

Artificial Turf

Exposures To Ground-Up Rubber Tires

Athletic Fields ■ Playgrounds ■ Gardening Mulch



ENVIRONMENT & HUMAN HEALTH, INC.




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ATHLETIC FIELDS ■ PLAYGROUNDS ■ GARDENING MULCH



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THE BOARD OF ENVIRONMENT AND HUMAN HEALTH, INC. IS ESPECIALLY GRATEFUL TO MARYJANE INCORVIA MATTINA, HEAD OF THE DEPARTMENT OF ANALYTICAL CHEMISTRY AT THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION, AND TO THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION FOR THEIR IMPORTANT AND CAREFUL TESTING OF THE GROUND-UP RUBBER TIRE CRUMBS.



Artificial Turf

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I. INTRODUCTION

This report is designed to place health and environmental exposures to ground-up recycled tires (“tire crumbs”) and mulch in a scientifically based qualitative and quantitative context. In the spring of 2007, Environment and Human Health, Inc. received numerous inquiries about health concerns with respect to children’s exposures to ground-up rubber tires that are the in-fill material in the new synthetic turf fields. Such fields have been installed, or are being proposed, in towns all over Connecticut and many other states.

The safety information about the new synthetic fields has mainly focused on the health benefits from the reduction of joint injuries due to the use of the rubber tire crumbs in the new fields. Public health analysis of the health risks from human exposures to the rubber tire crumbs has not been adequately addressed up to this point.

Research shows that the new synthetic fields are surfaced with a product called “in-fill” that is made from recycled rubber tires. This material, referred to as tire crumbs, constitutes the primary playing surface. We estimate these crumbs to be as much as 90% by weight of the fields. The tire crumbs are roughly the size of grains of course sand. They are made by shredding and grinding used tires. Tire crumb materials are spread two to three inches thick over the field surface and packed between ribbons of green plastic used to simulate green grass.



Review of the immediately available literature about these new fields found that similar health concerns had been raised in other states, as well as in other countries. In addition to athletic fields, shredded tires are being used on playgrounds and as gardening mulch.

There have been some studies done on the health effects from exposures to the rubber crumb material, but many of these studies present only partial assessments of the human health risk potential. In addition, many studies have major data gaps with respect to the chemicals released, as well as the actual levels of exposures in humans and the environment.

From the available information, it was found that tire crumbs contained volatile organic hydrocarbons (VOCs) with carcinogenic potential, which could be extracted from the crumbs in the laboratory. Health reports from workers in the rubber fabrication industry and in the rubber reclamation industry describe the presence of multiple volatile organic hydrocarbons, semi-volatile hydrocarbons, and other toxic elements in the air. Studies at tire reclamation sites report the leaching of similar sets of chemicals into the ground water. Occupational studies document a spectrum of health effects, ranging from severe skin, eye, and respiratory irritation to three forms of cancer.¹

The relationship between exposures affecting the rubber workers and those experienced by people using athletic fields, or children in playgrounds covered with ground-up rubber tire material is not known, but we do know that many of the same chemicals that rubber workers are exposed to are being released from the ground-up rubber tire crumbs.

Based on the uncertainty with respect to what these exposures mean for children's health, as well as the environmental leaching of the materials into the ground water, EHHI decided to initiate an exploratory study with the Connecticut Agricultural Experiment Station to determine the chemicals released into the air and water under ambient conditions.



Samples of ground-up rubber tire gardening mulch and tire crumbs used in the new synthetic fields were obtained for laboratory evaluation at the Connecticut Agricultural Experiment Station (see Appendix I). One set of experiments tested the *leaching potential* of the metals from samples of tire crumbs and one sample from commercial rubber mulch.

The second set of experiments tested the *chemicals released* from the tire crumbs used for “in-fill” and commercial rubber mulch. Ten metals were leached from the samples of tire crumbs and the tire mulch in the first experiment. Twenty-five chemical species were identified with 72% to 99% certainty in the mass spectrometry and gas chromatography analysis in the second experiment. Nineteen were identified with over 90% certainty and five with over 98% certainty. Confirmatory studies provided a definitive identification of four of the major chemicals released.



II. TOXICOLOGY AND HEALTH EFFECTS

In this report, Environment and Human Health, Inc. evaluates the information known about the potential health and environmental risks from exposure to crumb rubber made from recycled tires.

Health concerns have been documented in rubber tire fabrication workers that are attributed to exposure to chemicals and dusts. Use of recycled tire shreds or crumbs in athletic fields, gardening and playgrounds involves repeated and direct exposures for both children and adults to tire dust and some chemicals similar to those in tire plants. A comprehensive assessment of the information known about the health risks to the public is necessary to assess safety.

Determination of risks and safety from direct human exposures to mixtures of chemicals and dusts requires a systematic analysis of all data to assure a comprehensive evaluation of the hazard.

LABORATORY IDENTIFICATION OF COMPOUNDS RELEASED FROM TIRE CRUMBS AND RUBBER MULCH

The Connecticut Agricultural Experiment Station report (See Appendix I), found out-gassing and leaching from synthetic turf rubber crumbs under aqueous ambient temperatures. Several compounds were present, but four compounds gave the highest responses on GC/Mass spectrographic analysis. The four compounds conclusively identified with confirmatory tests were: *benzothiazole*; *butylated hydroxyanisole*; *n-hexadecane*; and *4-(t-octyl) phenol*. Approximately two dozen other chemicals were indicated at lower levels. These chemicals were released in laboratory conditions that closely approximate ambient conditions.

Those chemicals identified with confirmatory analytical studies at the Connecticut Agricultural Experiment Station study have the following reported actions:

- **Benzothiazole:** Skin and eye irritation, harmful if swallowed. There is no available data on cancer, mutagenic toxicity, teratogenic toxicity, or developmental toxicity.
- **Butylated hydroxyanisole:** Recognized carcinogen, suspected endocrine toxicant, gastrointestinal toxicant, immunotoxicant, neurotoxicant, skin and sense-organ toxicant. There is no available data on cancer, mutagenic toxicity, teratogenic toxicity, or developmental toxicity.
- **n-hexadecane:** severe irritant based on human and animal studies. There is no available data on cancer, mutagenic toxicity, teratogenic toxicity, or developmental toxicity.
- **4-(t-octyl) phenol:** corrosive and destructive to mucous membranes. There is no available data on cancer, mutagenic toxicity, teratogenic toxicity, or developmental toxicity.

The study also detected metals that were leached from the tire crumbs. Zinc was the predominant metal, but selenium, lead and cadmium were also identified.

The identification of toxic actions is based on research reported in the peer-reviewed literature and official listings, such as the Integrated Risk Information System (IRIS) and Toxic Substance Control Act (TOSCA). Many, if not most, of the compounds present in tire crumbs and shreds have been incompletely tested for human health effects. In some cases, a partial assessment can be based on the estimated actions of a chemical class or on structural activity characteristics.

Ascertaining the toxic actions of the chemicals identified in the analytical test is dependent on the levels of research that have been performed and reported in the appropriate literature. A qualitative analysis usually precedes the quantitative analysis to determine potency.


CANCER

Some of the compounds are identified as known or suspected carcinogens. The following is a discussion of the toxicity and health effects of the agents that have been released from tire crumbs under different conditions. The strongest data available with respect to cancer come from the International Agency for Research on Cancer's study of the rubber industry.² Strong and sufficient evidence for cancer in humans was demonstrated in a series of epidemiology studies of rubber fabrication facilities throughout the world. Cancer was also found in some other locations, but the data on exposures were insufficient to attribute a specific work task or exposure to the cancer.

One especially relevant report addressed exposures in a factory in Taiwan that made tire crumbs. In that study, mutagenic actions that were four to five times higher than in controls were shown in extracts of particulate matter collected in the air. These results indicate that the organic-dissolved portion of rubber particles contains various nitre-containing vulcanization stabilizers and accelerators, as well as process degradation products. Benzothiazole and 9-octadecenamide were identified as structures that would be converted to the N-nitrosamines under certain conditions.³

An unpublished 2006 Rutgers University study of tire crumbs taken from synthetic turf fields in New York City identified six polycyclic aromatic hydrocarbons (PAHs) at levels that reportedly exceeded the regulatory levels in New York State. These six compounds are highly likely to be carcinogenic to humans. The researchers caution that the availability of the carcinogens in the rubber is not established because solvent extraction was used to release the chemicals from the tire crumbs.





The Office of Environmental Health Hazard Assessment (OEHHA) of the California Department of Health prepared a report on potential risks, including carcinogenesis, from the use of recycled tire materials on playgrounds.⁴

A literature review of studies of the release of chemicals from recycled tires in laboratory settings and field studies found 49 chemicals, seven of which were carcinogens.

In a study that modeled gastric digestion 22 chemicals were identified.⁵ Hand-to-mouth activity was examined using wipe samples; researchers found four polycyclic aromatic hydrocarbons (PAHs) and one metal, zinc. There also were 46 separate laboratory or field studies that reported either volatile organic compounds (20 studies), semi-volatiles (20 studies), or metals (29 studies). Some mentioned particulate collection.

ALLERGIC RESPONSES

Allergies are addressed in studies from both California⁶ and Norway,⁷ indicating a moderate level of health concern. Inadequate data are available to address the concerns about allergic reactions, but it is possible that sensitized individuals will respond to the exposures. With so many children having asthma today, this is a real concern.

Furthermore, the Norway study⁸ indicates high levels of latex exposures from the tire crumbs and recommends that such fields not be installed because of the high prevalence in the population of latex sensitivity.

SKIN, EYE, AND RESPIRATORY IRRITATION

Skin, eye, and respiratory irritation is the most common action identified in the literature for these chemicals.⁹ That probably reflects the regulatory requirement for such testing before the chemical can be shipped in commerce. These studies are the most basic of the toxicology testing schemes expected for materials with continuous human exposures. Based on the chemical structures of the aliphatic chemicals present, it is not surprising that they are listed as severe irritants. The irritation potential of aliphatic compounds increases with chain length up to 10 carbons and with increased branching of the molecules.

THYROID EFFECTS AND NEUROLOGICAL EFFECTS

Other actions reported are thyroid effects, neurological effects, and systemic toxicity related to the liver and the kidneys. There is insufficient exposure information to assess whether these effects would be seen with the releases from ground-up recycled tires used on synthetic turf fields or in gardening mulch.

RELEASE OF METALS TO ENVIRONMENTAL MEDIA

The metals zinc, cadmium, and lead were also identified as contaminants from tire rubber released into ground water.¹⁰ With the exception of zinc, there are insufficient data to assess the health or environmental risks of any of these metals. It appears clear that the zinc levels are high enough to be phytotoxic if they enter the ground water or soil. It is doubtful that there is any human toxicity from zinc at the levels reported, but such a conclusion would have to be tested by more careful study.

PARTICULATES RELEASED TO THE AIR

Finally, the particulate exposures due to tire dust and chemicals contained in the dust that can be released in the lungs are especially troublesome. Nearly every test adequate to assess the risk that was reported found one or two dozen compounds released from particulates.¹¹ There are processes in the body that can release the chemicals contained in the rubber particles. Moreover, potent carcinogens are found in the tire dust. Only the assumption of limited exposure could support the conclusions of low cancer risk.

SUMMARY OF TOXIC ACTIONS

In summary, the toxic actions of concern from the materials that were released from recycled crumb rubber include:

- Severe irritation of the respiratory system
- Severe irritation of the eyes, skin and mucous membranes
- Systemic effects on the liver and kidneys
- Neurotoxic responses
- Allergic reactions
- Cancers
- Developmental effects



OTHER REPORTS ON RUBBER TIRE CRUMBS WITH ANALYTICAL DATA

A report from the Swedish Chemical Agency (KEMI) lists the materials in tires.¹² Tires contain over 60 different substances—40% is rubber; the rest is carbon black, high aromatic oils, sulfur and various metals. Rubber is elastic polymers. The most common types of synthetic rubber are styrene-butadiene rubber and ethylene propylene rubber. Vulcanizing agents are used in manufacture, and fillers, antioxidants and plasticizers are added for technical properties. A large number of high aromatic oils are added, including polyaromatic hydrocarbons, phthalates that can leach into water, phenols, metals including zinc, and low concentrations of lead.

Synthetic turf often contains rubber granules from waste tires, which in turn contain several particularly hazardous substances. Therefore, the Swedish Chemical Agency recommends that rubber granules from waste tires not be used in synthetic turf.



Other reported findings from environmental or laboratory testing, including direct analytical analysis of tire crumbs, are summarized in the California Report (OEHHA)¹³ and the Norwegian Public Health Report.¹⁴ These reports document the findings of volatile organic compounds, semi-volatile compounds, PAHs, and metals. These findings are listed in the tables of these reports (see Appendix I).

Both the OEHHA report and the Norwegian study summarized the known non-cancer actions of the volatile, semi-volatile and metal compounds released into the environment by recycled tire crumb rubber and mulch. The listed information included primarily classifications of acute toxicity and irritation. Few of the chemicals have been classified for possible long-term effects and allergies. Although both studies attempted to determine the possible health risks from projected exposures, their evaluations are restricted by an assumption of a single life-time exposure to 10 grams of tire crumbs or less (OEHHA) or estimated daily average exposures from periodic exposures of three to five weekly uses of synthetic turf fields.¹⁵

EHHI cautions that both of these exposure assumption approaches could underestimate the actual exposures that would occur by orders of magnitude. Even using these assumptions, human health effects were projected for acute and cancer effects of certain of the identified compounds.

The most striking limitation of both the Norwegian and OEHHA studies is the lack of needed data on the actions of some of the more prevalent semi-volatile compounds, such as benzo-thiazole. In fact, these chemicals are not included in the health analysis in either health assessment, which is a serious limitation because the compounds are important components of the chemicals that are released.

III. DISCUSSION OF RISK ASSESSMENTS

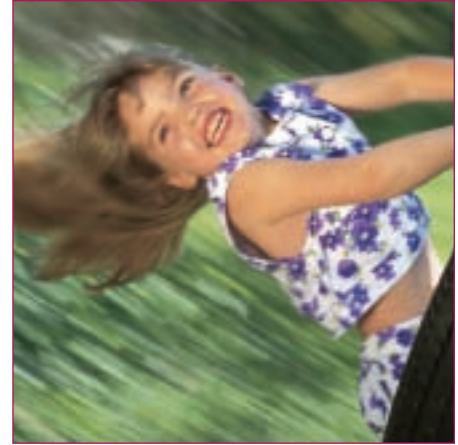
Four assessments that reviewed the information available from reasonably reliable sources are discussed below. The release of materials under ambient conditions was determined. The chemicals of concern were identified and the toxic actions listed. An attempt to determine the exposure potential was made and the human risk assessed. All four studies are limited by the application of the assessments only to the expected environmental and public health impact from crumb rubber at synthetic turf fields and the use of rubber mulch.



PEDIATRIC STUDY OF TIRE CRUMB USE ON PLAYGROUNDS

*“Case Study of Tire Crumb Use on Playgrounds: Risk Analysis and Communication When Major Clinical Knowledge Gaps Exist”*¹⁶

The report from the U.S. Environmental Protection Agency notes that children’s exposures may potentially occur by ingestion of tire crumbs or water, inhalation of the dust, or skin contact. Traditional published scientific literature identified one study, Birkholtz et al. (2003),¹⁷ which examined human and ecosystem hazards, and one or two other studies, but could not establish the products’ safety for children. Essentially no specific information was available regarding exposure to crumb rubber constituents from use on a playground. In addition to discussion of potential risks with parents who call with concerns, the authors do advocate for more relevant research.



CANADIAN EVALUATION OF HAZARD ASSESSMENT OF TIRE CRUMBS FOR USE ON PUBLIC PLAYGROUNDS¹⁸

A cooperative agreement developed between the Alberta Centre for Injury Control and Research and the Recycling Management Association of Alberta determined the potential exposure of children to surface runoff and puddles. The authors assumed that the potential for oral ingestion is unlikely, that the product is washed and thus free of dust, and that the only exposure pathways are skin contact and ingestion. Both were deemed unlikely and were not measured. The mutagenicity of solvent extracts of the tire crumbs was used to assess the carcinogenic potential. It was concluded that the limited response in the mutagenicity study ruled out the potential for cancer. No quantitative exposure data were collected to support either conclusion.

NORWEGIAN INSTITUTE OF PUBLIC HEALTH STUDY¹⁹

This study, discussed previously, used measured air levels of chemicals and an exposure model developed for participants in a building with synthetic turf. Although the study was limited by the absence of necessary toxicity data, it showed a potential for exposures and assessment of the level of risk. The approach used is more relevant for cancer risk assessment than for non-cancer risk assessment. Latex allergy was identified as the major risk. Margins of safety were calculated for each compound identified. The application of averaged exposures probably caused a 10-fold or greater reduction in the actual margin of safety in acute or short-term exposures.

CALIFORNIA OEHHA RISK ASSESSMENT FOR PLAYGROUND EXPOSURE²⁰

This study, described previously, considered single acute exposures by ingestion and chronic hand-to-mouth exposures for 22 chemicals found to be released by tire shreds. The individual

non-cancer risk was calculated by comparison to regulatory acute exposure levels. Seven of the 13 metals tested did not have acute exposure levels, so the risk could not be determined. Five of the eight VOCs lacked comparison data and seven of the eight semi-volatiles tested lacked comparison data. Even given this limitation, there were groups of chemicals that exceeded the hazard index of 1. The cancer risk assessment compared the accepted risk level for a single lifetime exposure to recycled rubber crumbs.

THE FRENCH STUDY

“Health Evaluation of the Use of Elastomer Granulates as Filling in Third-Generation Artificial Turf 2007”²¹

This study was conducted by ALIAPUR, the leading French government body responsible for used tires, along with ADEME, the French Agency for Environment and Energy Management.

“The main goal of the study was to determine the quality of water transferred into the natural environment after passing through the rubber granules and other infill materials from the artificial grass sports fields. In addition, the study obtained a detailed analysis and evaluation of the gas emissions generated by these fields.”



A Health Risk Evaluation (HRE) was performed by the French National Institute for Industrial Environment and Risks (INERIS) “in order to evaluate more precisely, in indoor situations, the health risks linked to the inhalation of the VOC and aldehydes of which these emissions have been quantified by the scientific and technical center of France.”

The study concludes with the statement: “the INERIS stipulates that the health risks associated with the inhalation of VOC and aldehydes emitted by artificial grass fields in outdoor situations give no cause for concern towards human health.”

It is necessary to examine the actual support for this conclusion of “no risk.” The authors base their conclusion on a chamber study in which 2.25 kilograms of used rubber tire crumbs were maintained at a temperature of 23 degrees centigrade (about 70 degrees F) for 28 days. VOC levels of 1,600 grams per cubic meter were found on day one and declined to under 200 grams per cubic meter on day 28. (Dimensions of the quantitative finding are vague in the report). The authors used the 28-day measure in which 112 different compounds were identified. Of the 112 released, the report examined the health risk of only 16 of the chemicals released into the chamber. The authors developed an indoor model to justify the dilution of the actual concentrations found and estimated the risk relative to that of a building materials code.



EHHI concludes that a test on a single sample of 2.25 kilograms of tire crumbs selected after 28 days of “conditioning”—and tested at 70 degrees F in a chamber—could not possibly be representative of the releases that would occur on a hot summer day when a synthetic turf field can reach temperatures of over 130 degrees F.

As well, evaluation of only 16 of 112 compounds released is simply inadequate to conclude that there are “no health risks.” Furthermore, such testing strategies will be of no value in assessing the health risks from “synthetic turf fields” to which several tons of rubber tire granules have been added. This study contains too many flaws, as well as problematic health risk endpoints, to be considered a credible human health evaluation study.

COMMENT ON THE STUDIES

These four studies and others provide useful information about the scale of the risk, **but none of the studies is sufficiently robust to be used in a public health safety evaluation.**

POTENTIAL FOR EVALUATION OF THE ACTUAL HEALTH RISK

The available information is sufficient and strong enough to raise plausible questions with respect to acute toxicity for susceptible persons, and for cancer risks. However, the status of the information about human exposures to recycled tire crumb rubber in-fill and gardening mulch is not sufficient to determine the safety of the use of the product in situations that involve continuous episodes of human exposure.

Given the complexity of the exposures, the limited research information on the actual toxic actions of these chemicals, and the limited experience with human exposures at sites other than tire fabrication facilities, identification of maximal safe exposure levels is not scientifically possible. Some researchers have compared projected exposures to background exposures in ambient air,²² but it is known that many of these compounds, such as the PAHs, are considered health risks in ambient air. There is little other than the Norwegian study²³ to give a scale to the potential exposures. A rough approximation can be obtained from the information in the Connecticut Agricultural Experiment Station study.



Before applying maximal safe exposure assumptions, it is necessary to actually identify the toxic actions of concern. Allergens are one example of exposures that are problematic for susceptible populations.

ESTIMATE OF THE SCALE OF EXPOSURES TO BENZOTHIAZOLE FROM TIRE CRUMB IN-FILL ON A SOCCER FIELD



The exposure potential on a soccer field could be quite large. A square foot of a field with between two and three inches of in-fill would have between five and seven kilograms of tire crumbs, which translates to between 11 and 15 pounds. If the findings from Table 2 in the Connecticut Agricultural Experiment Station study (page 30) are used as a reference, the emissions from the square foot of surface would approach four to six grams on a hot day when the surface approaches 60 degrees C (140 degrees F). Considering the actual size of the soccer fields, that would be substantial release into the ambient air. Actual exposure measurements are needed to determine the potential inhalation risks for players on the field or for spectators and nearby residents.

This same scale of analysis is needed for each of the agents shown to be released and the respirable dusts. If the tire crumbs are carried into a building or an automobile, similar analysis is necessary. EHHI has concluded that the currently available information is sufficient to raise plausible concerns for health risks, but is insufficient to determine how large those risks are.

PROBLEM STATEMENT

The use of recycled rubber as in-fill on athletic fields, as gardening mulch, or subsurface fill under playground equipment involves direct exposures by children and adults to dusts and chemicals that would be released from the tire crumbs. A review of findings from the currently available reports on health and safety found important gaps in the information needed to determine the public health and environmental risks involved. The following is not fully known for ground-up rubber tire products:

- What are the chemicals actually present in the exposure pathways
- How great is the release of chemicals present in rubber dust under the conditions of use
- What are the toxic actions of the chemicals that are released
- What is the amount of exposure(s) from inhalation, dermal contact or ingestion

The gaps in the available information make it difficult to determine whether the proposed use of recycled tire crumbs in playing fields or playgrounds can be deemed safe.

ADDITIONAL COMMENTS ON THE INADEQUACIES OF PRIOR STUDIES

A program to replace current grass playing fields with synthetic turf fields is underway in Connecticut and other states. The information supporting this effort essentially contains only the health benefits from reduction of injuries due to falls. The potential risk from human and environmental chemical exposures is not known. In its place are general reports with nonspecific data, such as that from the Consumer Product Safety Commission's *Handbook for Public Playground Safety*.²⁴

Although chemicals had been shown to be released from recycled tire in-fill, the Consumer Product Safety Commission (CPSC) inferred that "Oral ingestion is deemed to be low in overall hazard because ingestion of the tire crumbs on the ground is not likely and the gastrointestinal system is unlikely to be efficient in extracting toxic chemicals from tire crumbs." The CPSC report continues, "Tire crumb does not contain chemicals with high vapor pressures; thus, exposure via inhalation is deemed inconsequential and the resulting hazard is negligible.... Cancer hazard measured in *in vitro* predictive assays was deemed negative." In a single test, 3/4-inch pieces of tire chips sent to a testing laboratory to be tested with acid (stomach acid) resulted in the following report: "Visual examination of insoluble residue appeared to indicate only fibrous reinforcing strands were dissolved by the hydrochloric acid. The tire rubber did not appear to be affected in any way."



Based on that test, the CPSC concludes, "Therefore if a piece of rubber is swallowed it should not cause any acute or chronic problems." The report then goes on to discuss leaching and other data based on a single test and cites references with limited applicability to the determination of the risk from exposures. **None of the data are at the level needed for public health assessment.**

In contrast to the CPSC report, studies from the Norwegian Institute of Public Health and the Radium Hospital, 2006,²⁵ cited information showing that dozens of volatile organic compounds off-gas from tire crumb in-fill and are carried in respirable dust particles released from in-fill during playing of sports in an indoor arena. Similarly, the California OEHHA report²⁶ summarized 46 studies in the scientific literature that identified 49 chemicals released from tire crumbs. Seven of the chemicals leached from tire shreds were carcinogens. OEHHA calculated a cancer risk of 1.2 in 10 million based on a *one-time ingestion* of the tire crumb rubber over a lifetime.

OEHHA also conducted a gastric digestion experiment that found 22 chemicals were released. Five of the chemicals released were carcinogens. OEHHA concluded that the risk would be below the one in a million risk level considered to be acceptable. However, the analysis posits that there would only be one single exposure in a lifetime and extends the cancer risk over the lifetime. This is saying that a person would have only one exposure, which in the opinion of EHHI is unlikely.

The frequency of exposures from the use of tire crumbs in playing fields and gardens is not known, but would almost certainly exceed once in a lifetime. Both the Norwegian study and the California report describe attempts to assess the overall risk from the use of tire crumbs on synthetic turf and playgrounds, respectively. In both cases, the lack of reliable exposure measures and the absence of relevant toxicological tests restrict the quantitative determination of the actual health hazards.

A report from Switzerland by Hans J. Kolitzus,²⁷ cautions that the “the real effect of sports surfaces on sites to the environment cannot be determined using lab tests.” The report seems to caution that although no toxicity has been documented to date, the studies needed to evaluate the risk are not complete. EHHI concludes that neither the Norwegian study nor the OEHHA study is sufficient to determine the health risks to humans.

OCCUPATIONAL HEALTH DATA FROM THE MANUFACTURE OF TIRE CRUMBS

An occupational study in a Taiwan scrap-tire shredding plant²⁸ identified volatile organics and particulates in the air that were “frame shift” mutagens. While the report cited epidemiological studies of rubber workers showing acute and chronic respiratory effects, including reduced lung capacity, and increased risk of laryngeal, bladder, lung and skin cancers, no health studies had been done in workers in tire-shredding plants. With the exception of the more volatile solvents, similar types of chemicals are found in shredding facilities and manufacturing plants.



The scrap-tire shredding facility’s assessment listed materials present in the air. The volatile organics found include styrene, benzothiazole, phthalate esters and naphthalene. Airborne particulates in the respirable range constituted amines, aniline, quinoline, amides, and benzothiazole. Mass spectrographic analysis identified eight chemicals in the air, categorized as aromatic, ketone, monomer PAHs and esters. Octane, decane, benzene, toluene ethylbenzene, xylenes and ethyl methyl benzenes were also found. The particulate

contained 12 types of chemicals, including three amines, two additives, two amides, two PAHs, two acids and two esters. The results indicated that the organic-dissolved portion of rubber particles included nitre-containing vulcanization stabilizers and accelerators, as well as process degradation products.

EHHI concludes that the chemicals found in the air in tire-shredding facilities should also be considered to be potential contaminants at sites that use crumb rubber in-fill and gardening mulch, but at lower concentrations. The studies cited in the Norwegian and California reports support this conclusion.

PLAYGROUND SAFETY REPORTS

The OEHHA report²⁹ also addressed potential risks from the use of recycled tire materials on playgrounds. That study evaluated the release of chemicals that could cause toxicity on dermal contact in children. The report contains a literature review of studies that measured the release of chemicals from recycled tires in laboratory settings and field studies. Of the 49 chemicals listed, seven were carcinogens. Twenty-two chemicals were identified in a study that modeled gastric digestion. As noted earlier, a component of the OEHHA study that looked at hand-to-mouth activity using wipe samples found four PAHs and one metal, zinc. This study identified 46 separate laboratory or field studies that reported VOCs, semi-volatiles, and metals, and also mentioned particulate collection. There were three general groups of substances released: 15 metals, 20 volatile organic compounds, and 14 semi-volatile compounds.



The previously cited study by Birkholz et al.³⁰ concludes that there is little potential for exposure to cause adverse health effects in children and that no chromosome-damaging chemicals were present with solvent extraction. It does note slight aquatic toxicity. EHHI is concerned about the limited level of the exposure assessment performed in this study and by the sharply different findings from those found in more detailed studies that do identify both the presence of carcinogenic chemicals and mutagenic responses in recycled tire crumbs.

OTHER HIGHLY RELEVANT RESEARCH

Findings from two studies reported on the internet are important. The first is a report by William Crain and Junfeng Zhang (2007) that found carcinogenic PAHs released from tire crumb in-fill at levels that exceeded New York State Contaminated Soil limits. The findings of that study are totally consistent with the work cited by the Norwegian report, the California OEHHA report and the occupational report from Taiwan.

The second study, by Stuart Gaffin at Columbia University's Center for Climate Systems Research,³¹ determined that the temperature present on playing field tire crumb in-fill during summer afternoons approached 160 degrees F.



The findings from the study in Norwegian indoor sports facilities show a strong increase in the release of chemicals into the air with increased temperature, although none of the arenas in the study approached temperatures as high as those reported in New York.

In South Korea, the Ministry of Education and Human Resources Development has initiated a study of the safety of synthetic turf fields that have been installed in 605 elementary, middle, and high schools. The study is a response to complaints from teachers of nose and eye irritation and contact dermatitis, and complaints of headaches from both teachers and students.³²

Other reports in the literature cite current ongoing work to address the public and governmental concerns about potential exposures to recycled tires. One report from Norway³³ concluded that the use of recycled tire in-fill should be discontinued, based on a latex allergy concern.

Although the California report cited an animal study that did not find a positive response in animals, there is concern that types of allergic response cannot be properly tested in animal skin-exposure protocols. It is likely that, when allergens are inhaled by persons sensitized to latex, a systemic rather than contact response will be induced. Higher levels of latex allergy have been found in persons who live near highways. This is because the source of latex is in tires.

EHHI concludes that, given the significance of the potential health concerns, the findings that there are toxic chemicals and particulates present in areas that use recycled tires, the serious gaps in exposure information, and the partial information on the toxic actions of the chemicals released into the environment, *further assessment is absolutely necessary if the public is to be protected.*

Important policy questions raised with respect to tire rubber require analysis of both exposure potential and the toxicity of the mixture of components in air, soil, and dust. The question is thus addressed within the context of the contaminants of concern associated with exposure to the materials released, the health concerns of the communities with potential exposure, and the identification and quantitative assessment of the pathways of completed and potential exposures. The integration of these components constitutes a health hazard assessment on which health recommendations are based.

IV. HEALTH HAZARD ASSESSMENT

In order to determine the potential exposures, the first steps are to determine the completed pathways and the chemical agents released into the environment media.

IDENTIFICATION AND ASSESSMENT OF THE PATHWAYS OF COMPLETED AND POTENTIAL EXPOSURES

There are four components of completed exposure pathways:

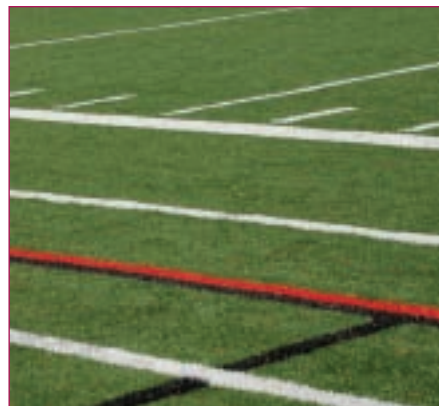
- Environmental media and transport
- Points of exposure
- Routes of exposure
- Receptor population

SYNTHETIC TURF EXPOSURE

With respect to the tire crumbs on synthetic turf fields or rubber tire mulch, both products can release compounds that are potentially carried to humans through direct contact or airborne dust. Indirect contact through surface or ground water runoff or contamination of local drinking water wells is also of concern. For the athletic playing fields, points of exposure occur primarily during athletic activities, while application of rubber mulch to gardens can cause contamination of ground water as well as soil.

Certain activities involve higher potential for exposures than others, such as playing contact sports or calisthenics that involve stretching on the ground. Inhalation of respirable particulates was found to be an important pathway in occupational settings and in closed arenas with synthetic turf fields.

Thus there are three routes of direct human exposure, but the primary one appears to be inhalation of dust and vapors. Dermal contact is also possible for those compounds that are leached from the tire materials or those that are allergens. Finally, ingestion by children or infants who come into contact with the materials might occur through accidental swallowing of the small tire crumbs found on new synthetic fields. Release from material in shoes has also been posited. Receptor populations include the student body of schools, teachers or members of athletic teams, and persons coaching or observing the contests.



GARDENING EXPOSURES

Gardeners and landscape personnel would similarly have dermal and potential inhalation contact with the rubber materials and material in dust or vapors while spreading mulch. Although rubber tire mulch and crumbs have been marketed as inert materials, off-gassing has been conclusively demonstrated by the Norwegian study.³⁴ However, there are no studies in the peer-reviewed academic literature that determine the human exposures from mulching activities.



A further factor to be considered is that the excessive amount of zinc found in ground-up rubber tires proves to be toxic to plants. “Tire manufacturing involves addition of zinc oxide to strengthen the rubber. Although zinc is essential for plant growth, most landscape soils... already contain adequate levels. Therefore, addition of zinc from any source may cause more problems than it resolves. Ground rubber, as either a mulch or a media amendment, increases the potential of zinc toxicity, especially when coupled with application of micronutrients in the fertilizer.”³⁵

CONTAMINANTS OF CONCERN ASSOCIATED WITH THE RUBBER TIRE CRUMBS AND RUBBER MULCH RELEASED INTO THE ENVIRONMENT

The purpose of this step in the health assessment is to identify chemical exposures that are likely to occur and determine the individual toxicity.

Four components that identify contaminants of concern include identification of:

- the compounds present
- the toxic actions of the individual compounds
- the toxic potency of compounds
- the maximal safe exposures levels

STUDIES THAT SHOULD BE VIEWED WITH CAUTION

Some risk assessments infer minimal health risk based on an assumption that exposures do not occur or are minimal, or that recycled tire crumbs are stable in the gastrointestinal (GI) tract. The studies cited in the background from Norway and California OEHHA clearly show that **neither** assumption is correct. The Connecticut Agricultural Experiment Station Report, 2007, conclusively identified four compounds that are released under ambient conditions in aqueous media. Other reports, as well, show that release of volatiles occurs under ambient conditions.

The Birkolz study³⁶ tested the use of tire crumbs on playgrounds. Exhaustive extraction of tire crumbs was used to obtain material for genotoxicity tests. Marginal toxicity—a 1.5-fold increase in response for some of the test species—was reported. Birkholtz concludes that “no DNA or chromosomal-damaging chemicals were present.” The authors go on to conclude that “ingestion of tire crumbs by small children will not result in unacceptable hazard of contracting cancer.”

In the human health hazard discussions, the authors further speculate that “Tire crumb does not contain chemicals with high vapor pressures; thus, exposure via inhalation was deemed inconsequential and the resulting hazard negligible.” The authors continue, “A carrier solvent more efficient than water would be needed to extract toxic chemicals from tire crumb in quantity and a non-polar vehicle skin layer for significant absorption would be required to penetrate protective skin layers.”



EHHI notes that the confirmed findings of emissions from aqueous solution at temperatures found in ambient exposures from the Connecticut Agricultural Experiment Station study would cause that statement to be viewed with extreme caution. Actual test data show that the rationale that the material is inert and not available is based on the flawed premise of biological unavailability of carcinogens.

The French Study, conducted by ALIAPUR, the leading French government body responsible for used tires, along with ADEME, the French Agency for Environment and Energy Management, also has major flaws. As discussed earlier in this report, EHHI concludes that testing a single sample of 2.25 kilograms of tire crumbs selected after 28 days of “conditioning”—tested at 70 degrees F and in a chamber—could not possibly be representative of the releases that would occur on a hot summer day, when a synthetic turf field can reach temperatures of over 130 degrees F.

In addition, evaluation of only 16 of 112 compounds released is simply inadequate to conclude that there are “no health risks.” This study not only has testing flaws, but also contains problematic health risk endpoints.

V. SUMMARY AND CONCLUSIONS

The Connecticut Agricultural Experiment Station study conclusively demonstrates that the tire crumbs and tire mulch release chemical compounds into the air and ground water. Thus, tire crumbs constitute a chemical exposure for humans and the environment.

It is clear that the recycled rubber crumbs are not inert, nor is a high-temperature or severe solvent extraction needed to release metals, volatile organic compounds, or semi-volatile organic compounds. The release of airborne chemicals and dust is well-established by the current information. The Connecticut Agricultural Experiment Station research conclusively demonstrates that release can occur under ambient conditions experienced in the summer in Connecticut.

Those published health assessments that indicate *de minimis* risk should not be applied to the synthetic turf paradigm and may not be appropriate for playgrounds with open layers of recycled tire crumbs.



Health endpoints of concern are numerous, including acute irritation of the lungs, skin, and eyes, and chronic irritation of the lung, skin, and eyes. Knowledge is somewhat limited about the effects of semi-volatile chemicals on the kidney, endocrine system, nervous system, cardiovascular system, immune system, developmental effects and the potential to induce cancers.

There are still data gaps that need to be filled in and additional studies are warranted.

It is prudent to conclude that there will be human exposures to chemicals released during the use of synthetic turf fields.

The excess amount of zinc in the rubber tire mulch makes it unacceptable to be used in gardens.



VI. RECOMMENDATIONS

- There is enough information now concerning the potential health effects from chemicals emanating from rubber tire crumbs to place a moratorium on installing any new fields or playgrounds that use ground-up rubber tires until additional research is undertaken.
- Exposures to already installed synthetic turf fields that contain ground-up rubber tire crumbs should be limited, pending the development of additional human exposure information.
- Synthetic turf fields should not be used on very warm days, as they can become extremely hot, sometimes reaching 140 degrees F.
- People who have a history of asthma or other allergic reactions should be careful when using fields or playgrounds containing ground-up rubber tires until additional information is available to assure that the released materials will not cause allergic reactions.
- People who are allergic to latex should be especially careful when using these fields or playgrounds because some rubber tires contain large amounts of latex.
- When weighing children's exposures to ground-up rubber tires, efforts to reduce their exposures over time should be considered.
- States should consider a detailed analysis of all health and environmental risk factors from recycled rubber tires in all their proposed uses.
- An epidemiological study of health effects, including skin irritation and allergic responses, should be conducted.
- The North Carolina Department of Agriculture's study shows that ground-up rubber tire mulch increases the potential of zinc toxicity and indicates that it is unsuitable for use in production of nursery plants. Therefore, EHHI is in agreement with this study and others that recommend ground-up rubber tire mulch not be used for gardens.

VII. APPENDIX I

Connecticut Agricultural Experiment Station's Report

EXAMINATION OF CRUMB RUBBER PRODUCED FROM RECYCLED TIRES

http://www.ct.gov/caes/lib/caes/documents/publications/fact_sheets/examinationofcrumbrubberac005.pdf

AC005 (8/07)

EXAMINATION OF CRUMB RUBBER PRODUCED FROM RECYCLED TIRES

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Introduction

In June 2007 the Department of Analytical Chemistry at the Connecticut Agricultural Experiment Station (CAES) was contacted by Environment and Human Health Inc. (EHHI), a non-profit organization headquartered in the greater New Haven area, to ascertain if our laboratory would be willing to examine crumb rubber produced from used tires. The product in question has been gaining widespread use as an enhancement on athletic fields constructed from artificial turf; other applications, such as on play areas for children, are also common. Private citizens questioned EHHI as to the human health and environmental neutrality of the product. The data to answer the inquiries were not available (Anderson et al., 2006).

Figure 1 shows the crumb rubber infill on a synthetic turf field. The photo is of an actual field installed in Connecticut and was provided to us by EHHI.

Given time and personnel limitations, the Department of Analytical Chemistry at the CAES agreed to conduct a very modest study of the material. Funding in the amount of \$2000 was received from EHHI to offset the cost of items such as analytical and instrumental supplies and chemical standards. This fact sheet contains scientific information, described in detail below, derived from the preliminary study. The experiments were conducted by Dr. Mehmet Isleyen, with contributions from Dr. Saim Ozdemir, both visiting scientists from

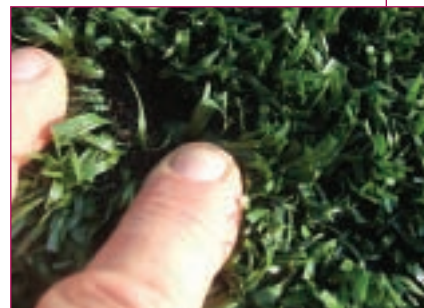


Figure 1

Sakarya University, Engineering Faculty, Environmental Engineering Department, Sakarya, Turkey, and with substantial input from William Berger of the Department of Analytical Chemistry. Dr. MaryJane Incorvia Mattina, the head of the Department of Analytical Chemistry, supervised the work.

Approach

It was deemed that answers to the following questions could be obtained within the time limitation imposed:

1. Are compounds volatilizing or out-gassing from the tire crumbs?
2. What is the identity of the volatilized compounds derived from the tire crumbs?
3. Can organic or elemental components be leached from the tire crumbs by water?

Experimental Details and Data

The crumb rubber examined is shown in Figure 2 and was provided to our laboratory by EHHI; the scale at the top of the photo is in centimeters (2.54cm/inch). Most of the crumbs were black, irregularly shaped particles <3mm in any dimension, although smaller particles may be seen in the photo. The material also contained lesser amounts of white crumbs similar in physical appearance to the black particles and presumed to be tire-derived rubber. The product was examined as received without any previous exposure to field conditions.

Because of the substantial interest in this project, considerably more experimental details are provided in this fact sheet than is typical for such a publication. Experiments were conducted in the laboratory under conditions which approximated field conditions for parameters such as temperature and leaching solvent. The method relied on solid phase micro-extraction (SPME), a well-known and reliable analytical technique (Zeng and Noblet and references therein). The SPME fiber used was coated with 100um thick polydimethylsiloxane (Supelco number 57342-U).



Figure 2

1. Are compounds volatilizing or out-gassing from the tire crumbs?

To obtain the data to answer this question 0.25g of tire crumbs were transferred to a glass, 2mL automated liquid sampling (ALS) vial. The vial was capped and the septum pierced with the SPME needle. The SPME fiber was exposed for 42 minutes to the headspace over the tire crumbs while the vial was warmed in a heating block to 60 °C. At the end of this period the SPME fiber was removed from the vial and desorbed in the inlet of a gas chromatograph (GC, Hewlett Packard model 6890) at 260 °C. A 30m X 0.25mm DB-5MS+DG column (J&W Scientific) was interfaced to the mass spectrometer (MS, Hewlett Packard model 5973) detector. The GC oven was programmed as follows: initial temperature 40 °C for 5 min, ramped at 2 °C/min to 50 °C, ramped at 5 °C/min to 160 °C, ramped at 10 °C/min to 300 °C and held for 10 min. Figure 3 shows a portion of the

total ion chromatographic (TIC) trace typically obtained from several replicates of this experiment. Peaks were identified using high probability matching of the actual mass spectrum with that in the NIST library supplied with the software.

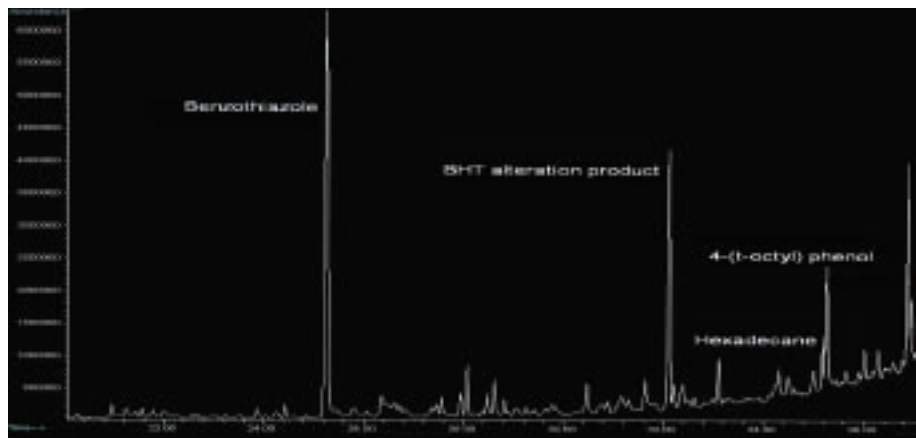


Figure 3

Using this approach of spectral matching several compounds were identified, some of which are summarized in Table 1:

Table 1. Organic Compounds Volatilizing from Tire Crumb

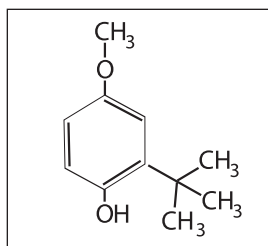
NAME	CAS NUMBER	RETENTION TIME (min)	STRUCTURE
Benzothiazole	95-16-9	25.2	
Butylated hydroxyanisole	25013-16-5	32.7	
n-hexadecane	544-76-3	35.2	
4-(t-octyl) phenol	140-66-9	35.3	

2. *What is the identity of the volatilized compounds derived from the tire crumbs?*

In order to confirm positively the four compounds cited in Table 1 which have good match between the archived NIST spectrum and the spectrum recorded in this experiment, authentic

standards were purchased from Sigma Aldrich. Solutions of the compounds were prepared in methanol and used to spike approximately 0.6 grams clean glass beads in 2 mL ALS vials. The same SPME procedure described above to collect volatile compounds from the tire crumbs was used to collect volatile compounds from the headspace over the spiked glass beads. The GC/MS analytical settings were also the same. The identity of the four compounds was confirmed with retention time (RT) match as well as mass spectral match. In order to assure that the compounds were not artifacts from laboratory background nor from any of the supplies used in the method, the following experiments were performed: (i) several consecutive desorptions of the SPME fiber in the GC inlet; (ii) SPME analysis of the headspace over clean glass beads in an ALS vial; (iii) SPME analysis of the headspace over glass beads in an ALS vial spiked only with methanol. None of the four compounds listed above was detected in any one of these three trials.

A comment must be made regarding butylated hydroxyanisole. Analysis of the purchased standard (Sigma catalogue number B1253-5G) resulted in detection of three peaks: RT=32.1, RT=32.5, RT=32.7 (major component). It should be noted that the structure matching this CAS number does not indicate a specific position of attachment of the t-butyl group relative to the hydroxyl group as shown above in Table 1. However, CAS 121-00-6 does correspond to 3-t-butyl-4-hydroxyanisole having the structure



Based on the mass spectral library match, we conclude that the compounds at RT 32.5 and 32.7 correspond to the two diastereomers of butylated hydroxyanisole. A search of the literature strongly suggests that the compound at RT 32.1, which has ions at m/z 236, 221, 205, 180, 165, 137, is 2,6-di-t-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (Brumley et al., 1989) designated as an alteration product of 2,6-t-butyl-4-methylphenol (BHT). Peaks at the three RTs for analysis of the standard were found as well in the analysis of the tire crumbs.

Experiments were conducted to determine approximate gas phase concentrations of the organic compounds which volatilized or out-gassed from the crumb rubber. In this trial standards at different concentrations were spiked onto glass beads in ALS vials and the SPME procedure conducted. Calibration curves were constructed using the spiked standards from which gas phase concentrations of the compounds of interest in the vapor phase over the tire crumbs were determined. We make the assumption that due to the non-porous nature of the glass beads, the entire amount of the organic compound spiked onto the glass beads volatilized into the gas phase in the ALS vial. From the original amount spiked and the volume in the vial remaining after the

volume of the beads is subtracted, we can calculate the amount of the compound in the headspace over the tire crumbs. These data in Table 2 should be considered a first approximation.

Table 2. Vapor phase concentrations of compounds out-gassed from crumb rubber

Compound	ng/mL air	ng/(mL air) normalized per gram of tire
Benzothiazole	225.87	866.72
Hexadecane	1.58	6.04
4-(tert-Octyl)-phenol	5.64	21.63
Butylated hydroxyanisole or BHT alteration product	13.89	53.32

3. Can organic and elemental components be leached from the tire crumbs by water?

To determine if materials of interest are extractable from the crumbs, portions of the crumb rubber were soaked over time in distilled, deionized water at ambient laboratory temperature in capped high density polyethylene (HDPE) jars. Approximately 17g of crumbs were soaked statically in 50mL water for seven weeks. After this period the leachate was filtered and 1.5mL transferred to ALS vials. The same SPME procedure was carried out as described above. A typical TIC trace for the headspace analysis is shown in Figure 4.

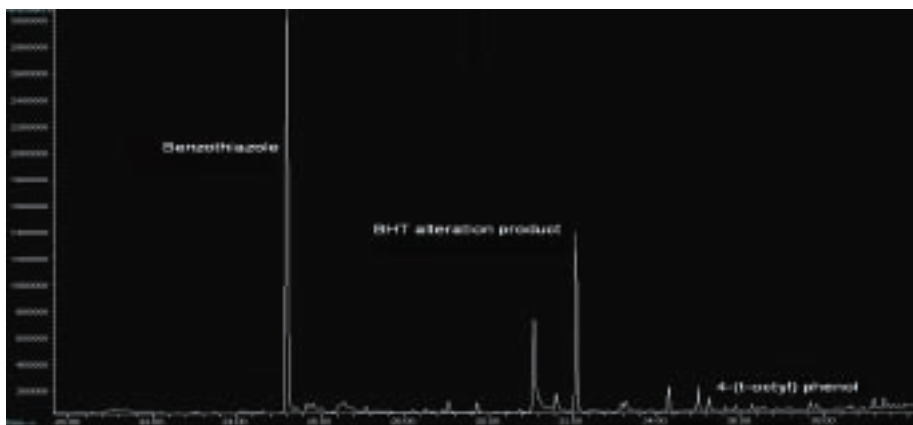


Figure 4

Figure 4 should be compared with Figure 3. Although relative amounts of the compounds of interest differ under the two experimental conditions, the same compounds are noted in both Figures. If the SPME fiber is immersed directly into the leachate rather than exposed to the headspace over the leachate and then desorbed in the GC inlet, the same set of compounds as shown in Figure 4 was detected.

We now provide the experimental procedures used to determine if elements are leachable into aqueous solution from the crumbs. In this case 2.0 grams of crumbs were transferred into 40mL of water in 50mL centrifuge tubes. The tubes were sealed and agitated on a wrist action shaker at ambient temperature for 18 hours. Following this agitation the tubes were centrifuged for 10 minutes at 3000rpm and the leachate was analyzed using inductively coupled plasma mass spectrometry (ICP/MS, Agilent model 7500ce). In a second regime the leaching water was acidified to pH 4.2 prior to the 18 hour agitation. This procedure is based on conditions recommended in EPA SW-846 Method 1312. Pertinent data, averages of four replicates for each trial, are presented in Table 3.

Table 3. Elements leached into water from crumb rubber

Element	Amount in water ($\mu\text{g}/\text{kg}$ tire)	Amount in acidified water ($\mu\text{g}/\text{kg}$ tire)
Zinc	20957	55010
Selenium	246	260
Lead	1.85	3.26
Cadmium	0.07	0.26

Conclusions

The laboratory data presented here support the conclusion that under relatively mild conditions of temperature and leaching solvent, components of crumb rubber produced from tires (i) volatilize into the vapor phase and (ii) are leached into water in contact with the crumbs. We note with interest that when we placed the black crumbs in direct sunlight at an exterior air temperature of 88 °F, a thermometer inserted directly into the crumbs registered 55 °C (=131 °F). Selection of 60 °C, therefore, is not beyond a reasonable temperature range accessible under field conditions.

Based on these data further studies of crumb rubber produced from tires are warranted under both laboratory, but most especially field conditions. In particular examination of compounds volatilizing from the crumbs under exterior conditions and collected at varying heights and seasonal conditions at installed fields should be compared with background levels. It is also logical to determine airborne particulate matter deriving from the product under the same conditions.

References

- M. E. Anderson, K. H. Kirkland, T. L. Guidotti, and C. Rose. A Case Study of Tire Crumb Use on Playgrounds: Risk Analysis and Communication When Major Clinical Knowledge Gaps Exist. *Environ. Health Persp.* 114: 1-3 (2006).
- W. C. Brumley, C. R. Warner, D. H. Daniels, S. Varner, J. A. Sphon. Electron Impact Mass Spectrometry of BHT and its Alteration Products. *Biomed. Environ. Mass Spectrom.* 18:207-217 (1989).
- Y. Chien, S. Ton, M. Lee, T. Chia, H. Shu, Y. Wu. Assessment of Occupational Health Hazards in Scrap-tire Shredding Facilities. *Sci. Total Environ.* 309: 35-46 (2003).
- E. Y. Zeng and J. A. Noblet. Theoretical Consideration on the Use of Solid-Phase Microextraction with Complex Environmental Samples. *Environ. Sci. Technol.* 36: 3385-3392 (2002).



APPENDIX II


TESTING METHODS

Samples of gardening mulch and tire crumbs were obtained for laboratory evaluation. One set of experiments tested the **leaching potential** of the metals from samples of tire crumb in-fill and one from commercial rubber mulch. The second set of experiments tested the **chemicals released** from the tire crumbs and the commercial rubber mulch. Ten metals were leached from the samples of tire crumbs and tire mulch in the first experiment. Twenty-five chemical species were identified with 72% to 99% certainty in the mass spectrometry and gas chromatography analysis in the second experiment. Nineteen chemicals were identified with over 90% certainty and five at over 98% certainty. Confirmatory studies provide a definitive identification of four of the major chemicals released. Below is an excerpt from the Connecticut Agricultural Experiment Station's report on their methods.

“To determine if materials of interest are extractable from the crumbs, portions of the crumb rubber were soaked over time in distilled, deionized water at ambient laboratory temperature in capped high density polyethylene (HDPE) jars. Approximately 17 g of crumbs were soaked statically in 50 ml water for seven weeks. After this period the leachate was filtered and 1.5 ml transferred to ALS vials. The same SPME procedure was carried out as described above. A typical TIC trace for the headspace analysis is shown in Figure 4.

Figure 4 should be compared with Figure 3. Although relative amounts of the compounds of interest differ under the two experimental conditions, the same compounds are noted in both Figures. If the SPME fiber is immersed directly into the leachate rather than exposed to the headspace over the leachate and then desorbed in the GC inlet, the same set of compounds as shown in Figure 4 was detected.

We now provide the experimental procedures used to determine if elements are leachable into aqueous solution from the crumbs. In this case 2.0 grams of crumbs were transferred into 40 ml of water in 50 ml centrifuge tubes. The tubes were sealed and agitated on a wrist action shaker at ambient temperature for 18 hours. Following this agitation the tubes were centrifuged for 10 minutes at 3000 rpm and the leachate was analyzed using inductively coupled plasma mass spectrometry (ICP/MS, Agilent model 7500ce). In a second regime the



leaching water was acidified to pH 4.2 prior to the 18-hour agitation. This procedure is based on conditions recommended in EPA SW-846 Method 1312.

The laboratory data presented here support the conclusion that under relatively mild conditions of temperature and leaching solvent, components of crumb rubber produced from tires (i) volatilize into the vapor phase and (ii) are leached into water in contact with the crumbs. We note with interest that when we placed the black crumbs in direct sunlight at an exterior air temperature of 88° F, a thermometer inserted directly into the crumbs registered 55° C (=131° F). Selection of 60° C, therefore, is not beyond a reasonable temperature range accessible under field conditions.”

EHHI began its assessment of the health effects from ground-up rubber tire crumbs by identification of the chemicals released from tire crumbs and gardening mulch under conditions that approximate their uses.

Information available from reliable sources, including published literature, documented research and official reports was reviewed. The potential for release of chemicals under typical conditions of use was determined. Chemicals of concern were identified and the toxic actions listed.

These studies conclusively demonstrate that the tire crumbs and the tire mulch release chemical compounds into the air and ground water. Thus, tire crumbs constitute a chemical exposure for humans and for the environment.

VIII. REFERENCES

- ¹ Chien, Y. et al. *Assessment of Occupational Health Hazards in Scrap-Tire Shredding Facilities*. Science of the Total Environment. 2003:35-46.
<www.ncbi.nlm.nih.gov/sites/entrez?db=pubmed&uid=12798090&cmd=showdetailview&indexed>
- ² International Agency for Research on Cancer (IARC) Summaries and Evaluations. The Rubber Industry (Group 1) Supplement 7, 1987, p. 332.
<<http://www.inchem.org/pages/iarc.html>>
- ³ Chien. Op. cit.
- ⁴ California Office of Environmental Health Hazard Assessment (OEHHA). Evaluation of Health Effects of Recycled Waste Tires in Playground and Track Products. January 2007: 8-12.
<<http://www.ciwmb.ca.gov/Publications/Tires/6220613.pdf>>
- ⁵ Ibid.
- ⁶ Id.
- ⁷ Norwegian Institute of Public Health and the Radium Hospital. *Pitches – An Assessment of the Health Risks for Football Players*. Oslo, Norway. January 2006:13-16, Tables 4-8. 8. Id.
<<http://64.233.169.104/search?q=cache:nOJynNVAhcEJ:www.iss.de/conferences/Dresden%25202006/Technical/Summary-artificial-turf-health-ISSS-TM-oct-06.pdf+synthetic+turf,+norwegian,latex&hl=en&ct=clnk&cd=1&gl=us>>
- ⁸ Ibid.
- ⁹ Environmental Defense Fund Scorecard. <<http://scorecard.org/chemical-profiles>>
- ¹⁰ Birkholz, Belton, Guidotti. Canadian Study. *Toxicological Evaluation of Hazard Assessment of Tire Crumb for Use on Public Playgrounds*. Jour of Air and Waste Mgt Assoc. 2003 53:903-907.
<<http://www.shercomindustries.com/industries/birkholz-crumb%20safety%20paper.pdf>>
- ¹¹ Norwegian Study. Op. cit.
- ¹² IARC. Op. cit.
- ¹³ OEHHA. Op. cit.
- ¹⁴ Norwegian Study. Op. cit.
- ¹⁵ OEHHA. Op. cit.
- ¹⁶ USEPA, Pediatric Environmental Health Specialty Unit. *Case Study of Tire Crumb Use on Playgrounds: Risk Analysis and Communication When Major Chemical Knowledge Gaps Exist*. *Environmental Health Perspectives*. Volume 114, No. 1, January 2006
<<http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=133264>>
- ¹⁷ Birkholz. Op. cit.

- ¹⁸ Ibid.
- ¹⁹ Norwegian Study. Op. cit.
- ²⁰ OEHHA. Op. cit.
- ²¹ “The French Study” — *Health Evaluation of the Use of Elastometer Granulates as Filling in Third-Generation Artificial Turf 2007*.
<<http://www.primenewswire.com/newsroom/news.html?d=125895>>
- ²² Birkholz. Op. cit.
- ²³ Norwegian Study. Op. cit.
- ²⁴ Consumer Product Safety Commission. *Handbook for Public Playground Safety*. Publication No. 325.
<<http://www.cpsc.gov/cpscpub/pubs/325.pdf>>
- ²⁵ Norwegian Study. Op. cit.
- ²⁶ OEHHA. Op. cit.
- ²⁷ Kolitzus, H. *Investigation and Assessment of Synthetic Surfaces in Switzerland Including Athletic and Soccer Facilities*. IST Switzerland, October, 2006.
<<http://www.iss.de/conferences/Dresden%202006/Technical/HJK%20Schweiz.pdf>>
- ²⁸ Chien. Op. cit.
- ²⁹ OEHHA. Op. cit.
- ³⁰ Birkholz. Op. cit.
- ³¹ “On Playing Fields, Grass Is an Endangered Species.” *New York Times*, David Gonzales, Reporter, August 13, 2007.
<http://www.nytimes.com/2007/08/13/nyregion/13citywide.html?_r=1&oref=slogin>
“Turf Wars Heat Up: Grass vs. Synthetic.” *The Boston Globe*, Connie Paige, Globe Correspondent, March 25, 2007.
<http://www.boston.com/news/local/articles/2007/03/25/turf_wars_heat_up_grass_vs_synthetic>
- ³² The Hankyoreh Newspaper, South Korea. July 2, 2007. Artificial turf causing skin disease at nation's schools.
<http://english.hani.co.kr/arti/english_edition/e_national/219645.html>http://english.hani.co.kr/arti/english_edition/e_national/219645.html >
- ³³ Norwegian Study. Op. cit.
- ³⁴ Ibid.
- ³⁵ Tucker, MR. Ground Rubber: Potential Toxicity to Plants. North Carolina Dept. of Agriculture and Consumer Services. *Media Notes for North Carolina Growers*. April 1997
<<http://www.ncagr.com/agronomi>>
<<http://www.ncagr.com/agronomi/pdffiles/rubber.pdf>>
- ³⁶ Birkholz. Op. cit.



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