying UF = 100 gives a subchronic screening level = 10 mg/kg-day
<b>Chronic:</b> using above subchronic study and applying another UF = 10 for subchronic to chronic extrapolation gives chronic screening level = 1 mg/kg-day (IRIS thought data insufficient for derivation of a chronic RfD)
<b>Phenanthrene</b> (classified as a group D carcinogen [not classifiable as to human carcinogenicity] by IRIS, 1990c)
<b>Acute:</b> no data located
<b>Subchronic:</b> no data located
<b>Chronic:</b> no data located
<b>Pyrene</b> (classified as a group D carcinogen [not classifiable as to human carcinogenicity] by IRIS, 1991b)
<b>Acute:</b> no data located
<b>Subchronic:</b> see chronic study below
<b>Chronic:</b> an oral RfD of 30 µg/kg-d was developed based on a 13 week subchronic study in which mice developed kidney effects (UFs of 10 for interspecies extrapolation, 10 for intraspecies extrapolation, 10 for subchronic to chronic extrapolation, and 3 for the absence of developmental/reproductive data and data from a second animal species; IRIS, 1991b)
<b>Styrene</b> (no evidence for increased sensitivity of the young; listed as a group 2B possible human carcinogen by IARC [1994] with inadequate evidence in humans and limited evidence in animals)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> Minimal Risk Level (MRL) = 0.2 mg/kg-day based on a 100 day study in rats identifying changes in hepatic enzymes (UFs of 10 for interspecies, 10 for intraspecies, and 10 for use of a LOAEL; ATSDR, 1992b)
<b>Chronic:</b> RfD = 2 mg/kg-day for effects in rbcs and livers of dogs (UF = 100 for intra and interspecies variability, they also included 10 for subchronic to chronic extrapolation which I have dropped since the study ran for 560 days; IRIS, 1990a)
<b>Toluene</b> (carcinogenicity judged not classifiable [Group D] due to absence of human data and inadequate animal data; IRIS, 1994b) (only minimal data indicating that neonatal humans may be more sensitive than adults)

<p><b>Acute:</b> Minimal Risk Level (MRL) = 0.8 mg/kg-day based on neurological changes (altered visual information processing) in rats following single-dose oral gavage (UFs of 10 for human variability, 10 for interspecies extrapolation, and 3 for use of a minimally adverse LOAEL; ATSDR, 2000c)</p>
<p><b>Subchronic:</b> Minimal Risk Level (MRL) = 0.02 mg/kg-day based on a 28 day drinking water study in mice identifying increased brain norepinephrine and dopamine (UFs of 10 for human variability, 10 for interspecies extrapolation, and 3 for use of a minimally adverse LOAEL; ATSDR, 2000c)</p>
<p><b>Chronic:</b> a chronic screening value of .022 mg/kg-day was identified from a subchronic mouse drinking water study producing immunological toxicity (UFs of 10 for interspecies, 10 for intraspecies, and 10 for subchronic to chronic extrapolation; OEHHA, 1999c); an RfD = 0.2 mg/kg-day was based on a subchronic rat gavage study which detected changes in liver and kidney weights (UF = 1000 for intraspecies and interspecies extrapolation, subchronic to chronic extrapolation, and limited developmental and reproductive toxicity data; IRIS, 1994b); maximum allowable dose level (MADL) = 7.0 mg/day (OEHHA, 2004b)</p>
<p><b>Trichloroethylene</b> (IARC considers the evidence for carcinogenicity to be sufficient in animals and limited in humans; OEHHA, 1999d) (no data were located showing that the young are more sensitive than adults)</p>
<p><b>Acute:</b> single-dose oral LD<sub>50</sub>s were 2400 mg/kg-d in mice and 7200 mg/kg-d in rats (ATSDR, 1997b)</p>
<p><b>Subchronic:</b> no screening level identified</p>
<p><b>Chronic:</b> a chronic screening level of 0.5 mg/kg-day was based on kidney nephropathy in rats (UFs of 10 for interspecies and 10 for intrahuman variability; OEHHA, 1999d); an excess individual cancer risk of 10<sup>-6</sup> was associated with a lifetime exposure of 0.077 µg/kg-d (OEHHA, 1999d)</p>

**Table 8: sVOCs: Oral route: Toxicity Values**

<b>1H-isoindole-1,3(2H)-dione (a.k.a. captan)</b> (no data were located on the carcinogenicity of 1H-isoindole-1,3(2H)-dione or whether children represent a sensitive subpopulation)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> an RfD of 130 µg/kg-d was developed based on decreased bodyweight in the rat (an UF of 10 was applied for interspecies and 10 for intrahuman extrapolation; IRIS, 1989)
<b>Aniline</b> (classified as a B2 probable human carcinogen by IRIS, 1994c)
<b>Acute:</b> Methemoglobinemia is the principle mechanism of acute aniline toxicity in man (Hazardous Substances Data Bank, 2004); a dose-dependent increase in methemoglobin resulted from single oral doses of aniline of 25-65 mg/person (Jenkins et al., 1972; IARC, 1982) with a NOEL at 15 mg (approximately 0.21 mg/kg); applying an UF of 10 for intrahuman variability yields an acute screening level of 0.021 mg/kg-day.
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> an excess cancer risk of 10 <sup>-6</sup> was calculated for a daily exposure of 0.175 µg/kg-d based on a two year feeding study in rats (IRIS, 1994c)
<b>Benzothiazole</b> (no data located on carcinogenicity or susceptibility of children) (used as a flavoring in foods at up to 0.5 ppm, listed as a GRAS substance ["generally recognized as safe"]; NTP, 2004)
<b>Acute:</b> Oral LD <sub>50</sub> s: rat = 380-479 mg/kg, mouse = 900 mg/kg (NTP, 2004)
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> no screening level identified
<b>Cyclohexanone</b> (no data were located on the carcinogenicity of cyclohexanone or whether children represent a sensitive subpopulation)
<b>Acute:</b> no screening level identified
<b>Subchronic:</b> no screening level identified
<b>Chronic:</b> an RfD of 5.0 mg/kg-d was developed based on decreased bodyweight gain in the rat (an UF of 10 was applied for interspecies and 10 for intrahuman extrapolation; IRIS, 1987)

**Phenol** (data considered insufficient to determine if children are more sensitive than adults; ATSDR, 1998) (data considered inadequate for carcinogenicity assessment in humans; IRIS, 2002)

**Acute:** no screening level identified

**Subchronic:** The chronic RfD of 0.3 mg/kg-d (see below) could be applied to subchronic exposures, since it is based on a developmental study with an exposure duration of 10 days

**Chronic:** an RfD of 0.3 mg/kg-d was developed based on decreased maternal weight gain in a rat developmental study (UFs = 10 for interspecies variability, 10 for intrahuman variability, and 3 for immunological and hematological effects noted in a 28 day mouse drinking water study; IRIS, 2002)

# Chapter 5: Evaluation of Toxicity Due to Ingestion of Tire Shreds Based on the Existing Literature of Tire Leachate Studies

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Table 9 lists 27 chemicals and the highest amount of each that leached per gram of tire, as found in the published literature, along with leaching conditions. Measurements were made in laboratory settings under a variety of different conditions. Aqueous solutions containing various salts and/or buffers were used, with the pH ranging from 2.1 to 12.1 across the studies, or not controlled. Perhaps even more problematic was the variable leaching times, ranging from 17 hours to six months. These studies also utilized different starting material: whole tires, tire shreds, chips and crumb.

The different brands of tires used in the different studies almost certainly contributed to the variable levels of chemicals released (Tables 2-4), since tire components, as well as the tire manufacturing process itself, vary across the industry. Keeping these uncertainties in mind, the highest leaching value for each chemical was chosen for calculating the dose. In this respect, the calculations represent worst-case scenarios. Using the laboratory leaching values in this way assumes that the same amounts of these chemicals would leach following ingestion of tire-derived shreds or crumb by a child. All such leaching chemicals were also assumed to be 100 percent bioavailable, representing another worst-case assumption.

The doses calculated in Table 9 are based on a one-time (acute) ingestion of 10 grams of tire shreds or crumb rubber by a 15 kg child. The value of 10 grams has been recommended for acute risk assessment for children who ingest large amounts of soil on 1-2 days out of the year (U.S. EPA, 2002; OEHHA, 2000c). This is not a typical behavior pattern observed in most children, but rather a poorly characterized behavior seen in a subset of young children (U.S. EPA, 2002). It seems reasonable to assume that a child ingesting 10 grams of soil in a single episode would also be capable of ingesting 10 grams of crumb rubber. A bodyweight of 15 kg is the 50<sup>th</sup> percentile value for both male and female children that are three years old (U.S. EPA, 2002).

As discussed earlier in this report, toxicity reference values from authoritative bodies were collected for acute, subchronic and chronic oral exposures to the substances released by tires. The acronyms for these reference values, together with their meanings and issuing bodies, are listed at the end of Table 9. These can be used as screening levels and compared to the estimated dose a child might ingest, to predict whether adverse noncancer health effects would occur. If the estimated dose were less than the screening level, then acute health effects would not be expected. Toxicity reference values for use as screening levels have not been developed for every chemical listed in Table 9; therefore, in some cases screening levels were calculated where adequate toxicity data were located in the published literature (toxicity data cited by chemical in Tables 6-8).

Since the exposure scenario being considered here is an acute, single-dose exposure, acute health effects are expected, and acute screening levels are most appropriate for use in risk calculations. However, Table 9 shows that an acute screening level was usually not available. In such cases, a subchronic screening level was used, and if this was also unavailable, a chronic screening level was used. The following reasoning was applied in these latter two cases; if the estimated dose was lower than the subchronic or chronic

screening level, then acute health effects were considered unlikely. When available, OEHHA values were used as screening levels. Conclusions reached from this comparison of screening level with estimated dose are listed in Table 9 for each chemical.

The dose levels of ingested chemicals presented in Table 9 are due to ingestion of tire shreds. For comparison, Table 10 shows the average daily intakes resulting from the presence of these chemicals in food, water and air. In many cases these average daily intakes are rough estimates. Nonetheless, it is useful to compare the tire-derived levels to the average daily intakes. Average daily intakes were located for 17 of the chemicals listed in Table 9. For 12, the average daily intakes equal or exceed the tire-derived exposures. In many cases the exposure due to ingestion of tire shreds is much lower than the average daily intake. Only for arsenic, iron, lead, nickel and zinc does the tire-derived exposure exceed the average daily intake. This indicates that particular care should be taken when comparing the tire-derived exposures to these chemicals to their corresponding health-based screening levels.

**Table 9. Comparison of ingested dose to health-based screening level for an acute ingestion of tire-derived crumb/shreds by a child based on published studies of tire leachate: noncancer health effects.**

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
<b>Metals</b>			
Aluminum	2.0 µg released per g of tire for slices of tire incubated in an aqueous solution at pH 3.5, 20-40°C for 24 h with agitation	1.3 µg/kg	Not acutely toxic in humans based on widespread presence in antacids, water and food; a 20 day human study was used to develop a chronic screening level of 18 µg/kg-d (OEHHA, 2001a)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is 14-fold lower than the chronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Arsenic	0.13 µg released per g of tire for shredded tires incubated in an aqueous solution whose pH ranged from 2.1 to 5.5 over 38 days	0.087 µg/kg	Acute MRL = 5 µg/kg-day (ATSDR, 2000a)
<i>Conclusion</i>	<i>The estimated dose is over 50-fold lower than the acute MRL, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Barium	1.7 µg released per g of tire shreds shaken for seven days in an aqueous solutions of 0-25 percent salinity	1.13 µg/kg	Subchronic screening level = 21 µg/kg-day (OEHHA, 2003b in Table 6)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is 19-fold lower than the subchronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Cadmium	0.27 µg released per g of tire (leaching conditions as for Al)	0.18 µg/kg	Chronic REL in adults = 0.5 µg/kg-day (OEHHA, 1999a)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 2.8-fold lower than the chronic REL, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Cobalt	0.1 µg released per g of tire (leaching conditions as for barium)	0.07 µg/kg	Intermediate MRL = 10 µg/kg-day (ATSDR, 2004b)
<i>Conclusion</i>	<i>The estimated dose is 143-fold lower than the intermediate MRL, suggesting a low risk of adverse effects from a one-time ingestion.</i>		

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
Copper	4.88 µg released per g of tire for shredded tires shaken for 17 h in an aqueous solution, pH = 4.9	3.25 µg/kg	The recommended daily allowance (RDA) for a 1-3 year old child is 23 µg/kg-day (USDA, 2006)
<i>Conclusion</i>	<i>Since the estimated dose is below the recommended daily allowance, adverse health effects are not expected.</i>		
Chromium	0.5 µg (fractions as trivalent and hexavalent not determined) released per g of tire (leaching conditions as for Al)	0.33 µg/kg	Chronic RfD (hexavalent) = 3.0 µg/kg-day (IRIS, 1998b)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 9-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Iron	1.1 mg released per g of tire (leaching conditions as for Al)	0.73 mg/kg	Upper intake level = 2.7 mg/kg-day for a 15 kg child (Institute of Medicine, 2002)
<i>Conclusion</i>	<i>The estimated dose is 3.7-fold lower than the upper intake level, suggesting a low risk of adverse health effects from a one-time exposure</i>		
Lead	0.92 µg released per g of tire (leaching conditions as for Al)	0.61 µg/kg	Acute screening level = 2.7 µg/kg (ATSDR, 1999c in Table 6); chronic screening level = 0.67 µg/kg-day (OEHHA, 1997b in Table 6)
<i>Conclusion</i>	<i>The estimated dose is 4.4-fold lower than the acute screening level in children. It is also below the chronic screening level. This suggests a low risk of adverse health effects from a one-time ingestion.</i>		
Manganese	5.8 µg released per g of tire for tire shreds shaken for 7 days in an aqueous solution at pH 6-7 and 25 parts per thousand salinity	3.9 µg/kg	Chronic RfD for nonfood sources of Mn in adults = 43 µg/kg-day (IRIS, 1996a in Table 6)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 11-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
Mercury	0.07 ng released per g of tire for ground tires shaken in aqueous solutions ranging in pH from 2.9 to 4.9 and for times ranging from 18 to 24 hours	0.05 ng/kg	Subchronic screening value of 1.6 µg/kg-day (OEHHA, 1999b)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is 32,000-fold lower than the subchronic screening level, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Nickel	12 µg released per g of tire (leaching conditions as for Cu)	8.0 µg/kg	Acute screening level = 233 µg/kg (OEHHA, 2001b in Table 6)
<i>Conclusion</i>	<i>The estimated dose is 29-fold below the acute screening level, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Selenium (elemental)	0.44 µg released per g of tire (leaching conditions as for Al)	0.29µg/kg	Chronic REL = 5 µg/kg-day (OEHHA, 2003a)
<i>Conclusion</i>	<i>The estimated dose is 17-fold below the chronic REL, suggesting a low risk of adverse health effects.</i>		
Zinc	2.32 mg released per g of tire chips shaken for 67 h in an aqueous solution at pH 2.5	1.55 mg/kg	Subchronic MRL = 0.3 mg/kg-day (ATSDR, 2003b)
<i>Conclusion</i>	<i>The estimated dose is 5.1-fold higher than the subchronic MRL, so adverse health effects are possible, but unlikely from an acute ingestion of tire shreds</i>		
<b>Volatile Organic Compounds</b>			
Acetone	0.115 µg released per g of tire chips incubated in water for at least 6 months prior to sampling	0.077 µg/kg	Subchronic MRL = 2.0 mg/kg-day (ATSDR, 1994)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is over 25,000-fold lower than the subchronic MRL, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Benzene	0.218 µg released per g of shredded tires incubated for 38 days in an aqueous solution, where the pH varied from 2.1 to 4.7	0.145 µg/kg	MADL = 0.34 µg/kg-day (OEHHA, 2004b)

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 2.3-fold lower than the chronic MADL, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Methyl ethyl ketone	0.017 µg released per g of tire chips (leaching conditions as for Acetone)	0.011 µg/kg	Chronic RfD = 0.6 mg/kg-day (IRIS, 2003a)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is over 50,000-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time exposure.</i>		
Methyl isobutyl ketone	1.15 µg released per g of tire chips (leaching conditions as for Acetone)	0.77 µg/kg	Subchronic screening level = 10 mg/kg-day (IRIS, 2003b in Table 6)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is more than 10,000-fold lower than the subchronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Toluene	0.28 µg released per g of tire shreds (leaching conditions as for benzene)	0.187 µg/kg	Acute MRL = 0.8 mg/kg (ATSDR, 2000c)
<i>Conclusion</i>	<i>The estimated dose is over 4,000-fold lower than the acute MRL, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Naphthalene	1.1 µg released per g of tire shreds (leaching conditions as for barium)	0.73 µg/kg	Acute oral MRL = 600 µg/kg-day (ATSDR, 2005)
<i>Conclusion</i>	<i>The estimated dose is over 800-fold lower than the acute MRL, suggesting a low risk of health effects from a one-time ingestion.</i>		
2-Methyl naphthalene	0.54 µg released per g of tire shreds (leaching conditions as for barium)	0.36 µg/kg	Chronic oral MRL = 40 µg/kg-day (ATSDR, 2005)
<i>Conclusion</i>	<i>The estimated dose is 111-fold lower than the chronic MRL, suggesting a low risk of health effects from a one-time ingestion.</i>		
Trichloroethylene	0.8 ng released per g of tire chips (leaching conditions as for acetone)	0.53 ng/kg	Chronic screening level = 0.5 mg/kg-day (OEHHA, 1999d)

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. The estimated dose is 900,000-fold lower than the chronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion</i>		
<b>Semi-volatile Organic Compounds</b>			
aniline	0.74 µg released per g of tire shreds incubated for 38 days in an aqueous solution, pH 12.0-12.1	0.5 µg/kg	Acute screening level = 0.021 mg/kg-day (Jenkins et al., 1972 and IARC, 1982 in Table 6)
<i>Conclusion</i>	<i>The estimated dose is 42-fold lower than the acute screening level, suggesting a low risk of adverse health effects from a one-time oral ingestion.</i>		
Benzothiazole	100 µg released per g of tire crumb shaken in water at 25°C for 5 days	67 µg/kg	On GRAS list; oral LD <sub>50</sub> in rats = 380-479 mg/kg (NTP, 2004)
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
2(3H)-Benzothiazolone	0.17 µg released per g of whole tire submerged in water for 2 weeks with aeration	0.11 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
2-Hydroxy-benzothiazole	36 µg released per g of tire crumb (leaching conditions as for Benzothiazole)	24 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
2-(4-Morpholin-yl)benzothiazole	2.0 µg released per g of tire crumb (leaching conditions as for Benzothiazole)	1.33 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
Phenol	0.01 µg released per g of ground tire incubated in aqueous solutions ranging in pH from 2.9 to 4.9 and for times ranging from 18 to 24 hours		

0.0

<b>Chemical</b>	<b>Highest amount released per g of tire and leaching conditions<sup>1</sup></b>	<b>Dose<sup>2</sup></b>	<b>Screening level<sup>3</sup></b>
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is over 42,000-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Phenoxazine	0.22 µg released per g of whole tire (leaching conditions as for 2(3H)-Benzothiazolone)		0.
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
4-(Phenyl-amino)-phenol	0.34 µg released per g of whole tire (leaching conditions as for 2(3H)-Benzothiazolone)		0.
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		

<sup>1</sup> See Table 2 for references.

<sup>2</sup>The dose is the amount of chemical assumed to leach from 10 grams of tire crumb/shreds following ingestion by a 15 kg child.

<sup>3</sup> See Tables 6, 7 and 8 for references associated with the screening levels covering metals, volatile organic compounds and semi-volatile organic compounds, respectively.

MRL = minimal risk level (ATSDR)

NSRL = no significant risk level (OEHHA)

REL = reference exposure level (OEHHA)

RfD = reference dose (U.S. EPA)

MADL = maximum allowable dose level (OEHHA)

GRAS = generally recognized as safe (FDA)

RDA = recommended daily allowance (NAS/NRC)

UL = upper intake level (Institute of Medicine)

**Table 10. Average daily intakes of chemicals released by tires<sup>1</sup>**

<b>Chemical</b>	<b>Source</b>	<b>Ave. daily intake in µg/kg</b>	<b>Reference</b>
<b><i>Metals</i></b>			
Aluminum	Total diet	13-270	OEHHA, 2001d
Antimony	Food and water	0.061	OEHHA, 1997c
Arsenic	Food and water	0.013	OEHHA, 2004a
Barium	Food and water	9-24	ATSDR, 2005b
Cadmium	Food and water	0.08-1.17	OEHHA, 1999a
Chromium (total)	Total diet	1.0	ATSDR, 2000d
Cobalt	Food	0.07-0.53	ATSDR, 2004b
Copper	Total diet	39	OEHHA, 1997a
Iron	All sources	120-230	HSDB, 2006a
Lead	Total diet	0.23	ATSDR, 2005c
Manganese	Food	100	HSDB, 2006b
Mercury (inorganic)	Food	0.06	OEHHA, 1999b
Nickel	Total diet	2.2	OEHHA, 2001b
Selenium	Total diet	1.5	ATSDR, 2003a
Vanadium	Total diet	A few tenths of µg	ATSDR, 1992c
Zinc	All sources	67-213	ATSDR, 2005d
<b><i>Organics</i></b>			
1H-isoindole-1,3(2H)dione (a.k.a. captan)	All sources	0.007-0.014	HSDB, 2006c
Benzene	Air	0.1	OEHHA, 2001c
Chrysene	Total diet	0.007	HSDB, 2006d
Fluoranthene	Air	0.00006	HSDB, 2006e
Naphthalene	All sources	0.27	HSDB, 2006f
Phenanthrene	Air and water	0.0007-0.0054	HSDB, 2006g
Pyrene	All sources	0.00001	HSDB, 2006h
Toluene	Air	0.27	HSDB, 2006i
Trichloroethylene	Air and water	186-757	ATSDR, 1997b
Total Polycyclic Aromatic Hydrocarbons	Food	0.023-0.23	ATSDR, 1995

<sup>1</sup> Intakes were normalized to bodyweights of 70 kg for adult data and 15 kg for data from 2 year old children

## *Comparison of ingested dose to screening levels: noncancer effects*

Comparison performed using the data from Table 9:

$\mu\text{g chemical released/gram tire shreds} \times 10 \text{ grams tire shreds ingested}/15 \text{ kg child} =$

$\mu\text{g chemical ingested} \times 10/15 \text{ kg child} \rightarrow \text{does dose exceed screening value?}$

### **Zn**

Addressing acute health effects, only the estimated dose of leachable zinc (1.55 mg/kg) exceeded its associated screening level: in this case 5.1-fold above a subchronic MRL of 0.3 mg/kg-day based on decreased erythrocyte SOD activity, hematocrit and serum ferritin in human females dosed daily for 10 weeks. These effects were probably due to zinc-induced changes in the copper and iron balance, causing the above-mentioned hematological effects to develop towards the end of the study (IRIS, 1992). Thus, zinc supplementation acted as an inducer of copper and iron deficiency.

Since nutritional deficiencies and their related health effects develop over extended periods of time, these effects are unlikely to occur in response to an acute ingestion of zinc. In addition, zinc is an essential element with a Recommended Dietary Allowance of 3 mg/day and a Tolerable Upper Intake Level of 7 mg/day for a 3-year-old child (National Academies, 2001). These considerations make it unlikely that an acute, oral ingestion of 1.55 mg/kg of zinc by a child would result in adverse health effects, other than the gastrointestinal distress observed in adults ingesting 2-8 mg/kg acutely (Table 6).

An additional area of uncertainty in the zinc risk calculations relates to the range of zinc leaching values listed in Table 2. The highest value (2.3 mg leached per gram of tire) was selected for use in the risk calculation described in Table 9. However, this value is from 2.6- to 2,300-fold higher than other zinc measurements listed in Table 2, and 18-fold higher than the value measured in the gastric digestion simulation experiment shown below in Table 16. Thus, using most zinc leaching values other than the maximum value in Table 9 would result in an estimated dose that was below the subchronic screening level for zinc. This underscores the importance of accurate leaching data.

### **Other chemicals**

Six of the chemicals listed in Table 9 could not be evaluated due to the absence of screening levels. In addition, 11 of the VOCs and sVOCs identified in Tables 3 and 4 as leaching from tires could not be evaluated due to the absence of information on the amount of tire rubber that was used to produce each leachate. Therefore, the acute risks from these chemicals remain uncharacterized. Other than for naphthalene and 2-methyl naphthalene, the data on polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons could not be evaluated since leaching data were not presented for individual compounds (Table 3).

It has become common practice to perform calculations to determine whether health effects are expected from exposures to complex mixtures of toxicants. The leachate from tires represents such a complex mixture. One methodology (CIWMB, 2004) is to calculate a Hazard Quotient for each individual toxicant by dividing the dose by the

associated health-based screening level, and then add all values together to give a Hazard Index (Table 11). A Hazard Index less than one suggests that health effects are unlikely, while an Index greater than one suggests that health effects are more likely. This approach is most meaningful when applied to chemicals that cause similar effects on the same target organ. Such is not the case here. It should also be noted that for most chemicals listed in Table 9 an acute screening level was not available, so that subchronic or chronic values were used instead. This undoubtedly led to higher individual Hazard Quotients than would have been calculated if acute screening values were available. On the other hand, for some chemicals there were no screening level data, so that a Hazard Quotient could not be calculated.

Nonetheless, the Hazard Index approach was used as a first tier screening procedure to estimate whether cumulative impacts would be expected from all the chemicals released by tire shreds. The Hazard Index based on all chemicals except zinc is 1.8, while that including zinc is 6.9. As discussed above, since zinc-induced copper or iron deficiencies develop over a period of weeks in which zinc is ingested daily, we believe it unlikely that zinc released from a one-time ingestion of tire shreds would cause health effects other than gastrointestinal distress. Since the Hazard Index for all chemicals other than zinc is close to one, this first tier screening suggests that this complex mixture of chemicals does not represent a serious health hazard.

**Table 11. Hazard Quotients and Hazard Index for an Acute Ingestion of Chemicals Identified in Published Studies of Tire Leachate**

Chemical	Dose <sup>1</sup> /screening value <sup>1</sup>	Hazard quotient <sup>2</sup>
<b>Metals</b>		
aluminum	1.3/18	0.072
arsenic	0.087/5	0.017
barium	1.13/21	0.054
cadmium	0.18/0.5	0.360
cobalt	0.07/10	0.007
copper	3.25/23 (RDA)	Not calculated
chromium (hexavalent)	0.33/3	0.110
iron	730/2700	0.27
lead	0.61/2.7	0.226
manganese	3.9/43	0.091
mercury	0.00005/1.6	0.00003
nickel	8/233	0.034
selenium (elemental)	0.29/5	0.058
zinc	1550/300	5.167

Chemical	Dose <sup>1</sup> /screening value <sup>1</sup>	Hazard quotient <sup>2</sup>
<b>Volatile Organic Compounds</b>		
acetone	0.077/2000	0.00004
benzene	0.145/0.34	0.426
methyl ethyl ketone	0.011/600	0.00002
methyl isobutyl ketone	0.77/10,000	0.00008
toluene	0.187/800	0.0002
naphthalene	0.73/600	0.001
2-methyl naphthalene	0.36/40	0.009
trichloroethylene	0.00053/500	1.1 x 10 <sup>-6</sup>
<b>Semi-volatile Organic Compounds</b>		
aniline	0.5/21	0.024
phenol	0.007/300	0.00002
<b>HAZARD INDEX (-) ZINC</b>		<b>1.8</b>
<b>HAZARD INDEX (+) ZINC</b>		<b>6.9</b>

<sup>1</sup>from Table 9, both in µg/kg    <sup>2</sup>calculated from second column of this table

In summary, serious noncancer health effects are not expected following a one-time ingestion of tire-derived shreds or crumb by a child. Gastrointestinal distress might occur as has been observed in adults ingesting high amounts of zinc (Table 6); however, the variable levels of zinc that leached from tire-derived material (Table 2 and the gastric digestion simulation experiment shown in Table 16) suggest that the amount leaching from ingested rubber would be significantly lower than that used in the calculation in Table 9, so that acute effects would not be expected. Chronic effects are also not expected due to the single-dose nature of the exposure (chronic health effects are examined more closely in a Chapter 7 dealing with chronic exposures via hand-to-mouth activity). Should a child ingest ten grams of tire shreds on more than one occasion, the methodology followed here would yield a proportional increase in ingested dose that could exceed some of the acute screening values listed in Table 9. Whether a child ingests ten grams of tire shreds often enough for such exposures to qualify as subchronic or chronic is unknown.

## *Estimating the increased cancer risk*

From among the chemicals listed in Table 9, seven (arsenic, cadmium, lead, benzene, trichloroethylene, aniline, naphthalene) are currently listed as oral carcinogens by the State of California (OEHHA, 2005). In general, data are lacking as to whether a one-time ingestion of most carcinogens is sufficient to cause cancer. Nonetheless, Table 10 calculates the increased cancer risk to a three year old assuming that a one-time ingestion of these seven chemicals is sufficient, however, the true risk may be greater or less than the calculated risk. The calculations were performed according to draft methodology recommended by the U.S. EPA (2003c). Following this methodology, the dose from

Table 9 was averaged over a 70-year lifetime, multiplied by the Cancer Slope Factor, and multiplied by a factor of three to cover the increased sensitivity of a three-year-old child to some carcinogens:

$\text{ingested dose}/(70)(365) \times \text{oral cancer slope factor} \times (3) =$ $\text{increased cancer risk in a three-year-old}$
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The increased cancer risk from exposure to each of seven chemicals (arsenic, cadmium, lead, benzene, trichloroethylene, aniline, naphthalene) is low, while the total increased risk is  $1.2 \times 10^{-7}$ . This is 3-fold higher than the increased cancer risk of  $3.7 \times 10^{-8}$  based on a “gastric digestion” experiment carried out by OEHHA (see Table 17). Thus, ingestion of tire-derived shreds by a three-year-old child is associated with a low cancer risk. The same U.S. EPA draft methodology that recommends the use of a safety factor of three for calculating the cancer risk to children between the ages of 2 and 15, also recommends the use of a safety factor of ten for children below the age of two (U.S. EPA, 2003c). Thus, multiplying the above total increased risk by 3.3 yields an increased risk of  $3.6 \times 10^{-7}$ .

Therefore, should a child below the age of two ingest ten grams of shredded tire rubber, the cancer risk would still be below the *de minimis* risk level of  $1 \times 10^{-6}$ , generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006). As for the noncancer health effects discussed above, calculating the increased cancer risk assumes a one-time ingestion of ten grams of tire shreds. Should this behavior be repeated in the same child, the risk would increase proportionately. However, lacking data as to whether ingestion of ten grams of tire shreds is a behavior that is repeated in some children, we have not calculated the increased cancer risk for other than a one-time ingestion.

**Table 12. Increased cancer risk in a 3 year old following a one-time ingestion of 10 grams of shredded tires based on published tire leachate studies**

Carcinogen	Dose ingested by a 3 year old in mg/kg <sup>(1)</sup>	Ingested dose averaged over 70 x 365 days in mg/kg-d	Oral Cancer Slope Factor in (mg/kg-d) <sup>-1(2)</sup>	Increased cancer risk in a 3 year old <sup>(3)</sup>
Arsenic	$8.7 \times 10^{-5}$	$3.4 \times 10^{-9}$	9.45	$9.6 \times 10^{-8}$
Cadmium	$1.8 \times 10^{-4}$	$7.0 \times 10^{-9}$	0.38	$8.0 \times 10^{-9}$
Lead	$6.1 \times 10^{-4}$	$2.3 \times 10^{-8}$	0.0085	$6.1 \times 10^{-10}$
Benzene	$1.45 \times 10^{-4}$	$5.7 \times 10^{-9}$	0.1	$1.7 \times 10^{-9}$
Trichloroethylene	$5.3 \times 10^{-7}$	$2.1 \times 10^{-11}$	0.013	$8.2 \times 10^{-13}$
Aniline	$5.0 \times 10^{-4}$	$2.0 \times 10^{-8}$	0.0057	$3.4 \times 10^{-10}$
Naphthalene	$7.3 \times 10^{-4}$	$2.9 \times 10^{-8}$	0.12	$1.0 \times 10^{-8}$

Calculated thus:  $\text{ingested dose}/(70)(365) \times \text{oral cancer slope factor} \times (3) = \text{increased cancer risk in a three-year-old}$

<sup>(1)</sup> From Table 9.

<sup>(2)</sup> From the OEHHA Toxicity Criteria Database, available at [www.oehha.ca.gov](http://www.oehha.ca.gov)

<sup>(3)</sup> Calculated by multiplying the Cancer Slope Factor in column four by the averaged dose in column three, and then multiplying by a factor of three for the increased sensitivity of 3 year old children to carcinogens released by tires (U.S. EPA, 2003c).

Chronic ingestion of excess zinc is not considered to be carcinogenic by the ATSDR (2003b), while IRIS (1992) classifies zinc into Group D: not classifiable as to human carcinogenicity.

# Chapter 6: Evaluation of Toxicity Due to Ingestion of Tire Shreds Based on OEHHA Gastric Digestion Simulation Study

## *Measuring the chemicals released from tire-derived shreds*

To estimate the kinds and amounts of chemicals that could potentially be extracted in a child's gastrointestinal tract, we performed the following gastric digestion simulation experiment. Three samples of shredded tire rubber were obtained from three recyclers; two located in California and one in Ohio. Forty grams of shredded tire rubber were added to each of three glass flasks. A fourth control flask received no rubber. Then 200 mls of a solution were added to simulate the environment of the human stomach. The chart below lists the components of this gastric digestion solution along with references. A citric acid-sodium citrate buffer was added to help maintain a constant pH.

**Table 13. Composition of "Gastric Digestion" Solution (Guyton and Hall, 2000; Semple et al., 2001)**

<b>Compound</b>	<b>Concentration</b>
Citric acid (buffer)	20.0 mM
Sodium citrate (buffer)	0.5 mM
Potassium chloride	15.0 mM
Sodium chloride	3.0 mM
Pepsin	1.0 mg/ml
All in distilled water with pH = 2.3	

Following addition of shredded tires and solution, each flask was sealed with parafilm, placed in a temperature-controlled rotary shaker, and gently shaken at 37°C for 21 hours. Each solution was then filtered through Whatman filter paper into a glass sample jar. Samples were immediately refrigerated, followed by transport to the analyzing laboratory (Sequoia Analytical, Morgan Hill, CA). Metals were analyzed by EPA Method 6020 and sVOCs (including sixteen PAHs) by EPA Method 8270C.

Table 14 lists the metals and sVOCs that were identified in the extract. The tire leachates contained 13 metals and 9 sVOCs that were present at lower levels or not at all in the control. No PAHs were detected. The control sample contained two sVOCs that were not detected in any tire samples. Unfortunately, these measurements give no information on bioavailability, which was assumed to be 100 percent for all chemicals.

All 13 metals were higher in the three rubber samples than in the control. Three sVOCs were also present in all three rubber samples but not in the control: benzothiazole, 2(3H)-benzothiazolone and aniline. Comparing the results of the digestion experiment to the studies gathered from the literature and listed in Tables 2-4, our digestion experiment

identified three metals and five sVOCs not previously identified as leaching from tire rubber: antimony, molybdenum, vanadium, cyclohexanamine N-cyclohexyl, cyclohexanone, formamide, N-cyclohexyl, 1H-isoindole-1,3(2H)dione and o-cyanobenzoic acid. In addition, two other metals and three other sVOCs leached at higher levels in the digestion experiment compared to the literature values: barium, copper, aniline, 2(3H)-benzothiazolone and phenol. Importantly, the amount of zinc released per gram of rubber was 18-fold lower in the digestion experiment compared to the highest value found in the literature and used in Table 9. Thus, our value for leaching zinc as well as the majority of zinc values gathered from the literature (Table 2), suggest that the value used in Table 9 overestimates the dose.

**Table 14. Chemicals leaching from three shredded tire samples in “gastric digestion” experiment (all units are µg/l, ND = below reporting limit)<sup>1</sup>**

Chemical	Reporting limit	Tire sample “G”	Tire sample “S”	Tire sample “O”	Control
<b>Metals</b>					
Antimony	0.50	110	42	1.7	ND
Arsenic	1.0	6.1	5.4	4.7	ND
Barium	1.0	130	110	870	4.2
Cadmium	0.25	2.2	2.8	1.1	0.44
Chromium (total)	2.0	41	57	35	16
Cobalt	0.50	45	50	33	ND
Copper	0.5-50	1500	960	1600	8.3
Lead	0.50	140	120	48	4.6
Molybdenum	1.0	11	18	8.5	ND
Nickel	1.0	27	27	22	1.1
Selenium	1.0	18	10	7.1	3.0
Vanadium	1.0	9.0	9.5	5.8	3.3
Zinc	5.0-500	17000	26000	13000	16
<b>Organics</b>					
o-cyanobenzoic acid	36-190	990	ND	910	ND
Cyclohexanamine, N-cyclohexyl-	190	190	410	ND	ND
Benzothiazole	36-190	320	450	390	ND
2(3H)-Benzothiazolone	36-190	640	450	480	ND

Chemical	Reporting limit	Tire sample "G"	Tire sample "S"	Tire sample "O"	Control
1H-isoindole-1,3 (2H)-dione	190	ND	490	ND	ND
Cyclohexanone	36	ND	ND	48	ND
Formamide, N- Cyclohexyl-	36	ND	ND	110	ND
Benzaldehyde, 3- Hydroxyl-4-methoxy-	19	ND	ND	ND	25
Hexanedioic acid, bis(2-ethylhexyl)	19	ND	ND	ND	28
Aniline	190-360	2800	3000	6700	ND
Phenol	19-360	190	ND	ND	ND

<sup>1</sup> Data reported in Appendix A in Work Order MOC0103. Ranges of reporting limits for some chemicals indicate that different reporting limits were associated with different samples.

#### COMPARISON OF CHEMICAL EXPOSURE DUE TO INGESTION OF TIRE SHREDS TO SCREENING LEVELS: NONCANCER EFFECTS

Comparison performed using the data from Table 14:

$$\mu\text{g chemical released/gram tire shreds} \times 10 \text{ grams tire shreds ingested/15 kg child} =$$

$$\mu\text{g chemical ingested} \times 10/15 \text{ kg child} \rightarrow \text{does dose exceed screening value?}$$

Exposure doses were calculated for chemicals that were detected in at least one rubber sample at a level that was either: 1) at least three times the control, or, if the control was a nondetect, at a level that was 2) at least three times one-half the reporting limit for that chemical. Multiplying the reporting limit by a factor of three has been recommended for setting the minimum level of quantitation (US EPA, 2004). In order to represent a worst case scenario, the highest value from among the three rubber samples was used in Table 16 for calculating exposure doses.

Chemicals released were assumed to be 100 percent bioavailable. It was also assumed that a 15 kg child might acutely ingest 10 grams of shredded rubber at one time, similar to the upper limit of soil ingestion recommended for estimating acute exposures in children (US EPA, 2002; OEHHA, 2000c). This kind of soil ingestion is not a typical behavior pattern observed in most children, but rather a poorly characterized behavior seen in a subset of young children (US EPA, 2002).

Estimated doses were calculated for each contaminant and compared to the corresponding screening value cited in Tables 6-8. Table 16 shows this comparison for noncancer health effects. As discussed in the previous section, acute screening levels were often lacking, so subchronic or chronic screening levels were used instead. The reasoning was that if the estimated dose was lower than the subchronic or chronic screening level, then acute health effects were unlikely. When available, OEHHA screening values were used.

The dose levels of ingested chemicals presented in Table 16 are due to ingestion of tire shreds. For comparison, Table 10 shows the average daily intakes resulting from the presence of these chemicals in food, water and air. In many cases these average daily intakes are rough estimates. Nonetheless, it is useful to compare the tire-derived levels to the average daily intakes. Average daily intakes were located for thirteen of the chemicals listed in Table 16. For nine, the average daily intake equals or exceeds the tire-derived exposure. In many cases the exposure due to ingestion of tire shreds is much lower than the average daily intake. Only for antimony, arsenic, lead and captan does the tire-derived exposure exceed the average daily intake. This indicates that particular care should be taken when comparing the tire-derived exposures to these chemicals to their corresponding health-based screening levels.

From among the 20 chemicals listed in Table 16, 15 yielded ingested dose levels that fell at or below the corresponding screening level. The remaining five chemicals had no associated screening levels, so that the risk of health effects could not be estimated. Thus, our measurements of chemicals that leach from tire rubber, under conditions approximating those in a child's stomach, suggest that acute health effects would not occur following ingestion of ten grams of shredded rubber by a 15 kg child. Should a child ingest ten grams of tire shreds on more than one occasion, the methodology followed here would yield a proportional increase in ingested dose that could exceed some of the acute screening values listed in Table 9. Whether a child ingests ten grams of tire shreds often enough for such exposures to qualify as subchronic or chronic is unknown

As in Chapter 5, the Hazard Index approach was again used as a first tier screening procedure to estimate whether cumulative impacts would be expected from all the chemicals released by tire shreds in the gastric digestion study (Table 15). The Hazard Index based on all chemicals is 2.2. Since the Hazard Index is close to one, this first tier screening suggests that this complex mixture of chemicals does not represent a serious health hazard.

**Table 15. Hazard Quotients and Hazard Index for an Acute Ingestion of Chemicals Identified in OEHA Gastric Digestion Simulation Experiment**

Chemical	Dose <sup>1</sup> /screening value <sup>1</sup>	Hazard quotient <sup>2</sup>
<b>Metals</b>		
antimony	0.37/1.4	0.26
arsenic	0.02/5	0.004
barium	2.9/21	0.138
cadmium	0.009/0.5	0.180
chromium (hexavalent)	0.19/3	0.063
cobalt	0.17/10	0.017
copper	5.3/23 (RDA)	Not calculated
lead	0.47/2.7	0.174
molybdenum	0.06/5	0.012

<b>Chemical</b>	<b>Dose<sup>1</sup>/screening value<sup>1</sup></b>	<b>Hazard quotient<sup>2</sup></b>
nickel	0.09/233	0.0004
selenium	0.06/5	0.012
vanadium	0.032/3	0.011
zinc	87/300	0.29
<b>Semi-volatile organic compounds</b>		
aniline	22.3/21	1.062
1H-isoindole-1,3(2H)-dione	1.6/130	0.012
<b>HAZARD INDEX</b>		<b>2.2</b>

<sup>1</sup>from Table 16, both in µg/kg    <sup>2</sup>calculated from second column of this table

Table 16. Comparison of ingested dose to health-based screening level for an acute ingestion of tire-derived shreds based on “gastric digestion” study: noncancer health effects.

<b>Chemical</b>	<b>Highest amount released per g of tire (from among the three shredded tire samples subjected to “gastric digestion” in Table 14)</b>	<b>Dose<sup>1</sup></b>	<b>Screening level</b>
<b>Metals</b>			
Antimony	0.55 µg	0.37 µg/kg	Chronic screening level = 1.4 µg/kg-day (OEHHA, 1997c)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 26% of the chronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Arsenic	0.031 µg	0.02 µg/kg	Acute MRL = 5 µg/kg-day (ATSDR, 2000a)
<i>Conclusion</i>	<i>The estimated dose is 250-fold lower than the acute MRL, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Barium	4.35 µg	2.9 µg/kg	Subchronic screening level = 21 µg/kg-day (OEHHA, 2003b in Table 6)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is 7-fold lower than the subchronic screening level, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Cadmium	0.014 µg	0.009 µg/kg	Chronic REL in adults = 0.5 µg/kg-day (OEHHA, 1999a)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 56-fold lower than the chronic REL, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		

<b>Chemical</b>	<b>Highest amount released per g of tire (from among the three shredded tire samples subjected to “gastric digestion” in Table 14)</b>	<b>Dose<sup>1</sup></b>	<b>Screening level</b>
Chromium	0.285 µg (fractions of trivalent and hexavalent not determined)	0.19 µg/kg	Chronic RfD (hexavalent) = 3.0 µg/kg-day (IRIS, 1998b)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 16-fold lower than the chronic RfD, suggesting that health effects are unlikely from an acute ingestion.</i>		
Cobalt	0.25 µg	0.17 µg/kg	Intermediate MRL = 10 µg/kg-day (ATSDR, 2004b)
<i>Conclusion</i>	<i>No acute screening level was identified. However, the estimated dose is 59-fold lower than the intermediate MRL, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
Copper	8.0 µg	5.3 µg/kg	The recommended daily allowance (RDA) for a 1-3 year old is 23 µg/kg-day (USDA, 2006)
<i>Conclusion</i>	<i>Since the estimated dose is below the recommended daily allowance, adverse health effects are not expected.</i>		
Lead	0.7 µg	0.47 µg/kg	Acute screening level = 2.7 µg/kg (ATSDR, 1999c in Table 6); chronic screening level = 0.67 µg/kg-day (OEHHA, 1997b in Table 6)
<i>Conclusion</i>	<i>The estimated dose is 5.7-fold lower than the acute screening level in children. It is also below the chronic screening level. This suggests a low risk of adverse health effects from a one-time ingestion.</i>		
Molybdenum	0.09 µg	0.06 µg/kg	Chronic RfD = 5 µg/kg-day (IRIS, 1993c)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 83-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		

<b>Chemical</b>	<b>Highest amount released per g of tire (from among the three shredded tire samples subjected to “gastric digestion” in Table 14)</b>	<b>Dose<sup>1</sup></b>	<b>Screening level</b>
Nickel	0.135 µg	0.09 µg/kg	Acute screening level = 233 µg/kg (OEHHA, 2001b in Table 6)
<i>Conclusion</i>	<i>The estimated dose is more than 2,500-fold below the acute screening level, suggesting a low risk of adverse health effects from a one-time oral exposure.</i>		
Selenium	0.09 µg	0.06 µg/kg	Chronic REL = 5 µg/kg-day (OEHHA, 2003a)
<i>Conclusion</i>	<i>The estimated dose is 83-fold below the chronic REL, suggesting a low risk of adverse health effects.</i>		
Vanadium	0.048 µg	0.032 µg/kg	Intermediate MRL = 3.0 µg/kg-day (ATSDR, 1992c)
<i>Conclusion</i>	<i>The estimated dose is 94-fold lower than the intermediate MRL, suggesting a low risk of adverse health effects from a one-time oral ingestion.</i>		
Zinc	130 µg	87 µg /kg	Subchronic MRL = 300 µg/kg-day (ATSDR, 2003b)
<i>Conclusion</i>	<i>The estimated dose is 3.4-fold lower than the subchronic MRL, suggesting a low risk of adverse health effects..</i>		
<b>Semi-volatile Organic Compounds</b>			
Aniline	33.5 µg	22.3 µg/kg	Acute screening level = 21 µg/kg-day (IARC, 1982 and Jenkins et al., 1972 in Table 10)
<i>Conclusion</i>	<i>The estimated dose is almost identical to the acute screening level, suggesting a low risk of adverse health effects from a one-time oral ingestion.</i>		

<b>Chemical</b>	<b>Highest amount released per g of tire (from among the three shredded tire samples subjected to “gastric digestion” in Table 14)</b>	<b>Dose<sup>1</sup></b>	<b>Screening level</b>
Benzothiazole	2.25 µg	1.5 µg/kg	On GRAS list; oral LD <sub>50</sub> in rats = 380-479 mg/kg (NTP, 2004)
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
2(3H)-Benzothiazolone	3.2 µg	2.1 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
Cyclohexanamine,N-cyclohexyl-	2.1 µg	1.4 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
Formamide, N-cyclohexyl	0.55	0.37 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		
1H-isoindole-1,3(2H)-dione (a.k.a. captan)	2.45 µg	1.6 µg/kg	Chronic RfD = 130 µg/kg-day (IRIS, 1989)
<i>Conclusion</i>	<i>No acute or subchronic screening levels were identified. However, the estimated dose is 81-fold lower than the chronic RfD, suggesting a low risk of adverse health effects from a one-time ingestion.</i>		
o-Cyanobenzoic acid	4.95 µg	3.3 µg/kg	No data located
<i>Conclusion</i>	<i>Inadequate screening level data.</i>		

<sup>1</sup>The dose is the amount of chemical assumed to leach from 10 grams of tire crumb/shreds following ingestion by a 15 kg child, based on the results listed in the second column of the table.

MRL = minimal risk level (ATSDR)

NSRL = no significant risk level (OEHHA)

REL = reference exposure level (OEHHA)

RfD = reference dose (US EPA)

MADL = maximum allowable dose level (OEHHA)

GRAS = generally recognized as safe (FDA)

RDA = recommended daily allowance (NAS/NRC)

UL = upper intake level (Institute of Medicine)

## ESTIMATING THE INCREASED CANCER RISK

From among the chemicals listed in Table 16, five (arsenic, cadmium, cobalt, lead, aniline) are currently listed as oral carcinogens by the State of California (OEHHA, 2005). However, data are lacking as to whether a one-time ingestion of these carcinogens is sufficient to cause cancer. Nonetheless, Table 17 calculates the increased cancer risk to a three year old assuming that a one-time ingestion is sufficient.

To do this, the dose from Table 16 was averaged over a 70 year lifetime, multiplied by the Cancer Slope Factor, and multiplied by a factor of three to cover the increased sensitivity of a three year old child to some carcinogens (US EPA, 2003c). These calculations could not be performed for cobalt, due to the absence of a Cancer Slope Factor. The increased cancer risk from exposure to each of four chemicals (arsenic, cadmium, lead, aniline) is low, while the total increased risk is  $3.7 \times 10^{-8}$ . This is 3-fold lower than the total increased cancer risk of  $1.2 \times 10^{-7}$  calculated above using published studies of chemicals that leached from tire shreds (see previous section).

The same US EPA draft methodology that recommends the use of a safety factor of three for calculating the cancer risk to children between the ages of two and fifteen, also recommends the use of a safety factor of ten for children below the age of two (US EPA, 2003c). Thus, multiplying the above total increased risk by 3.3 yields an increased risk of  $1.2 \times 10^{-7}$ . Therefore, should a child below the age of two ingest ten grams of shredded tire rubber, the increased cancer risk would still be below the *di minimis* risk level of  $1 \times 10^{-6}$ , generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006).

**Table 17. Increased cancer risk in a 3 year old following a one-time ingestion of 10 grams of shredded tires based on OEHHA “gastric digestion” study**

Carcinogen	Dose ingested by a 3 year old in mg/kg <sup>(1)</sup>	Ingested dose averaged over 70 x 365 days in mg/kg-d	Oral Cancer Slope Factor in (mg/kg-d) <sup>-1</sup> (2)	Increased cancer risk in a 3 year old (3)
Arsenic	$2 \times 10^{-5}$	$7.8 \times 10^{-10}$	9.45	$2.2 \times 10^{-8}$
Cadmium	$9 \times 10^{-6}$	$3.5 \times 10^{-10}$	0.38	$4.0 \times 10^{-10}$
Cobalt	$1.7 \times 10^{-4}$	$6.6 \times 10^{-9}$	Unavailable	-
Lead	$4.7 \times 10^{-4}$	$1.8 \times 10^{-8}$	0.0085	$4.6 \times 10^{-10}$
Aniline	$2.2 \times 10^{-2}$	$8.6 \times 10^{-7}$	0.0057	$1.5 \times 10^{-8}$

Calculated thus: ingested dose/(70)(365) x oral cancer slope factor x (3) = increased cancer risk in a three-year-old

(1) From Table 16.

(2) From the OEHHA Toxicity Criteria Database, available at [www.oehha.ca.gov](http://www.oehha.ca.gov)

(3) Calculated by multiplying the Cancer Slope Factor in column four by the averaged dose in column three, and then multiplying by a factor of three for the increased sensitivity of 3 year old children to carcinogens released by tire shreds (US EPA, 2003c).

## Conclusions

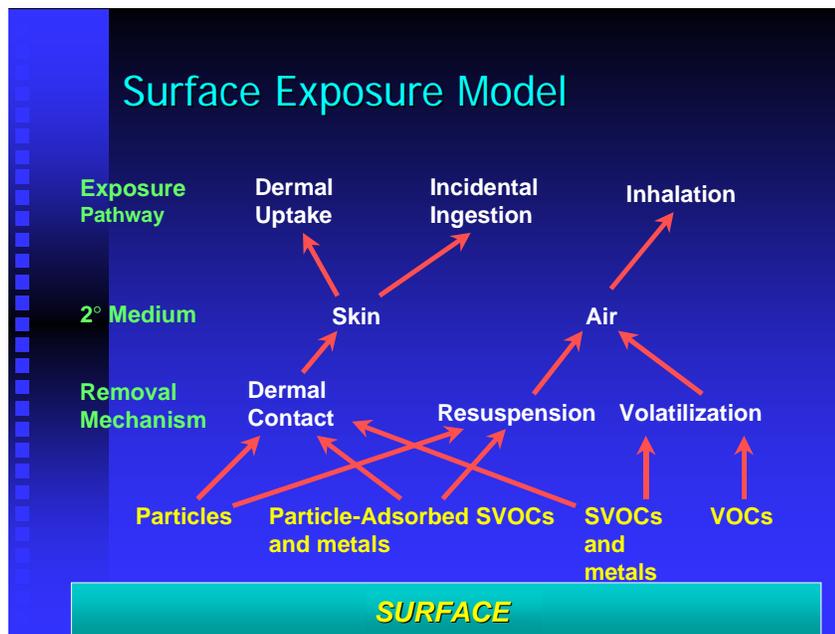
- Our gastric digestion experiment identified 22 chemicals released from tire shreds during a 21 hour incubation at 37°C in a solution that mimicked the gastric environment; these data were used to estimate the amounts of chemicals released following ingestion of 10 grams of tire shreds by a 15 kg child.
- All calculated exposure doses were at or below the corresponding screening value, suggesting a low risk of adverse noncancer health effects.
- Five of the leaching chemicals are currently listed by the State of California (OEHHA, 2005b) as carcinogens by the oral route.
- The acute ingestion of 10 grams of tire rubber by a 15 kg three year old child is associated with a  $3.7 \times 10^{-8}$  increased risk of cancer, based on the experimental results reported here; this is below the *di minimis* risk level of  $1 \times 10^{-6}$ , generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006).

# Chapter 7: Evaluation of Toxicity Due to Chronic Hand-To-Mouth Behavior Based on OEHHA Wipe Sampling of Playground Surfaces

## Exposure model

Figure 1 shows our model for estimating child exposure to toxicants released by unitary playground surfaces made of recycled tires. As discussed earlier in this report, unitary surfaces are solid surfaces that cannot be put into the mouth and ingested, unlike tire shreds. This eliminates the route of intentional ingestion (not shown in Figure 1). Since the playgrounds that are the subjects of this report are outdoors, we considered that any VOCs and sVOCs volatilizing from the rubber surfaces or fine particles becoming resuspended would enter the atmosphere and quickly disperse, precluding the inhalation of significant amounts by children. Thus, we did not consider the inhalation route in estimating exposure, nor did we measure VOCs released by these rubberized surfaces. Dermal uptake was estimated to be much less than incidental ingestion (hand-to-mouth), for reasons discussed in detail below. This left the route of incidental ingestion (hand-to-mouth) as the relevant route of exposure. This route is discussed in detail below.

Figure 1. Exposure model for children using rubberized playground surfaces



(courtesy of Chuck Salocks of OEHHA).

## Measuring the concentration of dislodgeable toxicants on the playground surface

To measure the chemicals that might be transferred to a child's hand through contact with a unitary playground surface made of recycled waste tires, the following wipe sampling study was performed by OEHHA. The protocol is modified from the US EPA (2003a) protocol used to wipe sample arsenic from CCA-treated wood. Polyester wipes (catalogue #TX1009) were purchased from ITW Texwipe (Upper Saddle River, New Jersey). These wipes are 9 inches by 9 inches and weigh approximately 8.3 grams. Prior to sampling, each wipe was put into a clean glass jar with 23 mls of distilled water (for metals or sVOCs) or isopropyl alcohol (for PAHs).

A cylindrical steel weight was kindly provided by Oakland Machine Works (Oakland, CA). It weighed 1.1 kg and had a surface at each end that was 8.26 cm in diameter. For each sample, the weight was wrapped in a clean disposable plastic bag and then wrapped with the wetted wipe. The weight was then dragged for twelve feet (366 cm) along a tape measure laid on the rubber or control surface. Dragging was then reversed without rotating the weight, and finally the dragging was done once more for a total of three passes along the same twelve foot path. The area wiped was 3021 cm<sup>2</sup>. The wipe was then returned to its glass jar. Clean nitrile gloves were used for each sample. Playground surfaces were sampled in duplicate per analyte class (metals, mercury, sVOCs, PAHs). Single field control wipes were performed on nearby sections of cement sidewalk. Two pour-in-place playground surfaces with bottom layers of recycled tires and top layers of EPDM were wipe tested. A single playground surface consisting of tiles made of 100% recycled tire rubber held together with a binder was also wipe sampled.

Samples were transported to Sequoia Analytical (Morgan Hill, CA) for analysis. The following methods were followed: calcium, iron, potassium and magnesium by EPA 6010B; mercury by EPA 7471A; all other metals by EPA 6020; sVOCs by EPA 8270C; PAHs by GCMS-SIM. Table 18 shows the chemicals that were detected in the wipe samples. Ten metals and six PAHs were detected. Another twelve metals and nine PAHs were not detected in any sample. In addition, no sVOCs were detected in any wipe sample.

**Table 18. Chemicals detected by wipe sampling three rubberized playground surfaces (A,B,C)<sup>1</sup>**

Chemical	Reporting limit	A	A (field control)	B	B (field control)	C	C (field control)
aluminum	2.0	91	75	-	-	370	330
antimony	1.0	2.8	4.2	155	220	170	170
barium	5.0	ND	ND	6.5	19	ND	ND
calcium	12	425	240	ND	ND	405	1300
copper	5.0	ND	ND	ND	6.3	ND	ND
iron	5.0	180	170	ND	ND	685	670
magnesium	2.5	78	58	ND	ND	210	220
mercury	0.005	ND	ND	ND	0.012	ND	ND

Chemical	Reporting limit	A	A (field control)	B	B (field control)	C	C (field control)
potassium	100	85	ND	ND	ND	145	120
zinc	10	ND	ND	73	66	105	26
benzo(b)-fluoranthene	0.10	0.13	ND	ND	ND	ND	ND
chrysene	0.10	0.25	ND	ND	ND	ND	ND
fluoranthene	0.10	0.25	ND	0.14	ND	0.1	ND
naphthalene	0.10	0.10	ND	ND	0.11	0.12	0.11
phenanthrene	0.10	0.14	0.10	ND	ND	0.25	ND
pyrene	0.10	0.39	0.10	0.28	ND	0.36	0.11

<sup>†</sup> All values are in µg/wipe. Playground surface values are averages of two duplicate wipes. Field control values are from single wipes. Surfaces A and B were pour-in-place with a top layer of EPDM. Surface C consisted of tiles that were 100% recycled tire rubber. ND = not detected.

**Surface A** data reported in Appendix B in Work Orders MOF0403 (rubber wipe samples A, B, D, E, G, H, J, K; background wipe samples C, F, I, L) and MOI0327 (rubber wipe samples UC1, UC2; background wipe sample UC3).

**Surface B** data reported in Appendix B in Work Orders MOF0623 (rubber wipe samples A, B, D, E, G, H, J, K; background wipe samples C, F, I, L) and MOI0327 (rubber wipe samples EC1, EC2; background wipe sample EC3).

**Surface C** data reported in Appendix B in Work Order MOF0858 (rubber wipe samples A, B, D, E, G, H, J, K; background wipe samples C, F, I, L) and MOI0327 (rubber wipe samples GR1, GR2; background wipe sample GR3).

## Results

Five chemicals in the above table were detected at levels that were at least three times the field control, or if the field control was a nondetect (ND), at least three times one-half the reporting limit. Multiplying the reporting limit by a factor of three has been recommended for setting the minimum level of quantitation (US EPA, 2004). One metal (zinc) and four PAHs (chrysene, fluoranthene, phenanthrene, pyrene) fell into these two categories. Therefore, the potential toxicity of these chemicals was evaluated.

The duplicate wipes of playground surface C gave an average zinc value of 105 µg/wipe, that was at least 3-fold higher than the field control wipe (26 µg/wipe). This surface was made of tiles composed of 100% shredded tire rubber held together with a binder. Zinc was not detected on pour-in-place surface A, and was only slightly above the field control for pour-in-place surface B. Both surfaces A and B had top layers of EPDM above a bottom layer of recycled tire rubber. A possible explanation for these findings is that the EPDM layer acted as a barrier to tire-derived zinc. This finding of zinc by wipe testing the tiles made of 100% recycled tire rubber is in good agreement with the results of the gastric digestion experiment. Digestion of shredded tire rubber identified zinc as the chemical released in the highest amount: 130 µg of zinc per gram of tire rubber (Table 14). Thus, it may not be surprising that zinc was identified by wipe sampling. As

discussed earlier, zinc oxide is used as an activator in the rubber vulcanization process (CIWMB, 1996).

From among the four PAHs that were evaluated, chrysene and fluoranthene were detected on playground surface A, phenanthrene on playground surface C, and pyrene on all three playground surfaces. These PAHs are all products of combustion, and are present in the exhaust from gasoline and diesel engines, as well as on barbecued foods. We were not able to determine whether the PAHs detected on the wipes originated from the rubber playground surface itself, or from automobile/truck exhaust fumes followed by atmospheric deposition onto the playground.

This toxicity evaluation uses the wipe values as surrogates for the amounts of chemicals a child would pick up on its hands after touching the playground surface. Therefore, since the wipe procedure sampled an area of playground surface equal to 3,021 cm<sup>2</sup>, then the dislodgeable chemicals that can be transferred to a child's hands are estimated to be:

- Zinc = 105 µg/3021 cm<sup>2</sup> = 34.8 ng/cm<sup>2</sup>
- Chrysene = 0.25 µg/3021 cm<sup>2</sup> = 0.0828 ng/cm<sup>2</sup>
- Fluoranthene = 0.25 µg/3021 cm<sup>2</sup> = 0.0828 ng/cm<sup>2</sup>
- Phenanthrene = 0.25 µg/3021 cm<sup>2</sup> = 0.0828 ng/cm<sup>2</sup>
- Pyrene = 0.39 µg/3021 cm<sup>2</sup> = 0.129 ng/cm<sup>2</sup>

#### **Estimating the child's body surface area that contacts the playground surface and from which toxicants can be transferred to the mouth**

Since unitary rubber playground surfaces are solid surfaces that cannot be picked up by a child and put into its mouth, hands touching the surface and then put into the mouth is considered the pertinent route by which dislodgeable residues could be ingested. Hand-to-mouth activity, a subset of the category often called nondietary or incidental ingestion, is an important route of child exposure to environmental contaminants (Hubal et al., 2000; Zartarian et al., 2000). The surface area of a three year old child's hands is approximately 400 cm<sup>2</sup> (50<sup>th</sup> percentile value), comprising approximately six percent of the total body surface area (US EPA, 2002).

However, less than 100 percent of the hand's surface area would be expected to contact the rubber surface. A maximum value of 50 percent was estimated to be the fraction of the hand's surface area that is available to pick up a toxicant from a contaminated surface (Zartarian et al., 2000). However, using modeling techniques this same study found that less of a child's hand (5 to 30 percent corresponding to 10 to 60 cm<sup>2</sup>) contacts the mouth per mouthing event. The US EPA (2001) recommends the use of 20 cm<sup>2</sup> per mouthing event, which falls within the range specified in the Zartarian et al. (2000) study. Therefore, this toxicity evaluation uses a value of 20 cm<sup>2</sup> as the area of the child's hand that transfers dislodgeable toxicants from a playground surface to the child's mouth.

#### **Estimating the frequency of hand-to-playground surface contact**

No data were found on the frequency of child hand-to-playground surface contact, and only limited data were located on the frequency of hand-to-floor contact. The data in Table 19 below show that the hand-to-floor data come primarily from children engaged in indoor activities. However, playground behavior encompasses outdoor activities. Unfortunately, there is poor agreement between the two studies that observed children

outdoors, with AuYeung et al. (2004a) reporting a hand-to-floor contact rate of 27/hour and Freeman et al. (2005) reporting a rate of 3/hr. Due to the dearth of data on hand-to-floor contact rates, the four values from the studies shown in the bottom three rows of Table 19 were averaged ( $40 + 21 + 3 + 27$ ) to give 23 contacts per hour. The data from Freeman et al. (2001) were not included since only a single child was observed per age group. Therefore, this toxicity evaluation will use 23 hand-to-playground surface contacts per hour for a three year old.

**Table 19. Hand-to-floor contact rates for children**

Study	Age and number of children (n)	Child mobility and setting	Hand-to-floor contacts
Freeman et al. (2001)	6 year old female (n=1)	Walker, indoors	5/hr
	8 year old female (n=1)	Walker, indoors	1/hr
Beamer et al. (2004)	6 and 24 months (n=11)	Walkers, mostly indoors	Mean = 40/hr
Freeman et al. (2005)	7-53 months (n=68)	Infants + toddlers, indoors	Median = 21/hr
		Infants + toddlers, outdoors	Median = 3/hr
AuYeung et al. (2004a)	1-6 years (n=38)	Mostly outdoors	Median = 27

### Estimating the frequency of hand-to-mouth activity

To estimate the frequency at which a child might transfer a dislodgeable toxicant from a rubber playground surface to its mouth, studies were located on the rate of hand-to-mouth activity. Such studies used direct observation or videotape analysis of children engaged in various activities, both indoors and outdoors. Table 20 shows the results of those studies.

**Table 20. Frequency of hand-to-mouth activity in children**

Study	Age and setting	Hourly hand-to-mouth contacts
US EPA, 2002	24-72 months, mostly indoors	Mean = 9
Tulve et al., 2002	10-60 months, indoors	Median = 11
AuYeung et al., 2004b	14-82 months, outdoors	Median = 8
Black et al., 2004	7-53 months, outdoors	Median = 5

The US EPA, in their Child-Specific Exposure Factors Handbook (US EPA, 2002), recommends the use of 9 contacts per hour for the frequency of hand-to-mouth activity in children age 24 to 72 months. This value is based mostly on data from children observed indoors. However, the playground is an outdoor environment, and children playing outdoors exhibited 2 to 3-fold less hand-to-mouth behavior than those playing indoors (AuYeung et al., 2004b; Black et al., 2004). Two recent studies in Table 20 provide

hand-to-mouth frequency data for children in outdoor environments: AuYeung et al (2004b) and Black et al. (2004). Using these two studies OEHHA calculates that 7 hand-to-mouth contacts per hour  $[(5 + 8) \div 2 = 7]$  represents the best available value for a three year old child playing outdoors. Therefore, we have used the value of 7 hand-to-mouth contacts per hour in the following calculations.

### **Estimating the efficiency of transfer of toxicants from the child's hand to the mouth**

Measurements of transfer efficiency (a.k.a. saliva removal efficiency) have been made for the transfer of pesticides and soil from the hands of children to their mouths. Maximum transfer efficiencies of 50 percent and 16 percent were measured for pesticides and soil, respectively (Zartarian et al., 2000). The lower value for soil may be related to a lower propensity of a child to extensively suck dirty hands compared to hands bearing a relatively tasteless and invisible chemical. In a more recent study the transfer of riboflavin from the hand to the mouth was measured in college-age volunteers (Cohen Hubal et al., 2005). The highest rate of transfer for a single mouthing event was 34 percent; however, the measured values were highly variable and often much lower. US EPA (2001) uses a standard value of 50 percent for hand-to-mouth transfer efficiency. Therefore, considering these data, this toxicity evaluation uses the value of 50 percent for the efficiency by which dislodgeable toxicants might be transferred from a child's hand to its mouth, thereby becoming ingested.

### **Estimating dermal loading**

The amount of toxicant accumulating on a child's hand as a result of touching a contaminated surface has been termed dermal loading, and is a prerequisite for estimating the amount of a toxicant that can be ingested through hand-to-surface-to-mouth activity. Dermal loading in this situation depends on how often the child touches the playground surface, how often it touches its mouth, the amount of a toxicant that is transferred from the surface to the hand at each contact, and the amount transferred to the mouth at each contact. Table 21 shows these parameters, all of which were discussed above.

**Table 21. Factors considered in estimating dermal loading**

Parameter	Variable measured	Value	Reference
Hand-to-surface	Frequency	23/hr	Beamer et al., 2004; Freeman et al. 2005; AuYeung et al. 2004a
Hand-to-mouth	Frequency	7/hr	AuYeung et al., 2004b; Black et al., 2004
Surface-to-hand	Amount of toxicant transferred	Wipe measurements in Table 15	This study
Hand-to-mouth	Transfer efficiency	50%	US EPA, 2001
Length of playground visit	time	2 hr (see below)	Gallup Organization (2003)

Assuming that 3 (23/7) hand-to-playground surface contacts occur between each hand-to-mouth contact, and 50 percent of the toxicant transfers from the hand to the mouth at each contact, then the amount of dermal loading per cm<sup>2</sup> occurring between each hand-to-mouth contact approaches 6 times the wipe value; i.e., where x is the amount of chemical detected by wipe sampling per cm<sup>2</sup>, then dermal loading at each successive hand-to-mouth contact would be 3x, 4.5x, 5.25x, 5.625x, 5.8125x, etc. (this calculation also assumes that the efficiency of loading does not change with sequential playground surface contacts). Thus, a three year old is estimated to load each chemical on its hands to the following levels:

- Zinc = 34.8 ng/cm<sup>2</sup> X 6 = 209 ng/cm<sup>2</sup>
- Chrysene = 0.0828 ng/cm<sup>2</sup> X 6 = 0.5 ng/cm<sup>2</sup>
- Fluoranthene = 0.0828 ng/cm<sup>2</sup> X 6 = 0.5 ng/cm<sup>2</sup>
- Phenanthrene = 0.0828 ng/cm<sup>2</sup> X 6 = 0.5 ng/cm<sup>2</sup>
- Pyrene = 0.129 ng/cm<sup>2</sup> X 6 = 0.77 ng/cm<sup>2</sup>

### Estimating the time and frequency of playground use

Three studies were located that measured the time and/or frequency that children spent in the playground. Table 22 lists those studies and their findings.

**Table 22. Time and/or frequency of playground use**

Study	Age	Time and/or frequency of playground use
Bjorklid-Chu, 1977	1 to 15 years	“practically every day” for 56% of those surveyed
Air Resources Board, 1991	Under 12 years	An average of 49 minutes per day for those surveyed
Gallup Organization, 2003	3-12 years	1)Daily or several times a week for 29% of those surveyed. 2)At least 1-2 hours per visit for 52% of those surveyed.

Data on the frequency of playground use by American children are sparse. The study by Bjorklid-Chu (1977) was conducted in a modern housing development in Sweden. The other two studies were performed in the United States, with the Air Resources Board (1991) study being performed in California and the Gallup study being a national survey. While the frequency of playground use and time spent in the playground per visit are hard to know with precision given the above data, it is clear that a significant fraction of children visit a playground daily or multiple times per week, and a large fraction of those visits last on the order of one or more hours.

Thus, it seems justified to consider child exposure to potential playground surface contaminants as a chronic exposure scenario. More specifically, the data in the table suggest that a significant subset of users visits a playground daily, for at least two hours per visit. Therefore, these are the values we use in the subsequent calculations. US EPA

(2005) recently completed an exposure assessment for children contacting chromated copper arsenate(CCA)-treated wooden playsets, in which two hours/day was considered the mean time that children used these playsets, either in public playgrounds or at home.

### Estimating exposure due to dermal absorption

Some chemicals that become deposited on human skin are able to enter the body by passing through the skin. This rate of dermal absorption varies greatly, depending upon the chemical and body part. While hands are the body parts which participate in hand-to-mouth transfer of environmental contaminants, dermal absorption can potentially occur at any place on the body. Considering children using the playground, we believe that hands are the body parts likely to come into repeated contact with the rubberized surface. The amount of dermal loading on the hands is discussed above. It is also estimated above that 50 percent of a toxicant picked up on a child's hands would transfer to the mouth every 8.6 minutes (7 times per hour).

Thus, for dermal absorption from the hands to make a significant contribution to the amount of a toxicant entering a child's body, its rate should not be much less than this 50 percent/8.6 minutes value. Table 23 below shows dermal absorption rates for 20 chemicals, covering a wide range of molecular weights and structures. For example, 0.02 percent of the applied dermal dose of zinc was absorbed in 8.6 minutes. All rates of dermal absorption were less than 1 percent/8.6 minutes except for 4,4'-methylene dianiline, which was 3.9 percent/8.6 minutes. Therefore, based on this survey of dermal absorption rates, we believe it unlikely that dermal absorption from the hands would contribute significantly to the amount of toxicant entering a child's body, due to the much higher rate of ingestion resulting from hand-to-mouth activity. Therefore, we will not calculate exposure via dermal absorption.

**Table 23. Dermal absorption rates of 20 chemicals found in published studies<sup>1</sup>**

Study	Species	Chemical	Dermal absorption <sup>2</sup>
Aoyama et al., 1986	human	tobramycin	0.21
Shah et al., 1987	rat	carbofuran	0.04
Agren, 1990	human	zinc	0.02
Agren et al., 1991	rat	zinc	0.02
Koizumi, 1991	rat	hexachlorobenzene	0.02
VanRooij et al., 1993	human	pyrene (a PAH)	0.57
Brunmark et al., 1995	human	4,4'-methylene dianiline	3.9
Moody et al., 1995	human	Benzo[a]pyrene	0.1
Timchalk et al., 1998	human	ortho-phenylphenol	0.74
Flarend et al., 2001	human	aluminum	<0.025
Qiao and Riviere, 2002	pig	pentachlorophenol	0.04
Meuling et al., 2004	human	chlorpyrifos	0.12
US EPA, 1992	pig	Caffeine	0.06

Study	Species	Chemical	Dermal absorption <sup>2</sup>
"	"	Benzoic acid	0.06
"	"	N,N-dimethyl-m-toluamide	0.02
"	"	Fluocinolone acetonide	0.01
"	"	Malathion	0.01
"	"	Parathion	0.04
"	"	Testosterone	0.01
"	"	Lindane	0.02
"	"	Progesterone	0.02

<sup>1</sup> All studies were performed *in vivo* except for the US EPA study which was performed *ex vivo*.

<sup>2</sup> Percent of applied dose entering the skin per 8.6 minutes.

#### **Calculating exposure via hand-to-mouth activity**

Using zinc as an example, the mass of ingested zinc was calculated as follows:

hand loaded zinc concentration ( $\mu\text{g}/\text{cm}^2$ ) **X** hand surface area transferring zinc to mouth ( $\text{cm}^2/\text{hand-to-mouth event}$ ) **X** total events (hand-to-mouth events/day) **X** hand-to-mouth transfer efficiency (dimensionless) =

$$0.209 \mu\text{g}/\text{cm}^2 \text{ X } 20 \text{ cm}^2/\text{event} \text{ X } 14 \text{ events}/\text{day} \text{ X } 0.5 = 29.3 \mu\text{g}/\text{day}$$

For a 15 kg child the ingested zinc dose would be 1.95  $\mu\text{g}/\text{kg}\text{-day}$

**Table 24. Estimated exposures from hand-to-mouth activity in a 15 kg three year old child at a playground where rubberized surfaces are present**

Chemical	Exposures
Zinc	1.95 $\mu\text{g}/\text{kg}\text{-d}$
Chrysene	0.005 $\mu\text{g}/\text{kg}\text{-d}$
Fluoranthene	0.005 $\mu\text{g}/\text{kg}\text{-d}$
Phenanthrene	0.005 $\mu\text{g}/\text{kg}\text{-d}$
Pyrene	0.007 $\mu\text{g}/\text{kg}\text{-d}$

The dose levels of ingested chemicals presented in Table 24 are due to contact with tire-derived playground surfaces. For comparison, Table 10 shows the average daily intakes resulting from the presence of these chemicals in food, water and air. In many cases these average daily intakes are rough estimates. Nonetheless, it is useful to compare the tire-derived levels in Table 24 to the average daily intakes. Average daily intakes were located for all five chemicals listed in Table 24. For zinc, chrysene and phenanthrene the average daily intake equals or exceeds the tire-derived exposure. Only for fluoranthene and pyrene does the tire-derived exposure exceed the average daily intake. This indicates

that particular care should be taken when comparing the tire-derived exposures to these chemicals to their corresponding health-based screening levels.

**Comparison of playground chemical exposure to screening levels: noncarcinogenic effects**

Table 25 below shows a comparison of the zinc exposure value for children using playground surfaces to screening values for subchronic and chronic zinc ingestion, and to its recommended daily dietary allowance (RDA). Chronic screening values were also located for the two PAHs, fluoranthene and pyrene, so that comparisons could be made to the chronic exposure values.

**Zinc**

The subchronic and chronic zinc screening values are based on the same study by Yadrick et al. (1989) in which healthy adult females were given zinc to supplement their normal diets for a period of ten weeks. The lowest observed adverse effects level (LOAEL, 0.83 mg/kg-day) was based on decreased red blood cell superoxide dismutase, hematocrit and serum ferritin. There was no NOAEL. Application of an uncertainty factor of 3 (for use of a minimal LOAEL and intrahuman variability) to the LOAEL yielded a subchronic MRL (ATSDR, 2003b) and a chronic RfD (IRIS, 1992) of 0.3 mg/kg-day. Since the zinc exposure is less than the MRL and RfD, subchronic and chronic health effects are not expected. This conclusion is supported by the RDA for zinc, also shown in Table 25. The RDA was developed for children 1-3 years old. It is slightly lower than the MRL and RfD, reflecting the importance of zinc in the human diet. The RDA is 100-fold greater than the exposure due to contact with the playground surface, suggesting that adverse health effects would not occur.

**Fluoranthene and pyrene**

In the case of fluoranthene, the exposure value is 8,000-fold lower than the RfD, which is based on nephropathy, increased liver weights, hematological changes and clinical signs in mice (Table 7). The calculated exposure to pyrene is 4,286-fold lower than the RfD, based on kidney effects in mice (Table 7). Thus, adverse health effects are not expected due to exposure to fluoranthene and pyrene. The absence of screening values for chrysene and phenanthrene makes it difficult to draw conclusions about those exposures, although the large margins of safety for the structurally related PAHs fluoranthene and pyrene suggest that exposure to similar dose levels of chrysene and phenanthrene would also be without health effects.

**Table 25. Playground-associated chemical exposures and associated noncancer screening values**

Chemical	Calculated ingested dose <sup>1</sup>	Noncancer screening value
Zinc	1.95 µg/kg-day	Intermediate MRL = 300 µg/kg-day (ATSDR, 2003b)
“	“	Chronic RfD = 300 µg/kg-day (IRIS, 1992)
“	“	RDA* = 200 µg/kg-day (The National Academies, 2001)

Chemical	Calculated ingested dose <sup>1</sup>	Noncancer screening value
Chrysene	0.005 µg/kg-day	None located
Fluoranthene	0.005 µg/kg-day	Chronic RfD = 40 µg/kg-d (IRIS, 1990b)
Phenanthrene	0.005 µg/kg-day	None located
Pyrene	0.007 µg/kg-day	Chronic RfD = 30 µg/kg-day (IRIS, 1991b)

<sup>1</sup> From Table 24

\* Normalized for a 15 kg child

MRL = minimal risk level; RfD = reference dose; RDA = recommended dietary allowance

### ***Risk characterization for noncancer effects***

#### ***Uncertainties that would increase exposure***

- Eating in the playground would tend to increase the transfer of toxicants from the surface of the hands to the food and into the mouth (Cohen Hubal et al., 2000; Black et al., 2004).
- Going barefoot in the playground would increase non-dietary ingestion in those children that exhibit toes-to-mouth activity (Freeman et al., 2001).
- Toxicants loaded onto the hands would be subject to hand-to-mouth transfer after the child had left the playground, unless its hands were washed.
- Objects that contact the playground surface and then are put into the child's mouth would increase non-dietary ingestion.

#### **Uncertainties that would decrease exposure**

- The transfer efficiency from a surface to the hand decreased with increasing number of hand-to-surface contacts (Cohen Hubal et al, 2005), and the loading of Cr, Cu and As onto children's hands did not increase with time (Hamula et al., 2006), both suggesting a saturation for loading.
- Hand-to-mouth events are often clustered, with few or no intervening hand-to-floor events (Ross, 2005). This suggests that hands become "fully loaded" for only a fraction of the total hand-to-mouth contacts.
- Some toxicants may be transferred from the child's hand to surfaces other than the child's mouth, such as playground equipment or clothes. This would decrease the amount transferred into the mouth.
- The duration of mouthing at each hand-to-mouth contact may decrease with increasing child age, leading to less toxicant transfer from the hands to the mouth (Cohen Hubal et al., 2000); however, at least one study suggests that mouthing times do not decrease between 1-3 months and 5 years of age (Dept. of Trade and Industry (UK), 2002).

- A bioavailability of 100 percent has been assumed for each chemical. It is likely that the true values are less, but this assumption represents a public health upper bound in the absence of empirical data.
- For the two hours per day a child is estimated to spend in the playground, it would be on the rubber surface for only a fraction of the total time.

## Zinc

In the Table 25 above, both the subchronic MRL and chronic RfD of 0.3 mg/kg-day for zinc were based on the same study by Yadrick et al. (1989), showing decreased red cell superoxide dismutase (SOD) activity (a copper-requiring enzyme), hematocrit and serum ferritin in human females dosed daily for 10 weeks. These effects were probably due to zinc-induced changes in the copper and iron balance, causing the above-mentioned hematological effects to develop towards the end of the study (IRIS, 1992). Thus, zinc supplementation acted as an inducer of copper and iron deficiency.

Similar hematological changes have been observed in subchronic studies performed in the rat, mouse, rabbit, cow and ferret, in which the animals' diets were supplemented with zinc either via the food or water (ATSDR, 2003b). Also, another subchronic study in humans identified a LOAEL based on reduced red cell SOD (Fischer et al., 1984). Lastly, a chronic study of zinc supplementation in the elderly identified a LOAEL based on reduced red blood cells (Hale et al., 1988). Thus, in a range of mammalian species, excess zinc caused hematological changes consistent with iron and copper deficiency, as might result from a competition between zinc and these cations. Therefore, these findings support the use of the MRL/RfD of 300 µg/kg-day for evaluating whether zinc-induced health effects would occur in children contacting rubberized playground surfaces.

Chronic ingestion of excess zinc is not considered to be carcinogenic by the ATSDR (2003b), while IRIS (1992) classifies zinc into Group D: not classifiable as to human carcinogenicity. Therefore, the zinc subchronic MRL and chronic RfD are the appropriate reference values for evaluating chronic oral exposures.

## Fluoranthene

The chronic RfD for fluoranthene is based on a 13 week study in mice gavaged daily with 0, 125, 250 or 500 mg/kg-d (IRIS, 1990b). At the two highest dose levels the animals exhibited a variety of adverse effects including increased serum alanine transaminase, kidney and liver pathology, increased clinical signs and hematological changes. Therefore, the NOAEL was 125 mg/kg-d. The following uncertainty factors were selected by IRIS: 10 for interspecies extrapolation, 10 for intraspecies variability and 30 for both subchronic to chronic extrapolation and a lack of reproductive/developmental data. Applying these uncertainty factors to the NOAEL yielded a chronic RfD of 40 µg/kg-d.

Carcinogenicity studies of fluoranthene (mostly via the dermal route) have also been performed in mice. Most have been negative with regard to tumor induction (IRIS, 1990b). However, these data were judged inadequate for determining the carcinogenicity. In addition, most studies in both mammalian cells and bacteria found that fluoranthene was not mutagenic (IRIS, 1990b). Thus, the RfD for fluoranthene shown in the table is the appropriate screening value for evaluating its long-term health effects.

## Pyrene

The chronic RfD for pyrene is based on a 13 week study in mice gavaged daily with 0, 75, 125 or 250 mg/kg-d (IRIS, 1991b). At the two highest dose levels the animals exhibited mild kidney lesions and reduced kidney weights. Therefore, the NOAEL was 75 mg/kg-d. The following uncertainty factors were chosen by IRIS: 10 for interspecies extrapolation, 10 for intraspecies variability, 10 for subchronic to chronic extrapolation, and 3 for both the lack of data from other species and the lack of reproductive/developmental data. Applying the uncertainty factors to the NOAEL yielded a chronic RfD of 30 µg/kg-d.

Pyrene did not induce tumors in mouse studies (intraperitoneal injection and dermal routes), however, the data were considered inadequate for judging this chemical's carcinogenicity (IRIS, 1991b). Most studies in mammalian cells and bacteria indicated that pyrene was not mutagenic (IRIS, 1991b). Thus, the RfD for pyrene shown in the table is the appropriate screening value for evaluating its long-term health effects.

### Estimating the increased cancer risk

From among the five chemicals identified by wipe sampling rubber playground surfaces, chrysene is currently listed as an oral carcinogen by the State of California (OEHHA, 2005). US EPA (2003c) draft methodology was followed to quantify the increased cancer risk to a child using these surfaces.

As discussed above in the section entitled "Estimating the frequency of playground use", survey data support the assumption that a significant percentage of children use playgrounds daily, although the data do not provide information as to how many years a child can be expected to use playgrounds. Thus, in order to calculate the cancer risk, estimates must be made as to when a child starts and stops using playgrounds. We believe it is reasonable to assume children start to use playgrounds with impact-attenuating surfaces at the time they begin to walk.

Prior to the walking stage, it is unlikely that a crawling child could access the equipment found in playgrounds such as rockers, slides, swings and climbers. It is well established that most children begin walking between the ages of 12 and 18 months (Bayley, 1936; Cratty, 1979; Bottos et al., 1989; Adolph et al., 1998). Therefore, we will consider 12 months as the age at which some children begin using these playgrounds. However, it should be kept in mind that should a child in the crawling stage have access to one of these surfaces, its exposure could be much higher due to a much higher hand-to-playground surface contact rate in crawlers compared to walkers.

The age at which most children stop using playgrounds is not well defined. We have not located any data addressing this question. Therefore, we will use the age of twelve years, which corresponds to the age when most children enter junior high school, where the playgrounds of elementary school are replaced by basketball courts, tennis courts, etc. This age range of 1 to 12 years is similar to the range of 1 to 13 years recently used as one of the target populations in an exposure assessment for children using playsets and decks made of CCA-treated wood (US EPA, 2005).

In the section above entitled "Estimating the frequency of playground use", it was concluded that a significant fraction of children use playgrounds daily. However, this is different from saying that a child uses a playground every day of the year. Obviously, on many days the weather could prevent playground use. Also, a child would not be expected to use the playground when sick. Recently, it was estimated that children

between the ages of one and six use public playgrounds an average of 185 days out of the year (US EPA, 2005). Therefore, this value has been applied to children between the ages of one and twelve in the cancer risk calculations presented below.

Table 26 below shows the values used to estimate the increased cancer risk to a child resulting from eleven years of hand-to-mouth activity in playgrounds with rubberized surfaces. The calculations follow the US EPA (2003c) draft methodology for assessing the cancer risk from exposures in childhood. The total increased risk of  $2.9 \times 10^{-6}$  is above the benchmark value of  $1 \times 10^{-6}$ , usually considered the maximum acceptable value for increased cancer risk.

**Table 26. Estimated increased cancer risk from exposure to chrysene via hand-to-mouth activity in a child (ages 1-12) frequenting a playground with a rubberized surface**

Age	Dose <sup>(1)</sup> in mg/kg-d	Cancer Slope Factor <sup>(2)</sup> in (mg/kg-d) <sup>-1</sup>	Duration of use normalized to 70 yr lifetime <sup>(3)</sup>	Days of playground use per year <sup>(4)</sup>	Safety Factor <sup>(5)</sup>	Increased cancer risk <sup>(6)</sup>
1-2 years	5 x 10 <sup>-6</sup>	2.0	1 yr/70 yrs	185 days/ 365 days	10	0.7 x 10 <sup>-6</sup>
2-12 years	5 x 10 <sup>-6</sup>	2.0	10 yrs/70 yrs	185 days/ 365 days	3	2.2 x 10 <sup>-6</sup>
Total increased cancer risk <sup>(7)</sup>						2.9 x 10 <sup>-6</sup>

<sup>(1)</sup>From Table 24.

<sup>(2)</sup>Available at [www.oehha.ca.gov/prop65/law/pdf\\_zip/6pahnsr162104.pdf](http://www.oehha.ca.gov/prop65/law/pdf_zip/6pahnsr162104.pdf)

<sup>(3)</sup>Estimated durations of playground use normalized to 70 year lifetime.

<sup>(4)</sup>Days in the year that included “public playset time” (US EPA, 2005).

<sup>(5)</sup>Safety factor for the increased sensitivity of a 0-2 year old (SF = 10) or 2-15 year old (SF = 3) child to some carcinogens (US EPA, 2003c).

<sup>(6)</sup>Calculated by multiplying columns 2, 3, 4, 5 and 6 according to US EPA (2003c) draft methodology.

<sup>(7)</sup>Calculated by adding the two individual increased cancer risks for the two age groups (US EPA, 2003c).

## ***Discussion of the increased cancer risk***

### ***Uncertainties that would increase exposure***

- Were a child in the crawling stage to use these surfaces, its exposure from hand-to-floor-to-mouth activity would be greater than that of a child of walking age.
- Use of the rubberized playground surfaces may continue past the age of 12.
- Eating in the playground would tend to increase the transfer of toxicants from the surface of the hands to the food and into the mouth (Cohen Hubal et al., 2000; Black et al., 2004).
- Going barefoot in the playground would increase non-dietary ingestion in those children that exhibit toes-to-mouth activity (Freeman et al., 2001).
- Toxicants loaded onto the hands would be subject to hand-to-mouth transfer after the child had left the playground, unless its hands were washed.
- Objects that contact the playground surface and then are put into the child’s mouth would increase non-dietary ingestion.

## Uncertainties that would decrease exposure

- The data on hand-to-floor contact rates presented in Table 19 above suggest that this rate decreases as the child grows older. While this toxicity evaluation uses a rate of 23 hand-to-floor contacts per 2 hours for a three year old child, it is likely that this rate is substantially less for at least the age range six through twelve. This would lead to a substantially decreased transfer of toxicants from the playground surface to the child's mouth during the second half of the proposed exposure period.
- Almost no data were located on the hand-to-mouth contact rates for adults, or for children older than six. Common experience tells us that this rate decreases as the child grows older, as discussed above for the hand-to-floor contact rate. Consequently, the transfer of toxicants from the playground surface to the mouth is most likely substantially less during the second half of the proposed exposure period, from ages six to twelve.
- The transfer efficiency from a surface to the hand decreased with increasing number of hand-to-surface contacts (Cohen Hubal et al, 2005), and the loading of Cr, Cu and As onto children's hands did not increase with time (Hamula et al., 2006), both suggesting a saturation for loading.
- Hand-to-mouth events are often clustered, with few or no intervening hand-to-floor events (Ross, 2005). This suggests that hands become "fully loaded" for only a fraction of the total hand-to-mouth contacts.
- Some toxicants may be transferred from the child's hand to surfaces other than the child's mouth, such as playground equipment or clothes. This would decrease the amount transferred into the mouth.
- The duration of mouthing at each hand-to-mouth contact may decrease with increasing child age, leading to less toxicant transfer from the hands to the mouth (Cohen Hubal et al., 2000); however, at least one study suggests that mouthing times do not decrease between 1-3 months and 5 years of age (Dept. of Trade and Industry (UK), 2002).
- A bioavailability of 100 percent has been assumed for each chemical. It is likely that the true values are less, but this assumption represents a public health upper bound in the absence of empirical data.
- For the two hours per day a child is estimated to spend in the playground, it would be on the rubber surface for only a fraction of the total time.

As enumerated above, there are many uncertainties associated with the exposure calculations. Some tend to increase the dose and therefore risk levels, while others decrease it. Another area of uncertainty to be considered is whether the chrysene measured on the surface of playground A originated from the rubber surface or resulted from atmospheric deposition. Referring to Table 18, two of three playground surfaces yielded chrysene values that were indistinguishable from field control wipes (all below the reporting limit).

These results, coupled with the finding that playground surface A yielded a wipe value for chrysene that was only 2.5 times the reporting limit (Table 18), indicate that more wipe tests should be performed on additional rubberized surfaces to determine if these surfaces consistently yield elevated levels of dislodgeable chrysene relative to field

controls. Seen in this light, the data collected from these playground surfaces suggest that if chrysene is elevated on these surfaces, regardless of its origin, the magnitude of the increase over background is small, and may occur only in a minority of playgrounds. In this regard, the wipes of the rubberized surfaces were always much dirtier than the control wipes performed on adjacent sidewalks, suggesting that the rubberized surfaces trap dirt more efficiently than concrete. If they also trap PAHs more efficiently, this might explain the increased PAH levels on wipes of the rubber surfaces.

The Cancer Slope Factor for chrysene shown in Table 26 was developed from intraperitoneal injection studies in neonatal mice, using an oral equivalent potency approach (OEHHA, 2004c). This approach first calculates the ratio of the potency of benzo[a]pyrene determined in the adult mouse by the oral route to that determined in the neonatal mouse by the intraperitoneal injection route. Then this ratio is applied to the neonatal intraperitoneal injection potency of chrysene, yielding the adult oral potency for chrysene used here.

Thus, it should be kept in mind that the Cancer Slope Factor for chrysene used here has its basis in intraperitoneal injection studies with neonatal mice. Those studies were performed with chrysene dissolved in DMSO, due to its very low solubility in water. Thus, its absorption from the intraperitoneal space in the carcinogenicity studies may differ from its absorption following ingestion due to hand-to-mouth activity in children (where DMSO is not used as a vehicle). These factors must be considered sources of uncertainty in applying the adult oral Cancer Slope Factor for chrysene to exposures in the playground.

Considering the uncertainty associated with both the exposure value and the Cancer Slope Factor for chrysene, the  $2.9 \times 10^{-6}$ -fold increased cancer risk calculated here could be either higher or lower than the true value. In addition, this relatively small increased cancer risk should be weighed against the beneficial impact-mitigating properties of rubberized surfaces, discussed elsewhere in this report.

## Conclusions

- Wipe sampling of tire-derived playground surfaces was performed to measure the amounts of dislodgeable chemicals subject to ingestion through child hand-to-surface-to-mouth activity.
- Ten metals and six PAHs were identified, with five at levels that were at least 3-fold above background: zinc, chrysene, fluoranthene, phenanthrene and pyrene.
- Chronic exposure assessment was performed for the five chemicals using published values for child hand surface area, hand-to-floor contact rate, hand-to-mouth contact rate, saliva removal efficiency, and frequency of playground use; this exposure assessment was associated with large degrees of uncertainty, some of which could increase exposure and some decrease exposure.
- The exposure values were then compared to the corresponding chronic health-based screening values; all exposures were below the corresponding screening levels, suggesting a low risk of adverse noncancer health effects.
- Chrysene was the only chemical from among the five listed above that was identified as a carcinogen by the State of California (OEHHA, 2005b).

- Assuming playground use from ages one through twelve, a total increased cancer risk of  $2.9 \times 10^{-6}$  was calculated due to the chronic ingestion of chrysene via hand-to-surface-to-mouth activity on rubberized playground surfaces. This risk is slightly higher than the benchmark of  $1 \times 10^{-6}$ , generally considered an acceptable cancer risk due to its small magnitude compared to the overall cancer rate (OEHHA, 2006).
- The calculation of cancer risk due to chrysene was associated with additional areas of uncertainty, regarding both the years of playground use during childhood, and whether the low levels of PAHs (including chrysene) on playground surfaces originate from the rubber surface itself or from atmospheric deposition.

# Chapter 8: A First-Step Evaluation of High School Running Tracks Containing Recycled Tire Rubber: Wipe Testing and Customer Satisfaction Survey

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## Introduction and Methods

In addition to playgrounds, the CIWMB also provides funds for the installation of running tracks made of recycled tires. One method of track construction follows that used for playground surfaces; a bottom layer primarily (80%) of recycled tire shreds is poured together with a chemical binder. After the bottom layer hardens, a top layer of synthetic rubber particles called EPDM is poured together with more binder. To determine if such tracks release chemicals following dermal contact, one such track at a northern California high school (funded by the CIWMB) was wipe sampled according to the methodology described above for sampling playground surfaces. Wipe sampling was performed twice, on two separate days. The field control wipes were performed on a concrete apron surrounding the track. Wipes were analyzed for metals, sVOCs and PAHs.

To obtain a first impression of how these rubberized track surfaces are performing, a customer satisfaction survey was taken among the track coaches at high schools awarded CIWMB grants. From among some twenty high schools contacted, six track or cross country coaches were kind enough to discuss their thoughts on track performance, with special attention paid to injury rates and athletic performance.

## Wipe testing results and discussion

Table 27 shows the results of wipe sampling a high school track made of recycled tires. Metals from wipes of the track surface were below the values of the field control wipes. No sVOCs were detected. Five PAHs were detected at higher levels on the track compared to the field control (chrysene, fluoranthene, naphthalene, phenanthrene, pyrene). Pyrene was detected at the highest levels, with good agreement between the two sampling days (4.5 and 3.1  $\mu\text{g}/\text{wipe}$ ); however, the background field control wipes for pyrene varied almost 7-fold over the two sampling days. The PAH fluorene was detected on the field control wipe but not on the track wipes.

**Table 27. Chemicals detected on a track surface made of recycled tires.**

Date	Chemical	Reporting limit <sup>1</sup>	Track wipe <sup>1,2</sup>	Field control wipe <sup>1,3</sup>
6/27/05	Phenanthrene	0.82	1.7	ND
6/27/05	Pyrene	0.82	4.5	1.8
9/6/05	Chrysene	0.10	0.27	ND
9/6/05	Fluoranthene	0.10	0.43	0.11
9/6/05	Fluorene	0.10	ND	0.22

Date	Chemical	Reporting limit <sup>1</sup>	Track wipe <sup>1,2</sup>	Field control wipe <sup>1,3</sup>
9/6/05	Naphthalene	0.10	0.12	0.10
9/6/05	Phenanthrene	0.10	1.0	0.15
9/6/05	Pyrene	0.10	3.1	0.26

<sup>1</sup> All values in µg/wipe.

<sup>2</sup> Each value is an average of two wipe samples.

<sup>3</sup> Each value represents a single wipe sample.

Data reported in Appendix B in Work Order MOF0960 (track wipe samples A, B, D, E, G, H, J, K; background wipe samples C, F, I, L) and Work Order MOI0327 (track wipe samples SM1, SM2; background wipe sample SM3).

In the preceding section, toxicity evaluations were performed for chemicals that were at least 3-fold higher in playground surface wipes compared to field control wipes (with one-half the reporting limit used for nondetects). Four PAHs from the above Table 27 fall into this category: chrysene, fluoranthene, phenanthrene and pyrene; however, it should be noted that while pyrene from track wipes exceeded the control wipe by almost 12-fold on 9/6/05, the margin was only 2.5-fold on 6/27/05. The reasons for this variability are unknown. On both days the samples were collected early in the morning when the skies were overcast with the typical morning fog. One possible explanation is that the PAHs detected on the track and cement apron resulted from atmospheric deposition, rather than from the material comprising the surfaces. Numerous studies have shown that the soil concentrations of various PAHs are increased in the vicinity of busy roads.

A comparison of exposure to health-based screening values was not performed for the high school students using this track surface, since their exposure to these chemicals was considered minimal for the following reasons: 1) hand-to-surface activity followed by hand-to-mouth activity was not considered an important route of exposure for these teenagers, 2) unlike the use of playgrounds by children, the use of this high school track by teenagers was considered a seasonal rather than daily activity.

### Customer satisfaction survey

The six high school track and cross country coaches that comprise this survey were uniformly complimentary in their opinions of the new rubberized track surfaces compared to the old surfaces of cinders, dirt, or crushed stone. Most coaches felt their athletes suffered fewer injuries on the rubberized surfaces, with improved athletic performance. In addition, the coaches saw increased student participation on track teams, most likely due to the attractiveness and comfort of the rubberized surfaces. Community use of the tracks also increased. Lastly, some coaches mentioned the superior performance of the rubberized surfaces in foul weather compared to traditional track materials, leading to more training days per school year.

**Table 28. Track Coach Satisfaction Survey**

<b>Track #1</b>
<b>Date Installed:</b> unknown

<b>Previous Surface:</b> dirt
<b>Injury Effects:</b> unknown
<b>Athletic Performance:</b> more students have joined the track team-in the opinion of the coach, this is in large part due to the attractiveness of the new rubberized track
<b>Track #2</b>
<b>Date Installed:</b> in 2005
<b>Previous Surface:</b> clay and dirt
<b>Injury Effects:</b> fewer injuries in general compared to old track, fewer shin splints in particular
<b>Athletic Performance:</b> better athletic performance, including faster times; they can now train in foul weather; greater community use of the track
<b>Track #3</b>
<b>Date Installed:</b> October, 2003
<b>Previous Surface:</b> dirt and “granite fines”
<b>Injury Effects:</b> reduced shin splints especially in female distance runners
<b>Athletic Performance:</b> more students have joined the track team-in the opinion of the coach, this is in large part due to the attractiveness of the new rubberized track; the athletes can train harder and more often; there is increased usage of the track by people living in the neighborhood
<b>Track #4</b>
<b>Date Installed:</b> 2003
<b>Previous Surface:</b> crushed brick
<b>Injury Effects:</b> fewer injuries in general, fewer shin splints in particular
<b>Athletic Performance:</b> greatly improved times in the highly technical events, such as high hurdles
<b>Track #5</b>
<b>Date Installed:</b> 2004
<b>Previous Surface:</b> cinder, granite and sand
<b>Injury Effects:</b> dramatic decrease in shin splints and “runner’s knee”
<b>Athletic Performance:</b> the softer rubberized surface allows the cross country team to train on the track, with more interval training-as a result, times for the distance events have decreased
<b>Track #6</b>
<b>Date Installed:</b> 2005
<b>Previous Surface:</b> unknown
<b>Injury Effects:</b> unknown but coach expects fewer injuries
<b>Athletic Performance:</b> unknown but coach expects more students will participate on the track team

# Chapter 9: Skin Sensitization Testing of Rubberized Playground Surfacing

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## Introduction

Tires contain varying amounts of natural rubber, in addition to the more prevalent synthetic rubber called styrene-butadiene. Natural rubber contains latex, which can form allergenic proteins leading to hypersensitization in susceptible individuals. Sensitized individuals become extremely sensitive to subsequent contact with material carrying latex allergens. These latex complexes have caused mild to severe allergic responses from dermal contact and through inhalation. This purpose of this study was to determine the potential of the recycled tire product in playground surfaces to cause skin sensitization in a laboratory animal model.

No data were located on either the latex allergen content of tires, or skin sensitization by vulcanized tire rubber in dermally exposed humans or laboratory animals. More importantly for this contract, data are also lacking for playground surfaces made from recycled tires. Such surfaces could potentially cause contact skin sensitization via latex allergens, or other unidentified allergens. Therefore, to quantitatively assess the skin sensitization endpoint, a laboratory study was performed in which guinea pigs were dermally exposed to pieces of playground surfaces made from recycled tires. The guinea pig has served as an effective animal model for identifying human contact skin sensitizers (Robinson et al., 1989), including latex (Sugiura et al., 2002).

As mentioned above, the major type of rubber in tires is the synthetic polymer styrene-butadiene. Manufacturers often refer to a playground surface made of tire pieces as SBR (styrene-butadiene rubber). Most schools and towns in California that install playground surfaces of SBR choose to add a top layer of virgin, synthetic rubber called EPDM, which contains no latex allergens. The EPDM layer is installed over the SBR layer, either in the factory (tiles) or directly in the playground itself (pour-in-place), and provides an attractive, weather-resistant surface. A survey of CIWMB grantees (see above) showed that 86 percent of responders installed a pour-in-place SBR base layer covered by a pour-in-place EPDM top layer. A few installed rakeable crumb rubber (SBR only), tiles of SBR only, or tiles of SBR constructed with an EPDM top layer. Therefore, we performed skin sensitization testing using tiles of SBR, EPDM, and loose crumb rubber (SBR).

## Materials and Methods

Delayed skin sensitization testing was carried out by a modified Buehler method for solid materials according to testing guidelines (US EPA, 1998) and in accordance with Good Laboratory Practices at Product Safety Laboratories (Dayton, NJ). Guinea pigs were the test animals. The test samples were SBR tiles (Unity Surfacing, Hicksville, NY), EPDM tiles (All About Play, Sacramento, CA) and loose SBR crumb (West Coast Rubber Recycling, Gilroy, CA). All SBR was from recycled tires.

Skin sensitization testing consisted of three 6 hr induction exposures, each exposure separated by one week from the preceding exposure. All test samples were applied to the animals' skin. Then, after an additional two weeks, the animals were challenged with the test sample for 6 hrs and examined after 24 and 48 hours for signs of erythema (skin reddening). The negative control substance was high density polyethylene sheeting (TOLAS Health Care, Feasterville, PA), often used in medical packaging for its very low

incidence of allergic reaction. The positive control substance was alpha-Hexylcinnamaldehyde (HCA), a standard skin sensitizer. Additional controls included exposing animals to high density polyethylene for the induction exposure only, followed by challenge exposure to SBR or EPDM. The nine treatment groups are shown below:

<u>Group</u>	<u>Induction</u>	<u>Challenge</u>	<u># of animals</u>
1	HD polyethylene	HD polyethylene	10
2	HD polyethylene	SBR crumb	10
3	SBR crumb	SBR crumb	10
4	HD polyethylene	SBR tile	10
5	SBR tile	SBR tile	10
6	HD polyethylene	EPDM tile	10
7	EPDM tile	EPDM tile	10
8	HCA <sup>1</sup>	HCA	10
9	none	HCA	5

<sup>1</sup> alpha-Hexylcinnamaldehyde (positive control)

Initially, the animals in the positive control group (#8) failed to exhibit skin sensitization reactions following the challenge exposure. No animals in any other group showed sensitization reactions either. Therefore, all animals were re-challenged seven days after the first challenge, in exactly the same manner with the same samples. The results of this re-challenge are shown below in the Results section.

The scoring system for characterizing skin reactions was as follows:

- 0 no reaction
  - 0.5 very faint erythema, usually non-confluent<sup>1</sup>
  - 1 faint erythema, usually confluent
  - 2 moderate erythema
  - 3 severe erythema with or without reaction
- <sup>1</sup> not considered a positive reaction

## Results

A single animal in group #4 was euthanized for humane reasons on the second day of the test. There was no reason to believe that the morbidity observed in this animal was treatment related. All other animals displayed normal clinical signs, food consumption and weight gain for the duration of the test. No animal showed a positive skin reaction (skin score 1, 2 or 3) following any of the three induction doses. However, no positive reactions were observed after the challenge dose, including the positive control group. This made it necessary to re-challenge the animals seven days later. The need to re-challenge is common with this protocol (Buehler, 1994).

The skin reaction results from the re-challenge exposure are shown below. Fifty percent of the animals (5/10) in the positive control group (#8) showed positive skin reactions (skin score of 1, 2 or 3) at 24 hours after re-challenge, indicating that skin sensitization had occurred. These positive skin reactions persisted to 48 hrs after re-challenge in four of the five animals. Persistent skin reactions are hallmarks of skin sensitization (Buehler, 1994). No other treatment group contained any animal with a positive response. Thus,

the SBR tiles, SBR crumb and EPDM tiles were considered not to be contact skin sensitizers.

**Numbers of animals showing positive skin reactions (skin score of 1, 2 or 3) following re-challenge<sup>1</sup>**

<b>Group</b>	<b><u>24 hrs after re-challenge</u></b>	<b><u>48 hrs after re-challenge</u></b>
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0
6	0	0
7	0	0
8	5/10	4/10
9	0	0

<sup>1</sup> Data reported in Appendix C.

**Discussion**

Tires contain some natural rubber, and natural rubber contains latex allergens. Following dermal contact, latex allergens can induce skin sensitization in susceptible individuals. It is also possible that tire rubber contains allergens other than latex. Children using playgrounds with surfaces made of recycled tires can be exposed to substances on those surfaces through dermal contact. Hands would probably be the most common points of contact, while children playing without shoes or socks would have multiple contacts through their feet. Thus, it is prudent to determine whether such dermal exposures lead to skin sensitization.

The protocol used here to test for skin sensitization is a standard protocol for identifying contact sensitizers (US EPA, 1998). The test animal of choice is the guinea pig. Of the 85 animals used in the current study, one animal became sick early on and was euthanized. All other animals remained healthy throughout the testing period, as demonstrated by their normal clinical signs and weight gain. The only animals showing sensitization were those in the positive control group that had been exposed to an induction and re-challenge dose of the skin sensitizer alpha-Hexylcinnamaldehyde.

Five of ten animals in this group exhibited positive skin reactions at 24 hours after re-challenge, with four of ten also exhibiting positive skin reactions at 48 hours. No animals in any other group displayed positive skin reactions. Thus, the validity of this test to detect skin sensitization was demonstrated, and no playground surface sample caused sensitization. The SBR tile and SBR crumb samples contained some natural rubber, and therefore they also contained some latex allergens. However, the allergens may have become denatured during the vulcanization process, thereby losing the ability to cause skin sensitization. EPDM does not contain latex allergens. Nonetheless, it was tested and did not elicit skin sensitization.

These results suggest that recycled tires (SBR) used in playground surfaces do not cause skin sensitization in children. In addition, skin sensitization was not induced by EPDM, the material that is often used as a top layer to cover a bottom layer of SBR.

In performing risk assessment for potential skin sensitizers in humans, it has been recommended that human skin testing should follow testing in the guinea pig (Robinson et al., 1989). Nonetheless, negative results in the guinea pig, as found in our tests of SBR and EPDM, have been accurate predictors of negative results in humans (Robinson et al., 1989). Thus, these test results stand as evidence that playground surfaces made of recycled tires do not constitute a skin sensitization risk to children.

## **Conclusions**

- Skin sensitization testing was performed with the guinea pig as test animal.
- Three materials used in rubberized playground surfaces were tested: 1) loose crumb rubber made from recycled tires, 2) tiles molded from tire shreds mixed with a binder, 3) tiles molded from particles of the synthetic rubber EPDM mixed with a binder.
- None of the components of rubberized playground surfaces caused any skin sensitization, while the positive control substance (alpha-Hexylcinnamaldehyde) produced positive reactions in 40-50 percent of the animals.
- These data suggest that playground surfaces made of recycled tires do not constitute a skin sensitization risk to children.

# Chapter 10: Ecotoxicity of recycled tires including Yulupa Elementary School tire chips fire

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## Introduction

This section addresses the potential of recycled tires as a source of soil or groundwater contamination, and if so, whether the contamination is sufficiently high to constitute a hazard to the ecology. In addition, the results of toxicity testing in sentinel organisms are presented as an indication of the potential of recycled tires to adversely impact the animals and plants that compose many local ecologies.

## Soil Contamination

Five studies contained measurements of metals and chemicals in soil either containing or within a few feet of recycled tire applications (Table 29). These applications were in a playground surface (CIWMB, 2004), in roadbed construction (Minnesota Pollution Control Agency, 1990), as cover for school parking lots and roadways (FCCJNC, 1999), as a rootzone amendment for the cultivation of turf grass (Boniak et al., 2001) and in a septic tank field (Amoozengar and Robarge, undated). A study by Newman et al. (1997) added ground tires to the potting medium used to grow hot-house flowers, while in a laboratory study by Smolders and Degryse (2002), fine tire debris was mixed with soil, allowed to weather, and filtered with water to measure the leaching of zinc.

Neither the playground study nor the roadbed study detected significant increases in metals or chemicals in the soil near the recycled tires (compared to background). For the turf grass application, the maximum increase in soil zinc was to 31 ppm: a level within the range of most agricultural soils in southern Illinois (Boniak et al., 2001). Soil zinc also increased in the laboratory study by Smolders and Degryse (2002), while both zinc and copper increased in the potting medium used to grow geraniums in a hot-house (Newman et al., 1997).

The parking lot study (FCCJNC, 1999) measured increases that correlated with the presence of recycled tire chips as cover for road surfaces: however, only the increase in iron appears to be significant based on the data presented in the report. As discussed previously in this report, the iron most likely originates from the steel belts and beads used in tire construction. At least 99 percent of this steel material is removed when tires are processed into crumb rubber for use in playground construction. Lastly, while the soil within 5 cm of rubber/gravel trenches of a septic field contained elevated levels of Zn, Se, Cr and Ni, the levels of the first three fell to background between 5 and 20 cm (Amoozengar and Robarge, undated).

None of the soil levels of metals or toluene measured in these studies exceeded either the U.S. EPA Region 9 Preliminary Remedial Goals for soil (U.S. EPA, 2003d), the screening values for soil-bound chemicals recently proposed by OEHHA (2005b), or the California Regional Water Quality Control Board Environmental Screening Levels (2003). Therefore, this limited data suggests that recycled tires do not leach sufficient chemicals into the surrounding soil so as to present a risk to human health.

## **Ecological toxicity**

With regard to ecological toxicity, the screening levels set by the California Regional Water Quality Control Board (2003) also address risks to the flora and fauna. None of the levels reported in Table 29 exceed those screening levels; thus, risks to the health of the non-human organisms are not expected by those criteria. However, another set of Preliminary Remediation Goals for Ecological Endpoints (Efroymson et al., 1997) include soil values for zinc (8.5 ppm) and selenium (210 ppb) that are exceeded by the corresponding values in the table. In the case of selenium, the screening value is based on toxicity in the White-footed mouse, while the screening value for zinc is based on toxicity in the American woodcock.

Thus, ecological effects from contaminated soil cannot be ruled out based on these Preliminary Remediation Goals, although the selenium level in the soil was only marginally higher than the PRG and the zinc levels were close to the normal background levels. It should be added that these PRGs (Efroymson et al., 1997) assume widespread soil contamination and unlimited access of the wildlife to the contaminated soil. Since the soil values in the table reflect measurements made no more than a few feet away from the tire rubber, it is quite possible that any detected contamination did not extend more than a few feet. In the case of the only playground for which soil data exist (CIWMB, 2004 in Table 29) this was the case, since only background levels of metals and chemicals were present where the soil was sampled at 1.5 feet below the rubber chip layer.

**Table 29. Soil analysis in the vicinity of recycled tires used in road/parking lot construction, a playground surface, or as a soil amendment.**

Citation	Methods	Findings
Amoozegar and Robarge, undated	Chipped tires mixed with gravel and used to fill trenches of a septic system	Soil within 5 cm of trenches was at least 3-fold above background for Zn, Se, Cr (total) and Ni; levels of all but Ni fell to background between 5 and 20 cm of trenches
Boniak et al., 2001	Crumb rubber mixed with soil for use as a rootzone mix at 20, 30 or 40% rubber/g soil; grass was planted and soil analyzed approximately one year later	Soil zinc content increased 7- to 16-fold to 31 ppm (but still within range of most soil in southern Illinois), soil phosphorous and potassium increased up to 2-fold
CIWMB, 2004	3-24 inches of tire chips used as playground surface for 5 years; soil sampled 1.5 feet below tire layer	Metals, VOCs, PAHs, dioxins and furans all at or below background levels
FCCJNC, 1999	Ground rubber used to cover dirt parking areas and internal roadways of a community college; soil sampled from directly beneath tire layer over 2.5 years	Toluene 63 ppb, antimony 500 ppb, copper 2.3 ppm, iron 960 ppm, lead 13 ppm, zinc 45 ppm, barium 10 ppm, selenium 253 ppb, all elevated compared to pre-installation baselines (largest increase was for iron, at least 50-fold); all levels of contamination were below state soil cleanup goals
Minnesota Pollution Control Agency, 1990	Shredded tires used in roadbed construction; soil sampled 3 feet from tire layers and 4 feet below the surface	Fifteen metals measured; 5 were elevated (about 2-fold) relative to background levels, however, the differences were not significant
Newman et al., 1997	Ground tire rubber mixed with peat and/or vermiculite for use as a medium for growing hot-house geraniums (2 months duration)	Medium containing rubber had zinc and copper levels that were 40- and 11-fold greater than controls.
Smolders and Degryse, 2002	Fine rubber tire debris mixed with soil and allowed to weather outside for eleven months	Leachates from soil/rubber mixtures analyzed for Zn: the Zn content of leachate from truck tire rubber/soil was not different from controls, while the Zn content of leachate from car tire rubber/soil was three-fold higher than control

## ***A Case Study of Possible Soil Contamination: Evaluation of the Construction Completion Report for the Yulupa Elementary School Tire Chip Fire, Sonoma County, June 2004 (CIWMB, 2004)***

### **Summary**

- A playground surface made of recycled tire chips burned at the Yulupa School. A clean-up followed.
- Environmental measurements were made by the US EPA and by DTSC of CAL EPA.
- The US EPA report showed:
  5. The soil/rubber material removed from the site was not hazardous waste and could be disposed of in a Class III landfill.
  6. The air above the burn site posed no health risks to clean-up workers.
  7. The soil below the burned layer posed no significant risks to human health.
- The DTSC report showed:
  1. The soil remaining after the clean-up contained only background levels of chemicals, suggesting the tire chips had not released chemicals into the soil.
  2. A human health risk assessment confirmed that the background levels of chemicals in the soil remaining after the clean-up were not expected to produce health effects in persons using the school site.

### **Introduction**

The Yulupa School fire occurred in August, 2003, in a playground surface composed of metal-free rubber chips derived from recycled tire side-walls. The chips had been in place for over five years. The chip layer varied from 3-24 inches deep. Under the chip layer was a bed of fill material of undetermined depth. Approximately 50 percent of the chip surface burned in the fire, which lasted about 15 minutes. The subsequent activities were aimed at removing all rubber material and a layer of soil under the rubber, followed by testing whether the remaining soil contained tire chip-derived toxicants that posed a health hazard to persons attending the school.

### **US EPA Assessment Sampling Report**

A contractor was hired by US EPA to assess the following:

1. Whether the soil below the burned chip layer had become contaminated with rubber-derived chemicals.
2. Whether the soil removed from the site should be classified as hazardous waste.
3. Whether the air sampled during one day of clean-up activities was contaminated with any rubber-derived chemicals or dust.

**OEHHA Evaluation:** While some soil samples from beneath the combusted tire chip layer contained levels of metals and/or chemicals that were above reporting limits, since

only a single background sample was analyzed, it was not possible to determine whether any substance detected below the tire chip layer was significantly higher than background. Accurate determination of background was particularly important in this instance, given that the entire playground was built on top of fill material brought in from another location. None of the reported levels approached the US EPA Region 9 Preliminary Remediation Goals for Soil or the OEHHA (2005b) Human-Exposure-Based Screening Numbers to Aid Estimation of Cleanup Costs for Contaminated Soil. Thus, human health effects were not expected.

A variety of procedures were used to demonstrate that the soil removed from the burn area was not hazardous waste. Thus, the soil could be disposed of in a class III landfill.

Two of four air samples taken from around the perimeter of the playground during the clean-up were slightly above the detection limit for zinc. It was concluded that no significant personal health risks were posed to clean-up workers by any of the monitored chemicals (zinc, dust, benzene, polycyclic aromatic hydrocarbons, total hydrocarbons, carbon monoxide or explosive atmospheres).

### **DTSC Confirmation Sampling Plan and Report**

After the tire chips had been removed along with a layer of fill extending 1.5 feet below the chip layer, the remaining soil was sampled for analysis of metals, VOCs, PAHs, dioxins and furans. Four background samples from nonimpacted areas at the school were analyzed for metals only. In addition, three soil samples were taken from points adjacent to the playground downwind of the fire. These “adjacent” samples were from under a six inch layer of wood chips.

**OEHHA Evaluation:** No VOCs were detected in any samples. A variety of PAHs were detected in samples from under the playground and adjacent/downwind of the playground fire. Although background PAH levels at nonimpacted locations were not determined, historical background levels measured in urban US soil (ATSDR, 1995) were actually higher than the levels measured in the Yulupa school samples. Similarly, levels of dioxins and furans in soil samples from under the burned chip layer were five-fold lower than the mean background levels in US rural soil and in California agricultural soil (Australian Government, 2004). These results suggest that neither the burned nor unburned tire chips released measurable amounts of these chemicals into the soil that remained after the clean-up (i.e., in soil at 1.5 feet below the chip layer).

Levels of five metals detected at one of three adjacent sites downwind of the playground were considered above background; however, the following suggest that these levels were not tire-derived:

1. The two other samples at adjacent/downwind sites were not above background for these metals.
2. No samples from under the chip layer were above background for these metals.

The soil measurements made by DTSC suggest that neither burned nor unburned tire chips in the Yulupa playground released chemicals into the soil that remained following the clean-up. Nonetheless, a human health risk assessment was performed based on the measured levels of both carcinogens and noncarcinogens. For carcinogens, the risk was determined to be less than  $10^{-6}$ , and for noncarcinogens the hazard index was less than 1. Thus, health effects were not expected for persons using the school site following the clean-up.

## Groundwater contamination

Although groundwater is a part of most local ecologies, its contamination usually represents only a human health risk in so far as it serves as a source of drinking water. However, groundwater can also be used for crop irrigation and as a drinking water source for livestock. Groundwater can also enter surface water systems such as lakes and streams. Thus, groundwater contamination has the potential to affect surface flora and fauna.

Five studies were located which analyzed groundwater for tire-derived metals and compounds (Table 30). For the studies by the Minnesota Pollution Control Agency (1990), Humphrey and Katz (2001) and Exponent (2003), the tire shreds were located below the water table; thus, the shreds were in constant hydraulic communication with the local groundwater. In the cases of storm runoff from crumb rubber-covered areas of a parking lot (FCCJNC, 1999) or storm seepage through a road embankment made of sand and tire shreds (Yoon et al., 2005), the rainwater entered the local groundwater followed by sampling of the groundwater.

Iron was noteworthy as the only substance identified in four of the studies as exceeding the US EPA National Drinking Water Standard (2005a); for iron the standard was a Secondary National Drinking Water Standard. Exceeding a Secondary Drinking Water Standard is associated with cosmetic or aesthetic effects. In the study by the Minnesota Pollution Control Agency (1990) the iron standard was exceeded by 1000-fold. As discussed earlier in this report, the source of iron in these studies was most likely the steel belts and beads used in tire construction. Since current methods for processing tires into crumb rubber for use in playgrounds includes a step that removes 99% of the steel material, the iron levels leaching from rubberized playgrounds should be at least 100-fold lower than those cited above.

Manganese exceeded its Secondary National Drinking Water Standard in two of the studies (maximum 26-fold higher). Like iron, it probably also originated from the steel belts and beads in the tires. Cadmium, chromium, aluminum and lead exceeded their National Primary Drinking Water Standards in the single study by the Minnesota Pollution Control Agency (1990). All other levels of compounds or metals either fell below their National Drinking Water Standard or had no standard established for them.

It should be noted that in the study by Humphrey and Katz (2001), almost all high values from within the tire trench fell to background at three meters downgradient from the trench. Similarly, Exponent (2003) reported that the iron concentration was only elevated in the area close to the tire shreds, and that leached iron was quickly diluted or precipitated within 2-10 feet of the tire trench. Iron was specifically discussed since it was believed to be responsible for the toxicity of the groundwater from the tire trench towards *Ceriodaphnia dubia*. Thus, these limited data suggest that the tire-derived contaminants in groundwater do not migrate very far from their source.

**Table 30. Groundwater analysis in the vicinity of recycled tires used in road and parking lot construction, and in underground test trenches.**

Citation	Methods	Findings
Exponent, 2003	Groundwater collected from shredded tire trench located in saturated soil below the water table; water samples taken from inside trench and at a well 2 feet downgradient from the trench	Concentrations above background, all in ppb: chloroethane 2; 1,1-dichloroethane 2; cis-1,2-dichloroethene 16; benzene 1.6; trichloroethene 0.8; toluene 2.6; N-Nitrosodimethylamine 7; N-Nitrosodiphenylamine 7; aniline 100; bis(2-ethylhexyl)phthalate 5; acetone 11; iron 80,000; manganese 570; zinc 90; barium 30
FCCJNC, 1999	Ground rubber used to cover dirt parking areas and internal roadways of a community college; groundwater sampled from wells within a few meters of rubber-covered areas; wells were "in hydraulic communication with the aquifer"	Concentrations above background, all in ppb: total xylenes 1.4; iron 1,500; chromium 4
Humphrey and Katz, 2001	Groundwater collected from shredded tire trench located in saturated soil below the water table; water samples taken from inside trench and at a well 3 meters downgradient from the trench	Concentrations inside trench and above background, all in ppb: 1,1-dichloroethane 6; 4-methyl-2-pentanone 58; acetone 28; benzene 4; chloroethane 4; cis-1,2-dichloroethene 24; aniline 71; phenol 33; m+p cresol 39; iron 33,000; manganese 1,300; zinc 26; almost all values were at background in the groundwater sampled 3 meters downgradient from the tire trench
Minnesota Pollution Control Agency, 1990	Road bed construction with tire shreds over a wetland area; groundwater sampled from wells within a few feet of road bed	Concentrations above background, all in ppb: aluminum 180,000; barium 2000; cadmium 32; chromium (total) 350; iron 300,000; lead 230; zinc 870
Yoon et al., 2005	Tires shreds used in constructing a road embankment; groundwater sampled from a well adjacent to and downgradient of the embankment	Metal concentrations above background, all in ppb: arsenic 19; barium 113; cadmium 1.1; chromium (total) 55; selenium 23

## Toxicity tests in sentinel organisms

Table 31 shows results of toxicity tests with sentinel organisms used as a means of identifying potential ecological toxicants. In almost all cases, whole tires, tire shreds or crumb rubber was used to produce concentrated leachates in the laboratory. The organisms used to test these concentrated leachates included single-celled bacteria (*Vibrio fischeri*) and algae (*S. capricornutum*, *R. subcapitata*), the aquatic invertebrates *Daphnia* and shrimp, three species of fish (rainbow trout, fathead minnows and sheepshead minnows), the frog species *X. laevis* and lettuce. In addition, four studies measured the effects of recycled crumb rubber on the growth of turf grass, while one study followed the growth of hot-house geraniums, all prompted by its use as a soil amendment.

The study by Birkholz et al. (2003) utilized crumb rubber manufactured specifically for use in playground surfaces. All other studies utilized either whole tires or tires processed into chips, shreds, plugs or powder.

Toxicity, often measured as lethality, was observed for all aquatic organisms (bacteria, algae, *Daphnia*, shrimp, minnows, trout, frog) exposed to recycled tires, although some individual studies were negative. Fathead minnows appeared to be less sensitive than rainbow trout, since 2/6 studies with the former detected toxicity compared to 3/3 studies with the latter. Three studies out of eight involving terrestrial plants documented adverse effects: decreased germination in turfgrass (Boniak et al., 2001), decreased growth rates for bermudagrass (Owings and Bush, 2001) and decreased growth rates and flower count in geraniums (Newman et al., 1997).

With regard to identifying the responsible toxicant(s), in *Daphnia* metals were thought to be responsible: zinc in the studies by Nelson et al. (1994) and Gaultieri et al. (2005) and iron precipitates forming on the feeding apparatus in the study by Exponent (2003). The lethality in rainbow trout was consistent with a nonvolatile (Day et al., 1993) and nonmetallic (Ontario Ministry of Environment and Energy, 1994) toxicant.

While these studies (mostly laboratory) show that recycled tire rubber has the potential to cause adverse effects in non-human organisms, whether this would occur in the environment surrounding rubberized playground surfaces would depend on the dilution, dispersion and precipitation of the relatively low levels of chemicals released by these surfaces. The chemicals released by tires could also be transformed through interactions with reactive chemicals already in the environment.

All but one of the studies with aquatic sentinel organisms discussed here utilized tire leachates produced in the laboratory. Chemicals in such leachates may be at lower or higher concentrations than would be achieved in the area surrounding rubberized playground surfaces. For the single study of tire leachate produced in the field (Exponent, 2003), only tire shreds below the water table released sufficient iron to cause toxicity, and then only within 2-10 feet of the tire trench. The tire trench above the water table did not release toxic levels of iron. This latter situation more closely represents what would be expected in the environment surrounding rubberized playground surfaces, where the surfaces are not in constant hydraulic communication with groundwater.

Table 31. Toxicologic responses of sentinel organisms to recycled tire rubber and its leachate.

<b>Citation</b>	<b>Methods</b>	<b>Findings</b>
<b>Bacteria</b>		
Birkholz et al., 2003	Playground crumb rubber used to produce leachate in lab; toxicity measured in luminescent bacteria <i>Vibrio fischeri</i>	Toxicity observed-less for crumb rubber aged by use in playground for 3 months
<b>Algae</b>		
Basel Convention, 1999	Powdered tire rubber shaken in water for 24 h; growth of <i>S. capricornutum</i> measured	No effects at highest dose tested
Gualtieri et al., 2005	Finely ground tire rubber shaken in water at pH 3 for 24 h; growth of <i>R. subcapitata</i> measured	Growth inhibited over the 72 h of incubation
Minnesota DOT, 1995	Chipped tires and chipped wood used to produce leachate in lab; survival and reproduction measured in green algae ( <i>S. capricornutum</i> )	Tire and wood leachates were equitoxic at lowest dose level tested
<b>Daphnia (aquatic invertebrate)</b>		
Basel Convention, 1999	Powdered tire rubber shaken in water for 24 h; testing for changes in mobility of <i>Daphnia magna</i>	No effects at highest dose level tested
Birkholz et al., 2003	Playground crumb rubber used to produce leachate in lab; lethality measured in <i>Daphnia magna</i> (exposure time not specified)	Lethality observed-less for crumb rubber aged by use in playground for 3 months
Day et al., 1993	Whole tires immersed in water in tanks for increasing times	No lethality observed
Exponent, 2003	Leachate from tire trench below and above water table; survival and reproduction measured in <i>Ceriodaphnia dubia</i>	Lower survival and less reproduction compared to controls for below water table application only-believed due to iron precipitates forming on feeding apparatus
Gualtieri et al., 2005	Finely ground tire rubber shaken in water at pH 3 for 24 h; toxicity to <i>D. magna</i> measured	Immobility/mortality was observed after 24 and 48 h of incubation

<b>Citation</b>	<b>Methods</b>	<b>Findings</b>
Minnesota DOT, 1995	Chipped tires and chipped wood used to produce leachate in lab; survival and reproduction measured in <i>Ceriodaphnia dubia</i>	Tire chip leachate was 5- to 8-fold more toxic than wood chip leachate
Nelson et al., 1994	Tire plugs immersed in lake water in lab for 31 days; 24 h LC <sub>50</sub> determined in <i>Ceriodaphnia dubia</i>	Lethality observed; believed due to Zn
Ontario Ministry of Environment and Energy, 1994	Whole tire immersed in water in tank for up to 2 weeks; water tested with <i>Daphnia magna</i> and <i>Ceriodaphnia dubia</i> in 48 hour incubations	No lethality observed
Wik and Dave, 2005	Finely ground tire rubber incubated in water for 72 h prior to addition of <i>Daphnia magna</i> for another 24 h	Variable toxicity in tire samples possibly due to nonpolar organic compounds
<b>Daggerblade Grass Shrimp (aquatic invertebrate)</b>		
Hartwell et al., 1998	Shredded tires used to produce leachate in lab at salinities of 5-25 percent; survival and growth measured over 96 hrs in grass shrimp <i>Palaemonetes pugio</i>	Lethality and growth inhibition both observed in response to tire leachate
<b>Minnows</b>		
Basel Convention, 1999	Powdered tire rubber shaken in water for 24 h; mortality of <i>Brachydanio rerio</i> measured	No mortality observed at highest dose level tested
Birkholz et al., 2003	Playground crumb rubber used to produce leachate in lab; lethality measured in the fathead minnow <i>P. promelas</i> (exposure time not specified)	Lethality observed-less for crumb rubber aged by use in playground for 3 months
Day et al., 1993	Whole tires immersed in water in tanks for increasing times; lethality measured in the fathead minnow	No lethality observed
Exponent, 2003	Leachate from tire trench below and above water table; seven day survival and reproduction measured in fathead minnow <i>P. promelas</i>	No effects observed

<b>Citation</b>	<b>Methods</b>	<b>Findings</b>
Hartwell et al., 1998	Shredded tires used to produce leachate in lab at salinities of 5-25 percent; survival and growth measured over 96 hrs in larval sheepshead minnows <i>Cyprinodon variegatus</i>	Lethality and growth inhibition both observed in response to tire leachate
Minnesota DOT, 1995	Chipped tires and chipped wood used to produce leachate in lab; survival and reproduction measured in fathead minnow ( <i>P. promelas</i> )	For survival and growth the leachate from tires was 2 to 3-fold more toxic than the leachate from wood
Ontario Ministry of Environment and Energy, 1994	Whole tire immersed in water in tank for up to 2 weeks; water tested with fathead minnow <i>P. promelas</i> in 4 day exposures	No lethality observed
<b>Trout</b>		
Day et al., 1993	Whole tires immersed in water in tanks for increasing times; lethality measured in rainbow trout	Lethality observed-lethality was stable for 2-3 days if tires removed, then slowly decreased over 32 days (believed due to break down of nonvolatile toxicants)
Ontario Ministry of Environment and Energy, 1994	Whole tire immersed in water in tank for up to 2 weeks; lethality measured in rainbow trout fry for exposures of up to 4 days	Lethality observed after 24 hours of exposure; toxicity completely removed by pretreating water with activated carbon
Stephensen et al., 2003	Whole tires immersed in water in tanks with rainbow trout; liver and bile examined from the fish	Tire-exposed fish exhibited the following: increased liver weight, increased hepatic CYP1A1, glutathione, glutathione reductase, glutathione S-transferase and glucose-6-phosphate dehydrogenase; bile contained hydroxylated PAHs and aromatic nitrogen compounds

<b>Citation</b>	<b>Methods</b>	<b>Findings</b>
<b><i>X. laevis</i> (frog) embryos</b>		
Gaultieri et al., 2005	Finely ground tire rubber shaken in water at pH 3 for 24 h; toxicity measured with <i>X. laevis</i> (frog) embryos incubated in Petri dishes	Lethality and malformations produced in the frog embryos during the 120 h incubation
<b>Plants</b>		
Boniak et al., 2001	Crumb rubber mixed with soil for use as a rootzone mix in the cultivation of turf grass (tall fescue and Kentucky bluegrass)	Smallest size of crumb rubber caused a dose-dependent decrease in germination rate and decrease in turf quality
Groenevelt and Grunthal, 1998	Crumb rubber mixed with soil used to grow turf grass	The Zn content of the turf grass approximately doubled, to over 80 mg/kg; no accompanying toxicity
Lisi et al., 2004	Crumb rubber installed as a drainage layer 30 cm beneath the root zone of a golf course putting green	No detrimental effects observed on turf grass quality, color or density
Minnesota DOT, 1995	Chipped tires and chipped wood used to produce leachate in lab; survival and growth of lettuce ( <i>Lactuca sativa</i> ) from seed measured	No effects observed on survival or growth
Minnesota Pollution Control Agency, 1990	Shredded tires used in roadbed construction	No differences observed in the diversity of plant species growing in the tire and control areas
Newman et al., 1997	Ground tire rubber mixed with peat and/or vermiculite for use as a medium for growing hot-house geraniums (2 months duration)	Plant growth and flower count were lower for plants grown in medium containing ground rubber, possibly due to released zinc and copper, both of which were elevated in the plant tissue

<b><i>Citation</i></b>	<b><i>Methods</i></b>	<b><i>Findings</i></b>
Owings and Bush, 2001	Growth of bermudagrass in containers of sand, peat moss and various concentrations of crumb rubber	Growth rates decreased, possibly due to released zinc and manganese
Tompkins et al., 1997	Crumb rubber as a soil amendment for the growth of turf grass	No effects observed on emergence rates; slightly better color was observed in the presence of the crumb rubber

## Conclusions

- Only a limited number of soil samples from locations adjacent to recycled tire shreds have been analyzed; while a number of metals were above background in some studies, most increases were small.
- In the single case where soil samples from under a playground surface made of recycled tires were analyzed, the metals, VOCs, PAHs, dioxins and furans were at or below background levels, suggesting no risk to the local ecology.
- Measurements of chemicals released from recycled tires into groundwater are also scarce.
- Groundwater in contact with tire shreds contained elevated levels of many chemicals; however, those levels rapidly approached background a few feet outside of the tire trench.
- Recycled tires released chemicals that were toxic to a variety of sentinel organisms including bacteria, algae, aquatic invertebrates, fish, frogs and plants; importantly, almost all of these studies in animals, bacteria and algae utilized concentrated leachate produced in the laboratory.
- Considering all the data, it seems doubtful that recycled tire rubber in outdoor applications such as playground surfaces releases high enough levels of chemicals to cause toxicity to animals and plants living in the vicinity.

# Chapter 11: Evaluating the Risk of Serious Head Injury Due to Falls on California Playground Surfaces Made of Recycled Tires

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## Abstract

Recycled tires continue to be used in the construction of rubberized playground surfaces in California. To function as an effective means of reducing the incidence of serious head injury when children fall in the playground, these surfaces should meet standards for impact attenuation, as cited in the California Code of Regulations (sections 65700-65750). This study was conducted to determine whether rubberized surfaces are meeting the standards for impact attenuation, and whether those properties change as the surfaces age. Data have been gathered from 32 rubberized playground surfaces and 5 surfaces made of wood chips/engineered wood fiber.

An accelerometer was used to measure maximal deceleration rates ( $G_{\max}$ ) and Head Impact Criterion (HIC) values for the surface below each play structure (131 tested) within the playgrounds, which were then compared to the American Society for Testing and Materials (ASTM) F1292 standard for impact attenuation by playground surfaces. Approximately 33 percent of the play structures on rubberized surfaces failed to meet the HIC standard, compared to no failures on wood chips. Approximately 69 percent of the rubberized playground surfaces contained at least one failing structure. Failing structures over rubberized surfaces included swings, climbers, slides, upper body rings and elevated platforms.

As the heights of the play structures in rubberized playgrounds increased, so did the likelihood that the surface below would fail to meet the HIC standard, although some of the highest structures had underlying surfaces that met the standard. There appeared to be little or no difference in impact attenuation by surfaces less than one year old compared to surfaces that were between one and two years old. In addition, HIC values in two pour-in-place surfaces were stable for at least the first two to three months following installation. Lastly, HIC values of pour-in-place surfaces increased with increasing surface temperature. These results demonstrate the importance of testing rubberized playground surfaces following installation, to verify that the surfaces meet the standards for impact attenuation.

## Introduction

Nationwide, up to 80 percent of serious playground injuries are the results of falls to the surface (Tinsworth and McDonald, 2001). Most were injuries to the upper limbs (Altman et al., 1996; Chalmers et al., 1996), although this varied with age; for children younger than five years old the head or face was injured most frequently, while for children 5-14 years old injuries to the hand or arm predominated (Tinsworth and McDonald, 2001).

Epidemiologic studies performed with data from hospitals and daycare centers demonstrated that as the height of playground equipment increased, the injury rate from falls also increased (Briss et al., 1995; Chalmers et al., 1996; Mott et al., 1997; Macarthur et al., 2000). Less clear, however, is the influence of playground surface type on

frequency and kind of injury. In some instances impact-absorbing surfaces such as wood chips, sand, rubber tile/mats and rubber shreds were effective at reducing injuries from falls compared to hard surfaces such as asphalt, cement, turf and dirt (Chalmers et al., 1996; Mott et al., 1997; Mowat et al., 1998; Norton et al., 2004b), while other studies found little or no benefit (Sosin et al., 1993; Briss et al., 1995; Waltzman et al., 1999).

There are too few data to draw reliable conclusions on impact attenuation and injury reduction by rubber playground surfaces compared to other surfaces. An epidemiologic study by Mott et al. (1997) found that playgrounds with “rubber surfaces” (rubber surface type not specified) performed better than those consisting of bark or concrete. However, as discussed above, other epidemiologic studies have failed to detect any significant differences among surfaces.

Turning to laboratory studies where impact attenuation was measured with mechanical devices under controlled conditions, in two studies rubber chips outperformed sand, wood chips and gravel (Mack et al., 2000; CPSC, undated), while in a third study wood chips outperformed rubber mats (Lewis et al., 1993). Clearly, data collected from playgrounds being used by children are needed in order to determine whether the different types of rubber surfacing (crumb, shreds, pour-in-place, molded tiles) lower the injury rate compared to other impact-absorbing surfaces.

Therefore, discussions were held with members of the Injury Surveillance and Epidemiology Section of the California Department of Health Services and the Department of Epidemiology in the UCLA School of Public Health, in an effort to locate injury data collected from playgrounds both before and after installation of rubberized surfaces. No such data were located, including no information on insurance savings directly attributable to decreased playground injuries. Thus, OEHHA decided to collect impact attenuation data from California playground surfaces made of recycled tires, from which to estimate the risk of serious head injury from falls.

That lowering the number of playground injuries would produce a large reduction in health care-related costs is demonstrated by the estimate that playground-related injuries in the United States cost 1.2 billion dollars to treat in 1995 (U.S. Centers for Disease Control, 2005). If ten percent of these occurred in California, then approximately 120 million dollars were spent in this state. Since approximately 80 percent of these injuries resulted from falls (Tinsworth and McDonald, 2001), then reducing the injury rate from falls by only ten percent has the potential to save almost 10 million dollars in California (higher savings in 2006 dollars). An accompanying reduction in injury severity would save even more.

It may also be particularly important to compare injury rates for specific types of injuries, such as head concussions and long-bone fractures of the arm. Some studies suggest that impact attenuation properties vary between surfaces, such that head injury might be optimally prevented by one surface, while long-bone injury might be optimally prevented by another (Briss et al., 1995; Rabinovitch and Chiu, 1998; Petridou et al., 2002; Norton et al., 2004a; Norton et al., 2004b). This was in fact demonstrated in a laboratory study that used a test dummy to simulate the short-distance falls that children experience when falling out of bed (Bertocci et al., 2003). While similar “g” forces for head impact were measured on playground foam compared to padded carpet, the foam produced significantly less axial tension to the femur. Similar data are needed for the different types of rubberized playground surfaces.

More than 40 million waste tires are generated each year in California (CIWMB, 2006). Increasingly, these used tires are being recycled into rubberized playground surfaces. Such surfaces can be made thick enough to provide significant impact attenuation when children fall from play structures in the playground, thereby reducing the chance of serious head injury (U.S. CPSC, 1997). This is accomplished by deformation and/or displacement of the surface in the local area of the impact, thereby absorbing some of the energy of impact. While the standards for impact attenuation by playground surfaces are cited in the California Code of Regulations (sections 65700-65750), these standards have never been enforced.

Thus, it is currently unknown whether the standards are being met, either by the relatively new playground safety surfaces made of recycled tires, or by more traditional surfaces also in use in California including sand, wood chips and pea gravel. The primary objective of this study was to determine whether California playground surfaces made of recycled tires are in compliance with the California standards for impact attenuation. In addition, since these surfaces are exposed to the environment, we studied whether their impact attenuating properties are influenced by temperature and whether they change over time.

### **Materials and Methods**

We tested playgrounds of municipalities and school districts awarded grants by the CIWMB for the installation of playground surfaces made of recycled tires. These were located in San Francisco and surrounding regions. In a number of instances, grantees had additional playgrounds with rubberized surfaces made of recycled tires that were not funded by the CIWMB. Permission was obtained to test both the CIWMB-funded and non-funded surfaces. There were no obvious differences in the types or sizes of playground structures contained in these two groups. One private childcare facility with a rubberized playground surface made of recycled tires was included in the study.

A total of 32 rubberized playground surfaces were tested for impact attenuation. Twenty-six were pour-in-place surfaces consisting of a bottom layer of shredded tires and a top layer of the synthetic rubber called ethylene propylene diene monomer (EPDM). Pour-in-place surfaces are made by mixing shredded tire rubber with polyurethane binder on site, and pouring the mixture into the playground to harden into a unitary surface. The top layer of EPDM is then added using a similar process. Four playground surfaces were constructed out of tiles made of shredded tires. Such tiles are pre-molded by the manufacturer and transported to the playground site, where they are attached to each other by glue or other method to form a unitary surface. Two surfaces were tested that consisted of loose-fill shredded tires. This material is raked into place, and requires periodic maintenance that includes removal of foreign objects and evening of the surface. Five playgrounds were tested that had surfaces made of wood chips/engineered wood fiber. These surfaces are also raked into place, and require regular maintenance similar to that required by the loose-fill rubber surfaces. Table 32 lists some of the advantages and disadvantages of these safety surfaces, including sand.

**Table 32. Advantages and disadvantages of different playground safety surfaces (adapted with modification from Huber, 2001)**

<b>Pour-in-place or tiles made of shredded tires</b>
<i>Advantages:</i> low maintenance and easy to clean; consistent shock absorbency; does not harbor foreign objects; does not readily support microbial growth; not subject to displacement during children's play; accessible to the disabled; good footing; unattractive to dogs and cats as a place

to defecate; cannot be swallowed by children
<i>Disadvantages:</i> high installation cost; shock absorbency may decrease somewhat over a time frame of years; can become uncomfortably hot on warm days; flammable
<b>Loose-fill shredded tires</b>
<i>Advantages:</i> low installation cost; drains well; depth easily increased to increase shock absorbency; does not readily support microbial growth; less attractive to dogs and cats as a place to defecate; less subject to compaction over time
<i>Disadvantages:</i> requires regular maintenance; gets dirty over time; harbors/hides foreign objects; subject to displacement during children's play; can be thrown by children; flammable; less accessible to the disabled; can be swallowed by children; difficult footing; smaller particles prone to being tracked indoors by children
<b>Wood chips/engineered wood fiber</b>
<i>Advantages:</i> low installation cost; drains well; depth easily increased to increase shock absorbency; stays relatively cool on hot days
<i>Disadvantages:</i> requires regular maintenance; combines with dirt over time; harbors/hides foreign objects; subject to displacement during children's play; can be thrown by children; supports microbial growth; used by cats and dogs as a place to defecate; flammable; can become compacted over time; less accessible to the disabled; can be swallowed by children
<b>Sand</b>
<i>Advantages:</i> low installation cost; drains well; depth easily increased to increase shock absorbency; nonflammable; does not readily support microbial growth
<i>Disadvantages:</i> requires regular maintenance; combines with dirt over time; harbors/hides foreign objects; subject to displacement during children's play; can be thrown by children; used by cats and dogs as a place to defecate; can become compacted over time; not accessible to the disabled; can be swallowed by children; difficult footing; loses shock absorbency when water saturated
<b>Pea Gravel</b>
<i>Advantages:</i> low installation cost; drains well; depth easily increased to increase shock absorbency; nonflammable; does not readily support microbial growth
<i>Disadvantages:</i> requires regular maintenance; combines with dirt over time; harbors/hides foreign objects; subject to displacement during children's play; can be thrown by children; used by cats and dogs as a place to defecate; can become compacted over time; not accessible to the disabled; can be swallowed by children; difficult footing; can be inserted by the child into its body openings such as ears and nose

Measurement of surface impact attenuation (HIC,  $G_{max}$ ) was performed with a Triax2000 triaxial accelerometer (Playground Clearing House, Trenton, New Jersey) according to the American Society for Testing and Materials (ASTM, 2004) standard number F1292: Standard Specification for Impact Attenuation of Surfacing Materials Within the Use Zone of Playground Equipment. HIC and  $G_{max}$  data can be used to predict whether serious head injury would result from a fall onto a surface. According to this standard, the surface below each play structure is tested at its fall height at three locations within its use zone. Fall heights and use zones were according to ASTM standard F1487 and United States Consumer Products Safety Commission publication No. 325: Handbook for Public Playground Safety.

The Triax2000 utilizes a ten pound headform (Figure 2). For reference comparison and quality control purposes, the accelerometer in the headform was routinely tested by performing drops onto a rubber reference pad supplied by the manufacturer. Those HIC and  $G_{max}$  values were always within 2% of the reference pad values specified for our accelerometer, as required by the ASTM F1292 standard (ASTM, 2004).

All testing was conducted on days when it had not rained, and on dry surfaces (other than surface dampness that might be due to fog or morning dew). Prior to testing, loose-fill surfaces were compacted with a hand tamper as described in ASTM F1292. Temperatures of both the surface and ambient air were recorded.

## Results

Figure 3 shows the results of drops at 368 locations around 121 playground structures standing on rubberized surfaces. For a drop location to meet the ASTM F1292 standard, the  $G_{max}$  value must be less than or equal to 200, and the HIC value must be less than or equal to 1000. A number of drops failed the HIC standard, while a smaller number failed the  $G_{max}$  standard. Every drop that passed the HIC standard also passed the  $G_{max}$  standard. In contrast, many drops that passed the  $G_{max}$  standard failed to pass the HIC standard. Thus, the HIC=1000 standard is a more sensitive test of impact attenuation by these rubber surfaces, and in subsequent graphs only the HIC value was plotted for each drop location.

Figure 4 contains the HIC data from Figure 3 plotted as a function of playground structure fall height. Data from five playgrounds with surfaces made of wood chips/engineered wood fiber are included. Both sets of data show increasing HIC with increasing fall height, although the increase appears to be greater for the drops on rubber. As stated in the Methods section, each structure was tested at three drop locations within the use zone. Many of the drops on rubber surfaces exceeded the HIC=1000 standard, leading to a playground structure compliance rate of 67 percent (Table 33), and an overall playground surface California regulatory compliance rate of 31 percent. There were no failures out of ten structures tested on surfaces made of wood chips.

While the data in Figure 4 show a generally greater likelihood of rubberized surfaces to fail the HIC=1000 standard at higher fall heights, a number of drops at heights up to almost twelve feet yielded values that met the standard. This demonstrates that rubber surfaces in the use zones of quite tall playground structures can be constructed to meet the standard.

The data from Figure 4 have been plotted in Figure 5 so as to show how the playground structure compliance rate decreased as the fall height increased. Only a single structure failed the HIC standard at < six feet. However, above six feet the compliance rate fell continuously up to nine feet. At structure drop heights greater than nine feet, the small number of structures makes it difficult to know the true compliance rate.

The structures failing the HIC standard are shown in Table 34, where they have been categorized according to structure type. No specific type of play structure stood out as being responsible for the failure rate observed here.

To determine whether rubberized playground surfaces failed the HIC standard at only a single location or at multiple locations, the number of failing structures per playground were plotted in Figure 6. While the largest group (ten playgrounds) contained only a single failing structure, three surfaces each contained three failing structures and two

surfaces each contained four failing structures. Clearly, some rubberized playgrounds did not comply with the HIC standard over much of their surface.

Some municipalities were able to supply the installation dates for their particular playground surfaces. Figure 7 uses these data to calculate surface age, and compare those ages to the corresponding HIC compliance rate. The small numbers of surfaces greater than two years old make those data unreliable. Comparing surfaces in their first year following installation to those in their second year, the compliance rates were not significantly different according to a 2-tailed Fisher's Exact Test, suggesting that the surfaces experienced little or no change in impact attenuation over their first two years of life. However, since other explanations are possible, we followed impact attenuation over time at the same locations in the same playgrounds.

Figures 8 and 9 show surface HIC values as a function of time, over the first two to three months of surface life. The playground represented in Figure 8 was first measured two days after installation of the top EPDM layer, while the playground in Figure 9 was first measured at four days after installation. Both surfaces were pour-in-place with bottom layers of recycled tire rubber and tops layers of EPDM. Normally, these two layers are poured on consecutive days. Thus, these data give an indication of how quickly the surfaces hardened, and to what extent the hardness changed over the first few months of surface life. Because surface hardness is affected by temperature, the air temperatures measured in the shade are presented, showing that the HIC data were collected over a relatively narrow temperature range. The data show little or no change in hardness over the first two to three months, indicating that these surfaces provide stable impact attenuation soon after they are poured, and for months thereafter. Taken together, the data in Figures 7-9 are consistent with stable impact attenuation by these surfaces for at least the first two years of surface life.

Two surfaces composed of loose-fill shredded tire rubber were also tested. One had play structures that were less than two feet high, yielding HIC values of 129 or less (data not shown). The second playground had structures up to eight feet tall. The HIC testing data for this playground are shown in Figure 10. The values fluctuated over a wide range. For example, the three testing locations for the swing set ranged from a low of 558 to a high of 2821. Also, comparing the platform values to the rings values, both tested at a fall height of 6.5 feet, the platform values were approximately three fold higher than those of the rings. Since this surface consisted of loose-fill shredded tire rubber, each drop location was inspected to determine thickness of the rubber layer. It was immediately obvious that the locations with high HIC values were spots where most of the rubber shreds had been kicked away, leaving only a relatively thin layer behind. Thus, variability in surface thickness was responsible for the variability in HIC values. We believe it likely that for pour-in-place surfaces, variability in surface thickness is also the primary cause of the variability in HIC values, as exemplified by the data in Figure 4.

As mentioned briefly above, the temperature of the pour-in-place surface had a small but reproducible effect on its HIC value. The data in Figures 11 and 12 show HIC values for three drop locations as a function of surface temperature. These data were collected in a single playground, beginning early in the morning when the temperature was cool until the last measurements were made during the heat of the day (Figure 11), or starting in the hottest part of the afternoon with measurements lasting until just after sundown (Figure 12). At all three locations, the HIC values increased with increasing temperature. The largest increases were at location #1 in Figure 11, where the HIC values increased approximately 20 percent as the surface temperature rose from 52 to 114 degrees

Fahrenheit. Counterintuitively, the surface became harder as it warmed and softer as it cooled.

To substantiate the findings regarding surface temperature, two series of drops were performed at location #1 over a range of fall heights, one at a surface temperature of 49 degrees Fahrenheit and one at 108 degrees. Figure 13 shows that the higher temperature was associated with higher HIC values at every drop height, and that the temperature effect increased with increasing fall height. Thus, the surface was consistently harder at the higher temperature. This temperature experiment was repeated at a second playground (playground II, Figure 14), over a lower range of HIC values (approximately 200 to 500) compared to playground I in Figure 13 (approximately 400 to 2000). As for playground I, every fall height in playground II gave higher HIC values when measured at the higher temperature. The smaller temperature effect in playground II may have been due to the smaller temperature difference: 36 degrees F for playground II compared to 59 degrees F for playground I. These results demonstrate the importance of controlling the temperature of these surfaces for obtaining consistent HIC values. In addition, these data indicate that testing pour-in-place surfaces for compliance with the ASTM standards is best done on warmer days rather than cooler days, to help ensure that the surface is compliant throughout the entire year.

## **Discussion**

### **Extent and nature of injuries**

A total of 1,299 Californians (presumably children) were admitted to California hospitals in 2003 due to fall-related playground injuries (California Department of Health Services, 2006). The USCPSC estimates that for each playground injury requiring hospitalization, there are at least 22 emergency room “treat and release” playground injuries (USCPSC, 2006). Therefore, there were an estimated  $1,299 \times 22 = 28,578$  fall-related playground injuries in California in 2003 serious enough to require an emergency room visit. Thus, injury due to falls in the playground represents a significant public health problem. Furthermore, since fall-related injuries comprise about 80 percent of all playground injuries (Tinsworth and McDonald, 2001), impact-attenuating surfaces represent an effective means for reducing the playground injury rate. (Chalmers et al., 1996; Mott et al., 1997; Mowat et al., 1998).

However, care must be taken to ensure that such safety surfacing is thick enough and installed correctly to provide sufficient impact attenuation (U.S. CPSC, 1997). Various standards have been promulgated to help achieve this goal. California is one of the few states with regulatory playground surface safety standards. The Code of Regulations, sections 65700 through 65750 specify compliance with the U.S. CPSC Handbook for Public Playground Safety (Publication Number 325, 1997) and ASTM standard F1487-98 (ASTM, 1998), both of which cite ASTM standard F1292. It is F1292 (ASTM, 2004) that specifies the actual physical measures of impact attenuation ( $G_{\max} \leq 200$  and  $HIC \leq 1000$ ) and the methodology for their measurement. Prior to our work, none of the playground surfaces comprising this study had been tested after installation to determine compliance with these regulatory standards.

### **Development of the regulatory standard**

$G_{\max}$  is the maximum deceleration produced by contact between the falling Triax2000 headform and the surface. HIC is derived by transforming the deceleration versus time data and integrating under the curve (ASTM, 2004). Both values have a history of use by

those concerned with predicting head injury, including the automotive and airline crash test communities (Bandak et al., 1996; Nahum and Melvin, 2002) and the sports helmet industry (Camacho et al., 2001; Duma et al., 2005). However, significant uncertainty is associated with the use of these measures to predict serious head injury. This uncertainty is due to many factors, including the limited dataset used to define the relationship of  $G_{max}$  and HIC to serious head injury, and a general paucity of child head injury data. Evidence indicating that as children develop, their skulls become harder (Goldsmith and Plunkett, 2004) and their brains become more viscous (Thibault and Margulies, 1998) illustrates the difficulties raised by this gap in child head injury data. Nonetheless, ASTM standard F1292 states that a playground surface must have a  $G_{max}$  value  $\leq 200$  and an HIC value  $\leq 1000$ .

An HIC value of 1000 is associated with a risk of critical head injury from a head-first fall of from 5 percent (ASTM, 2004) to 16 percent (Prasad and Mertz, 1985). The threshold for fatal head injury has been estimated as low as HIC = 840 to as high as HIC = 1475 (Cory et al., 2001). To give an idea of how high the HIC = 1000 value is, the mean HIC value for an impact to the football helmet of an NFL player that resulted in a concussion was 400, while the blows of an Olympic boxer produced HIC values below 100 (Viano et al., 2005). ASTM F1292 states that playgrounds with surfaces not meeting the standard should be closed until the surface is brought into compliance.

#### **$G_{max}$ vs. HIC**

Since values for  $G_{max}$  and HIC were collected for every test drop performed with the accelerometer, it was a simple matter to plot these data to study the relationship between these two parameters. Figure 3 shows that for the rubber surfaces made of recycled tires, the HIC values tended to increase faster than the  $G_{max}$  values. As a result, the HIC = 1000 standard was often exceeded while the corresponding  $G_{max}$  value remained in compliance at  $\leq 200$ . In fact, in no instance either on rubber or any other material did the surface pass the HIC standard pass but fail the  $G_{max}$  standard. Thus, it may well be a general finding that the HIC = 1000 standard is a more sensitive test of playground surface impact attenuation than the  $G_{max} = 200$  standard.

#### **Compliance as a function of fall height**

Plotting the HIC data from Figure 2 as a function of fall height (Figure 4), there is a clear trend towards a greater HIC failure rate as the fall height increases. These data also illustrate a generally large degree of variability in the HIC values associated with any given fall height. For example, at a fall height of slightly less than eight feet, the HIC values range from less than 500 up to almost 2000. While a number of explanations are possible for these HIC failures and variability, we believe the simplest one is that of a failure to install a surface of sufficient thickness. This was shown to be the case for the loose-fill surface in Figure 10, where a rubber layer of varying thickness yielded a number of high HIC values.

This hypothesis is also supported by the finding that surfaces under some quite high play structures easily passed the HIC standard. For example, one structure just over nine feet tall yielded two drops with HIC values around 500 (Figure 4). Two structures over eleven feet tall also had surfaces that were in compliance at some or all drop locations. From these observations, we conclude that rubberized surfaces under high playground structures can be constructed to meet the HIC standard. The determining factor in surface thickness may only be cost, not technological infeasibility or absence of a performance standard.

In comparison to rubberized surfaces, surfaces of wood chips yielded HIC values that were always in compliance with the standard, and the HIC values at any given fall height appeared to vary less than those for the rubber surfaces (Figure 4). These results could be explained if wood chips were routinely installed at relatively great depth providing a high degree of impact attenuation. The approximately 10-fold lower cost of installing wood chips compared to pour-in-place rubber provides a possible reason for why municipalities might have the resources to install a surface of great depth out of wood chips but not of pour-in-place rubber.

### **Number and location of failures**

Approximately 33 percent of all playground structures over rubber surfaces failed the HIC standard (Table 33). ASTM standard F1292 states that if a single drop location within the use zone of a single structure fails the standard, then the playground fails and should be closed until the problem is corrected. Since most playgrounds contained multiple structures, the overall failure rate of rubberized surfaces was considerably higher, at 69 percent (Table 33).

To get a better sense of whether failing surfaces were failing at only one or many locations within the playground, the numbers of failing structures per playground were plotted (Figure 6). The data show that many surfaces failed due to a single structure. Thus, correcting these inadequacies might be a cost-effective approach towards bringing these surfaces into compliance. However, other surfaces failed at multiple structures, suggesting that most if not all of the rubberized surfaces in those playgrounds were noncompliant. If, as discussed earlier, this is due to the surfaces being of insufficient thickness, a completely new and thicker surface may be required to bring these playgrounds into compliance. Alternatively, the playground structures could be lowered.

### **Compliance as a function of surface age**

Pour-in-place surfaces made of recycled tires require considerably less day-to-day maintenance than traditional surfaces such as wood chips or sand. In addition, the unitary rubber surfaces are expected to be long lasting, with advertised useful lifetimes of 5-10 years or more. These desirable characteristics are important considerations when deciding whether to pay the relatively high cost of installing a pour-in-place surface. If the useful lifetime of these surfaces is on the order of 10 years or greater, it is important to determine if their impact attenuating properties change as a function of surface age.

For example, a surface that hardens over time in response to environmental factors could be in compliance with F1292 during the first few years following installation, but not in subsequent years. We have addressed this question by comparing the playground structure failure rate to surface age (Figure 7). Because the use of recycled tires in playground surfaces is a relatively recent development, most of the surfaces we tested were less than two years old.

Nonetheless, the failure rates were not significantly different between the first and second years post-installation, suggesting that surface hardness had not changed over this period. However, other explanations are possible. Therefore, to better address the effects of surface age, we also measured surface hardness at the same locations within the same playgrounds over the first two to three months of surface life. There was little or no change in HIC values at three locations in each of two playgrounds (Figures 8 and 9), suggesting that once these pour-in-place surfaces harden, they provide stable impact attenuation.

## Discussion of the head injury standard

As mentioned above, there is much uncertainty associated with the estimate that an HIC = 1000 yields a less than 5 percent risk of critical head injury (ASTM, 2004). Much of this uncertainty stems from the small data set that was used to construct the head injury risk curve (King, 2000; Melvin and Lighthall, 2002). Since only a small subset of these data were from children, application of the HIC standard to predict child head injury is even more problematic (Goldsmith, 1981; Goldsmith and Plunkett, 2004). Thus, a surface with an HIC value that is significantly lower than 1000 may be highly desirable to provide a greater level of protection against critical head injury. In addition, a lower HIC might help protect against minor head/brain injury, which actually comprises 60-80 percent of all head injury, with unknown health consequences over the long term (Fearnside and Simpson, 1997).

An HIC value below 250 has been recommended to reduce the chance of such relatively minor brain injury (Pellman et al., 2003). Looking at the data in Figure 4, it is hard to escape the conclusion that the surfaces of wood chips currently in use in California playgrounds provide a greater margin of safety than those of pour-in-place rubber. This need not be the case, since those same data show that pour-in-place surfaces can be constructed to provide as great a margin of safety as the surfaces of wood chips.

While the HIC was developed to predict serious head injury, a recently published study by Sherker et al. (2005) indicates that reducing the HIC value of a given surface also helps reduce the risk of arm fracture. This is welcome news since arm fracture is a more common playground-related fall injury than head injury (Tinsworth and McDonald, 2001). However, the high coefficient of friction associated with pour-in-place rubber surfaces may increase the likelihood of long bone fractures relative to smoother surfaces or surfaces of loose-fill material. Further studies are needed to address these issues.

In summary, our study indicates that California surfaces made of recycled tires commonly fail to meet the HIC standard for impact attenuation specified in state regulations. It is likely that these failures resulted from installation of surfaces that were not sufficiently thick, given the heights of the play structures in the playgrounds. It seems that a relatively simple way to prevent this would be for future purchasers to require that the installer test the surface after installation, to verify that all structures in the playground had surfaces below that met the HIC standard. Given the temperature dependence of the HIC measurements, it would probably be public health protective to make the measurements on a day when the ambient temperature was near the maximum expected for that location. That testing after installation is rarely done is suggested by our finding that none of the surfaces comprising this study had been tested prior to our work.

## Conclusions

- The head impact criterion (HIC) standard = 1000 was a more sensitive measure of impact attenuation by rubberized playground surfaces than the  $G_{\max}$  standard = 200.
- As the fall height of playground structures increased, the underlying rubberized playground surface was more likely to fail the HIC standard; however, even at fall heights of 9-12 feet, some rubberized surfaces passed the standard.

- Only 31 percent of rubberized playground surfaces (32 tested) passed the HIC standard below every play structure, compared to 100 percent for surfaces made of wood chips (5 tested).
- The large proportion (69 percent) of new rubberized playground surfaces in California not meeting impact attenuation standards represents a missed opportunity for prevention of playground fall injuries, which are estimated to be in the thousands and which include serious trauma such as brain injury.
- Some rubberized surfaces failed the HIC standard at multiple locations, indicating a widespread deficiency in impact attenuation for those surfaces.
- HIC values were not influenced by surface age, either during the first 2-3 months following installation or during the first 2 years.
- HIC values of rubberized surfaces increased with increasing surface temperature; in one playground the HIC value measured at dawn increased almost 20 percent when measured again in the afternoon during the heat of the day.
- These data point out the importance of testing the impact attenuation of rubberized playground surfaces following installation, to ensure that they meet the standards.
- Given the uncertainty associated with the  $HIC \leq 1000$  standard, as well as the seriousness of the endpoint (critical head injury), customers should consider installing rubberized surfaces that provide as low an HIC value as possible.

**Table 33. HIC standard compliance rates (HIC ≤ 1000) for playground surfaces: rubber vs wood.<sup>1</sup>**

	<u>No. tested</u>	<u>percent passing HIC standard</u>
Structures over rubber surfaces	121	67
Structures over wood surfaces	10	100
Entire rubber playground surface	32	31
Entire wood playground surface	5	100

<sup>1</sup>Rubber surfaces were made of recycled tires and wood surfaces were made of wood chips/engineered wood fiber.

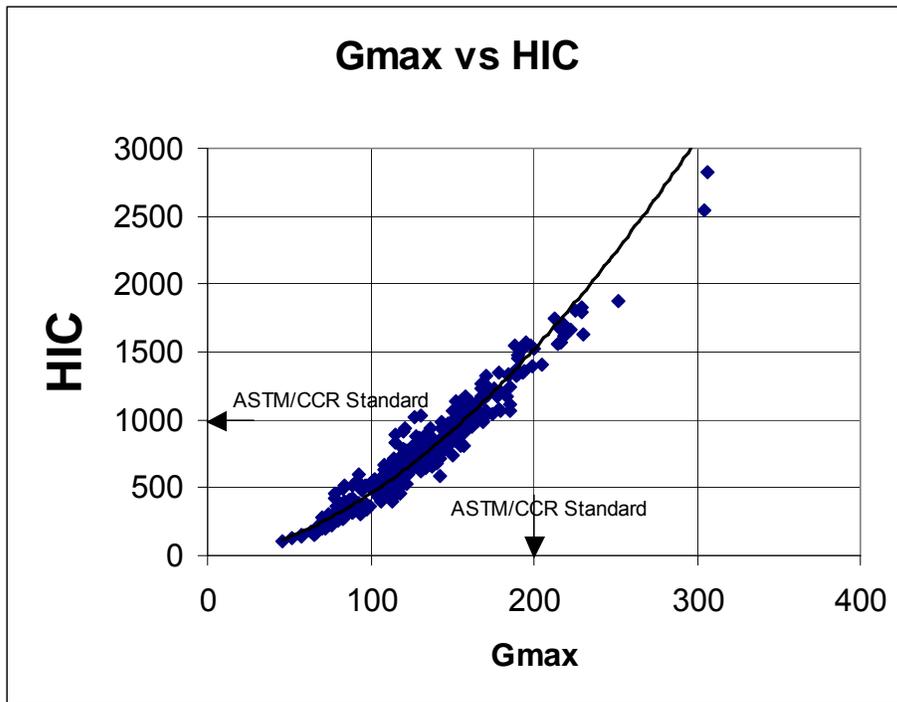
**Table 34. Types of playground structures failing the HIC standard<sup>1</sup>**

	<u>No. of failing structures/No. tested</u>
Standard swings	12/22
Tot swings	8/18
Slides	4/13
Climbers	8/16
Upper body rings	6/11
Platforms	5/29

<sup>1</sup> A total of 121 structures were tested (these six types and other types not shown), with these 43 having at least one HIC value greater than 1000.

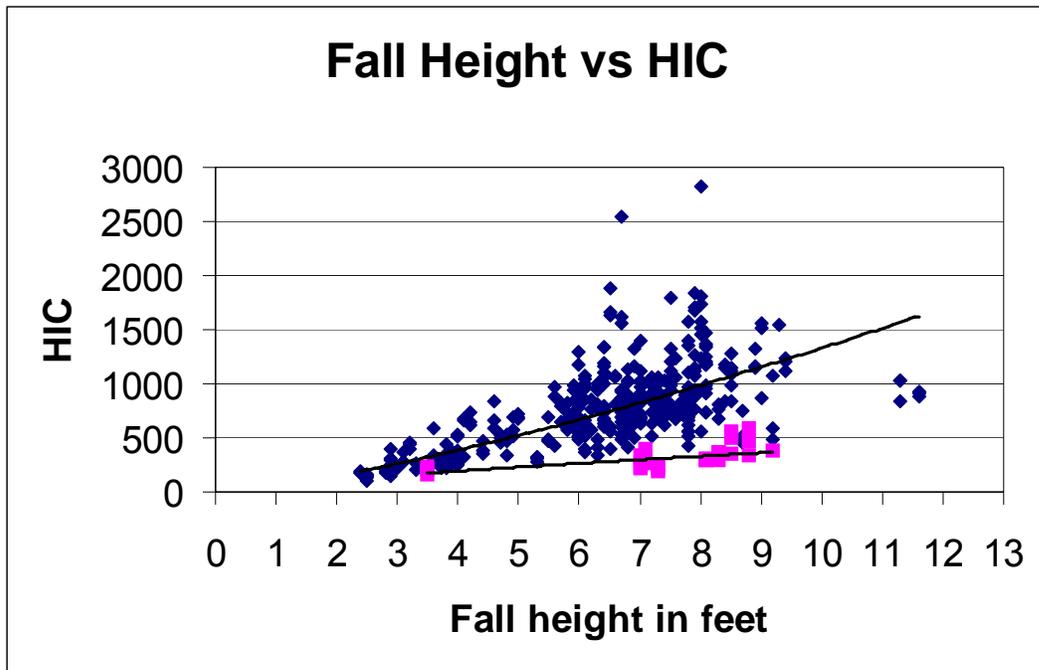


Figure 2: Triax2000 triaxial accelerometer.



**Figure 3: HIC as a function of  $G_{max}$ .**

Data points represent 368 individual drop locations in 32 rubberized playground surfaces (26 pour-in-place, 4 tiles, 2 shredded rubber). The trend line was fitted by regression analysis according to a power function. ASTM/CCR standards:  $G_{max} \leq 200$  and  $HIC \leq 1000$ .



**Figure 4: HIC as a function of playground structure fall height.**

Data points represent individual drop locations in 32 rubberized playgrounds (diamonds) and 5 playgrounds with surfaces of wood chips/engineered wood fiber (squares). Trend lines were fitted by regression analysis according to power functions.

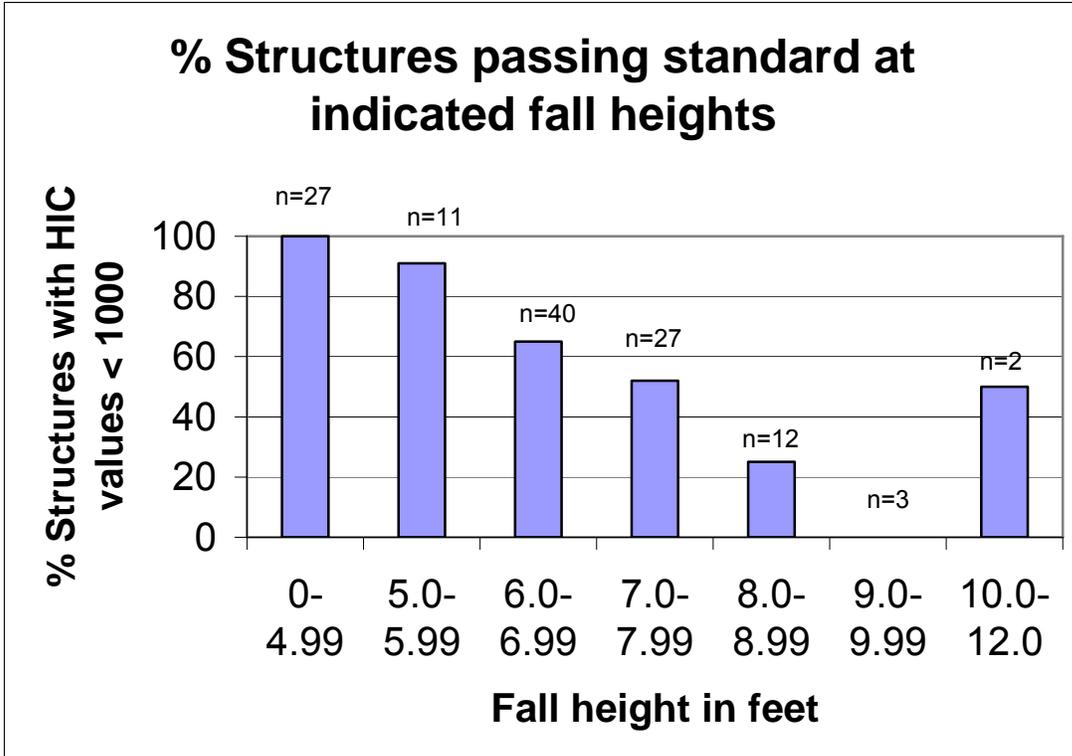
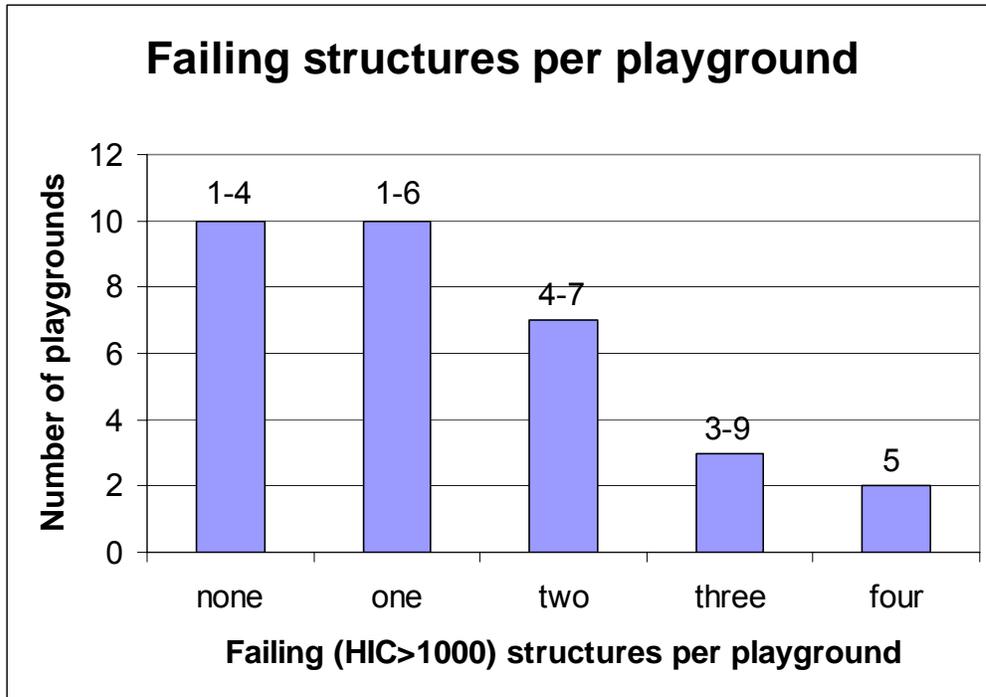
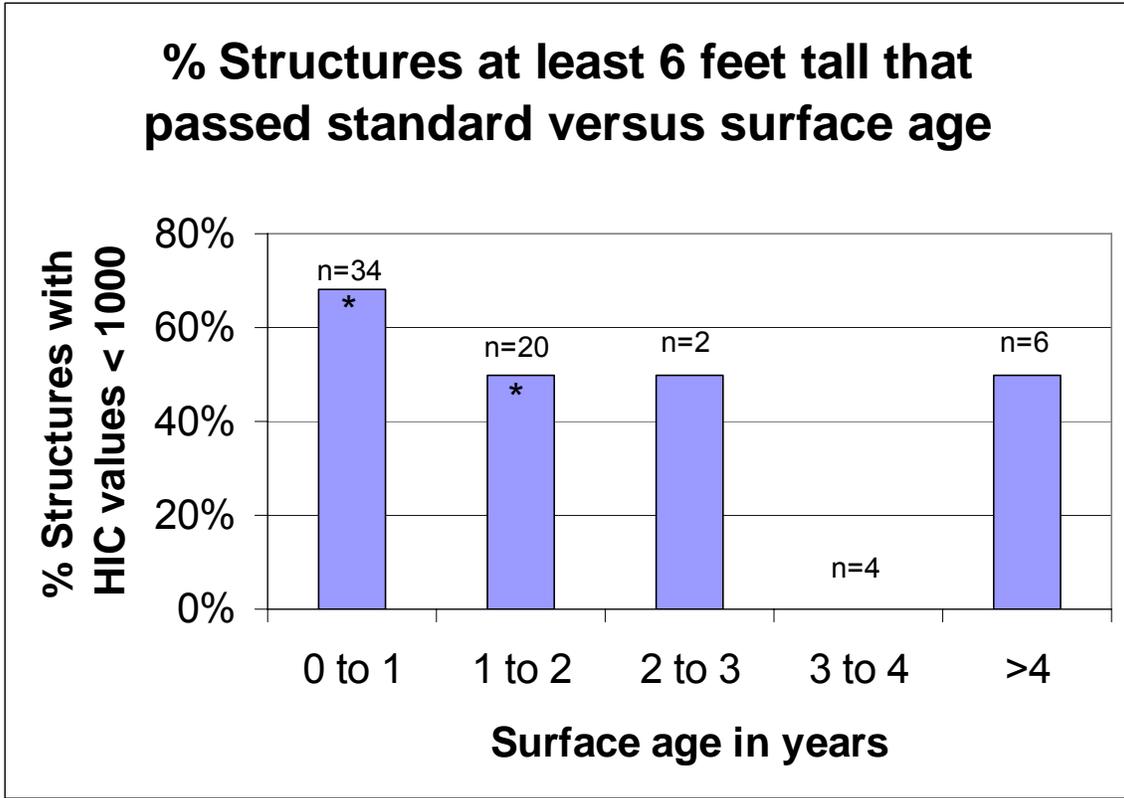


Figure 5: Percentages of playground structures on rubberized surfaces passing the HIC standard at increasing fall height.



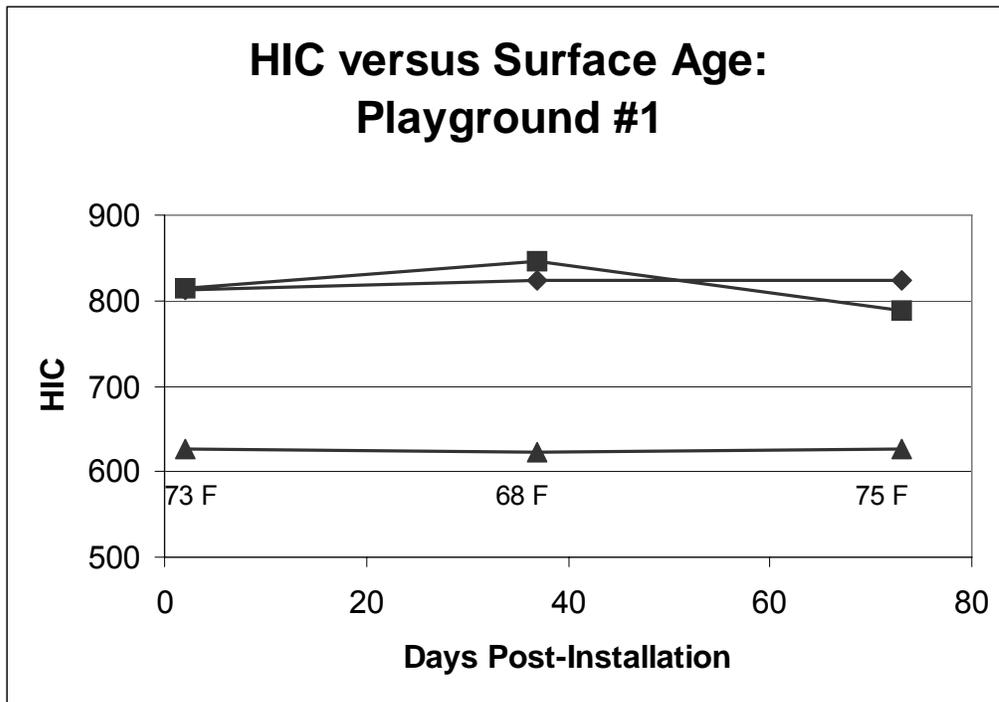
**Figure 6: Numbers of failing structures (HIC > 1000) per rubberized playground surface.**

A total of 131 structures in 32 playgrounds were tested. Ranges at the top of each bar indicate the numbers of structures per playground.



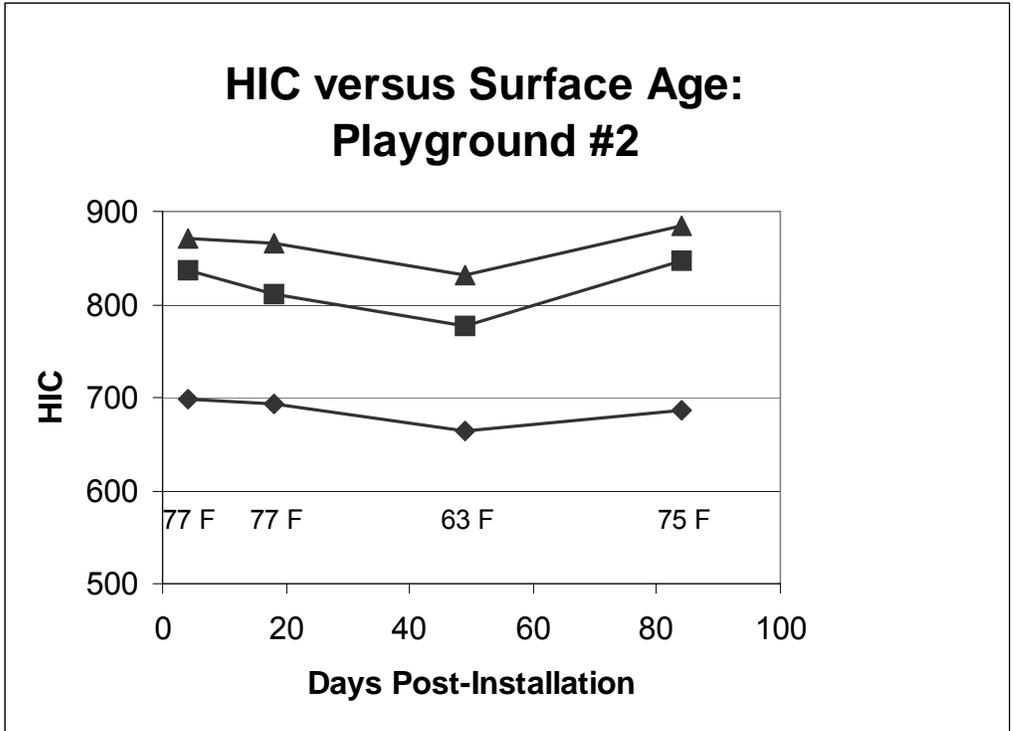
**Figure 7: Percentages of playground structures with fall heights  $\geq 6$  feet yielding HIC values  $\leq 1000$  as a function of rubberized surface age.**

Data from pour-in-place and tiled surfaces were included. Each n represents the total number of structures tested at the indicated surface age. Asterisks (\*) indicate no significant difference between the two bars in a 2-tailed Fisher's Exact Test.

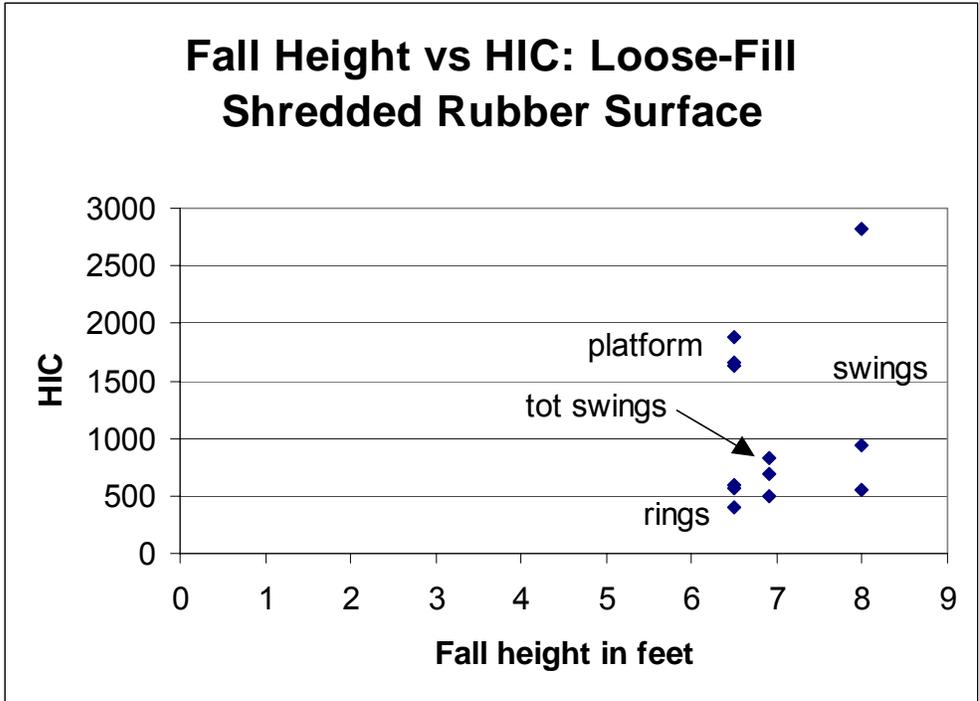


**Figure 8. HIC as a function of surface age during the first two to three months following installation.**

This pour-in-place playground surface consisted of a bottom layer of recycled tire rubber and a top layer of EPDM. At two days after the top layer was poured, HIC measurements were made at three locations (squares, triangles or diamonds) on the surface from a drop height of seven feet. Measurements were repeated on the indicated days at the same locations. The temperature of the air in the shade was recorded on each day as indicated on the graph.

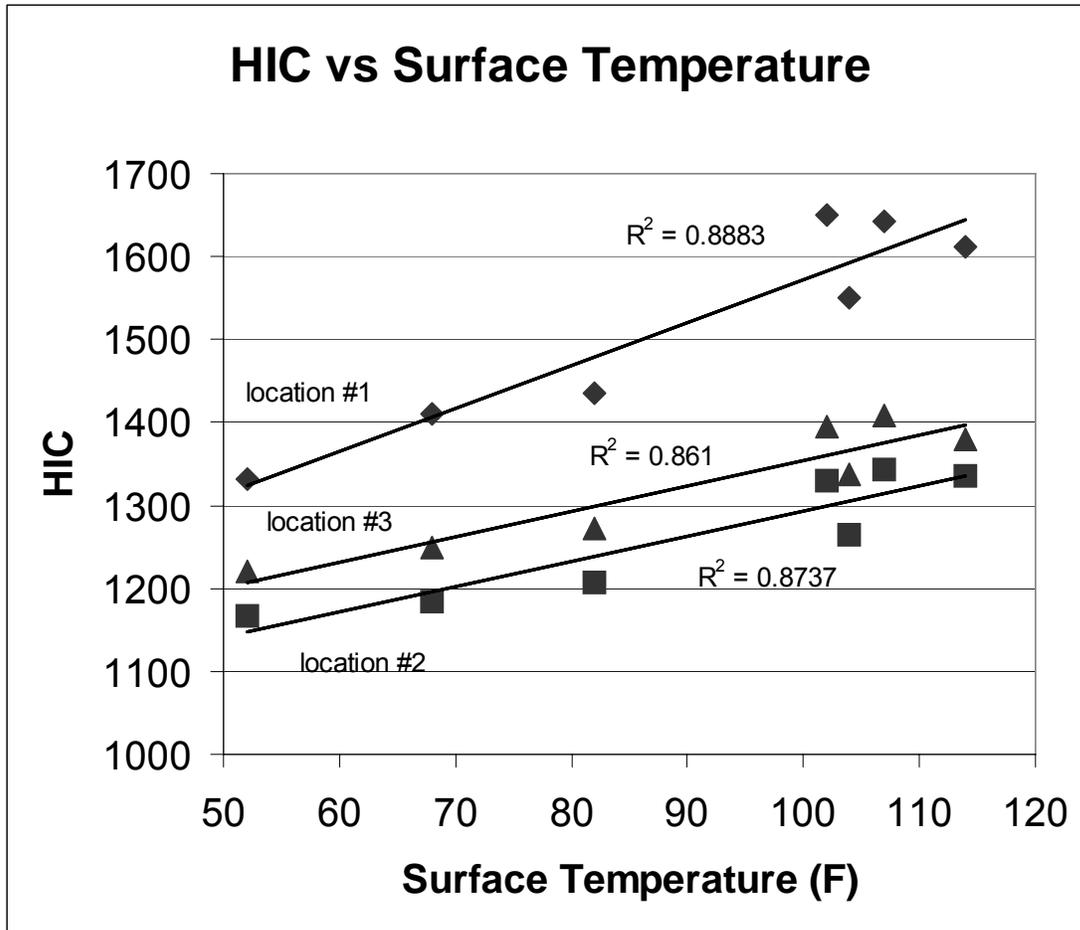


**Figure 9: Same as for Figure 8, except that for this playground the first measurement day was at four days after installation of the top layer.**  
 Three different locations on the playground were followed, represented by the squares, triangles or diamonds.



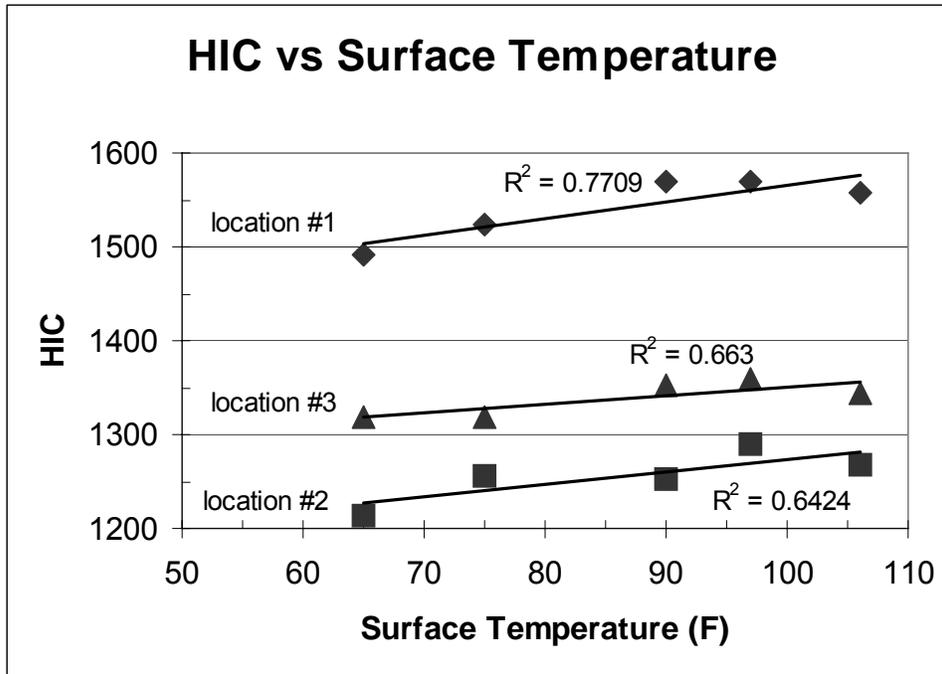
**Figure 10: HIC values for four playground structures on a loose-fill surface of shredded tire rubber.**

Each datum point represents the HIC value for one of three drop locations around each playground structure.



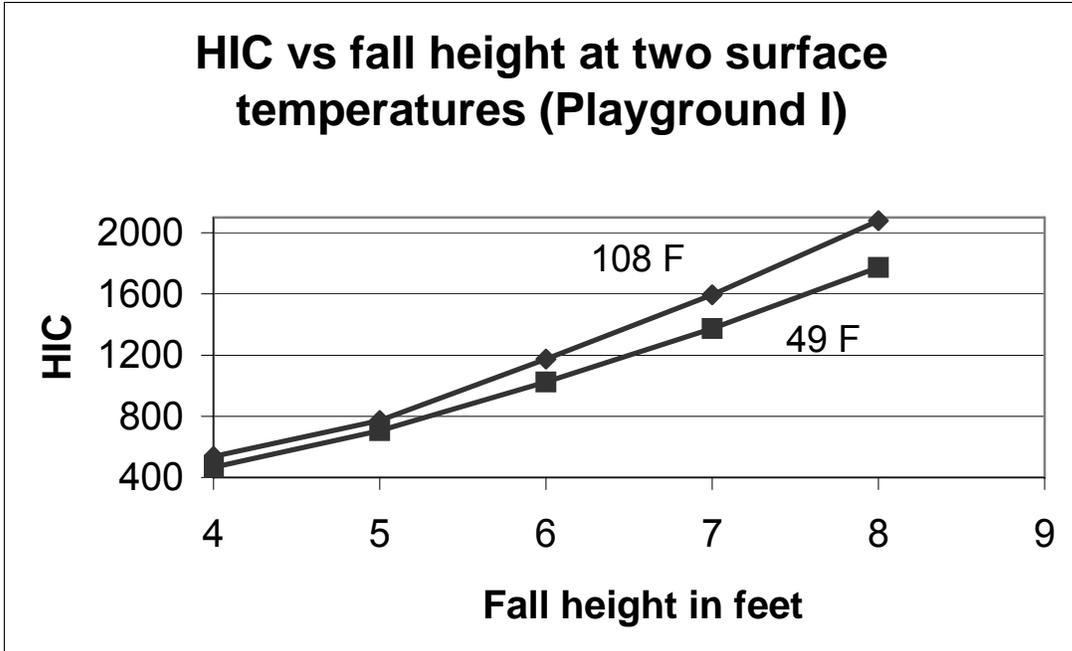
**Figure 11: Temperature dependence of HIC measurements on a pour-in-place surface: cold to hot.**

HIC measurements were made at three locations in a single playground. The drop height was seven feet. Measurements began at 8:00 am in the coolest part of the day, and finished at 2:00 pm during the heat of the day. Curves were fit by linear regression and correlation coefficients are also shown.



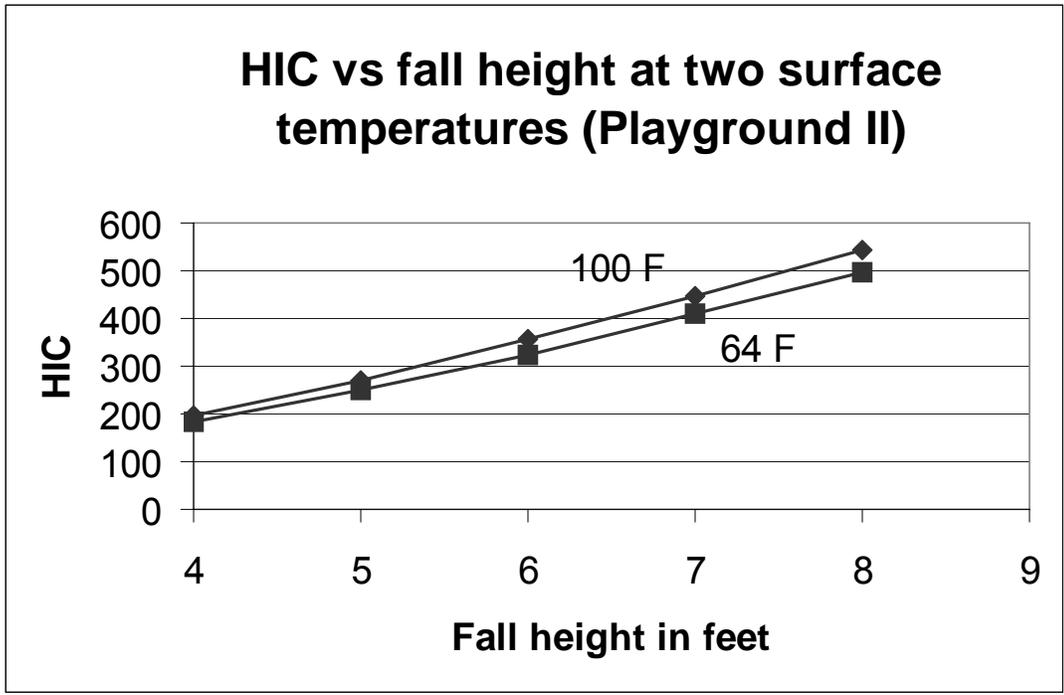
**Figure 12: Temperature dependence of HIC measurements on a pour-in-place surface: hot to cold.**

Same playground and protocol as for Figure 11 except that measurements began at 3:00 pm during the heat of the day and ended at sundown at 7:20 pm. Curves were fit by linear regression and correlation coefficients are also shown.



**Figure 13: HIC as a function of fall height measured at two different surface temperatures: Playground I.**

Drops were performed at the same location #1 shown in Figures 11 and 12. The drops at 108 degrees Fahrenheit were performed during the heat of the day at 2:00 pm, while the drops at 49 degrees Fahrenheit were performed shortly after sunrise at 7:45 am.



**Figure 14: HIC as a function of fall height measured at two different surface temperatures: Playground II.**

Drops were performed at the same location on two different days, with the surface temperature varying by 36 degrees F between.

# Abbreviations

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ASTM	American Society for Testing and Materials International
ATSDR	Agency for Toxic Substances and Disease Registry
C	Centigrade
CCA	Chromated Copper Arsenate
CDC	Centers for Disease Control
cm <sup>2</sup>	square centimeters
CIWMB	California Integrated Waste Management Board
DOT	Department of Transportation
DTSC	Department of Toxic Substances Control
EPDM	ethylene propylene diene monomer
F	Fahrenheit
FCCJNC	Florida Community College at Jacksonville Nassau Center
FDA	Food and Drug Administration
g	grams
GCMS-SIM	Gas chromatography mass spec selective ion monitoring
G <sub>max</sub>	maximum acceleration during impact
GRAS	Generally recognized as safe
HCA	alpha-Hexylcinnamaldehyde
HD	high density
HIC	Head impact criterion
hr	hour
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
kg	kilogram (approximately 2.2 pounds)
kg-d	kilograms per day
l	liter
LD <sub>50</sub>	Lethal dose 50 percent
LOAEL	Lowest observed adverse effect level
m <sup>2</sup>	square meters
m <sup>3</sup>	cubic meters
MADL	Maximum Allowable Dose Level
mg	milligram

ml	milliliter
mM	millimolar
MRL	Minimal Risk Level
n	number
NAS	National Academy of Sciences
ND	not detected
ng	nanogram ( $10^{-9}$ grams)
NOAEL	No observed adverse effect level
NRC	National Research Council
NSRL	No Significant Risk Level
NTP	National Toxicology Program
OEHHA	Office of Environmental Health Hazard Assessment
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PEL	Permissible Exposure Limit
pg	picogram ( $10^{-12}$ grams)
PHG	Public Health Goal
ppb	parts per billion
ppm	parts per million
PRG	Preliminary Remediation Goal
RDA	Recommended Daily Allowance
REL	Reference Exposure Level
RfC	Reference concentration
RfD	Reference dose
SBR	styrene butadiene rubber
SF	safety factor
SOD	superoxide dismutase
sVOC	semi-volatile organic compound
UF	uncertainty factor
µg	microgram ( $10^{-6}$ grams)
ul	microliter ( $10^{-6}$ liters)
U.S. CPSC	United States Consumer Products Safety Commission
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic compound

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