STATE OF KNOWLEDGE REPORT
FOR TIRE MATERIALS AND TIRE WEAR PARTICLES

July 30, 2008

Prepared by
ChemRisk, Inc. - Pittsburgh, PA; San Francisco, CA, USA
DIK Inc., - Hannover, Germany

TABLE OF CONTENTS

FIGURES AND TABLES

1.0 INTRODUCTION

The Tire Industry Project Group (TIPG) working through the World Business Council on Sustainable Development was formed to address environmental health and ecological impacts associated with tire materials and tire wear particles. The participating companies include: Bridgestone Corporation, Continental AG, Cooper Tire & Rubber Company, The Goodyear Tire & Rubber Company, Hankook Tire Company, Kumho Tire Company, Inc., Group Michelin, Pirelli Tyre SpA., Sumitomo Rubber Industries, Ltd., Toyo Tire & Rubber Company Ltd., and Yokohama Rubber Co., Ltd. To meet those objectives, two main steps were envisioned. The first step consisted of tasks designed to compile information to determine the state of knowledge regarding potential human and ecological health risks from both the tire materials and the tire wear particles. The second step will be designed to fill the gaps in the knowledge. This report presents the results of the first step - compiling information.

Five tasks were conducted as part of the first step including:

- Global search and review of the scientific literature pertaining to information which could be used in the assessment of environmental health risk of tire materials and tire wear particles
- Identification of international environmental regulatory policies and research plans that may impact tire materials and tire wear particles
- Summarization of the state of knowledge for tire materials and tire wear particles
- Determination of data gaps/needs for risk assessment purposes
- Prioritization of research to fill data needs

1.1 OVERVIEW OF TIRE MANUFACTURING AND TIRE MATERIALS

Independent of the application, all tires must fulfill a fundamental set of functions like cushioning, damping, transmitting of driving and braking torque, dimensional stability, abrasion resistance, low rolling resistance, and durability throughout the life of the tire. To meet these requirements modern tires consist of five primary components, namely: tread, sidewall, steel belts, body plies, and the bead. As such, tires are manufactured from many different materials including natural and synthetic rubber, textiles and steel. The construction of one typical passenger car tire is shown in Figure 1(1).

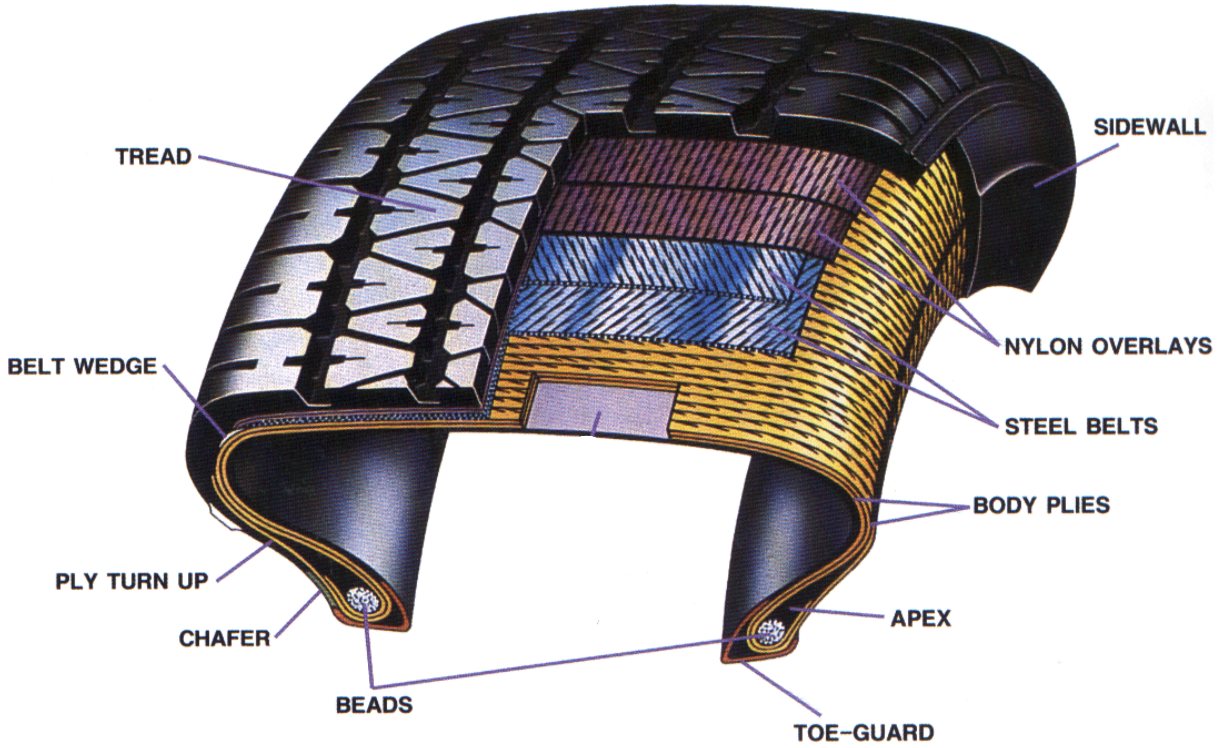


Figure 1. One Typical Construction of a Passenger Tire

Depending on the specific function and performance of a tire, different rubber formulations based on different polymers, fillers and low molecular weight ingredients are necessary for the various tire components. The rubber components are made using chemically stable and reactive/unstable materials including:

Stable materials
Polymer
Carbon black (filler)
Silica (filler)
Mineral oil (plasticizer)
Resins
Waxes
Zinc oxide (activator)
Processing aids (fatty acids, esters, glycol derivatives)

Reactive materials
Silanes (coupling agents)
Adhesives
Accelerators (cross linking)
Sulfur (cross linking)
Stearic acid (activator)
Retarders (cross linking)
Antioxidants

During the tire making process, reactive materials are generally consumed during the curing process, so that little if any of these materials are found in the finished product. The tire production process consists of three primary steps: preparation of the component materials, production of the components, and building of the tire. Figure 2 provides a simplified description of the process.

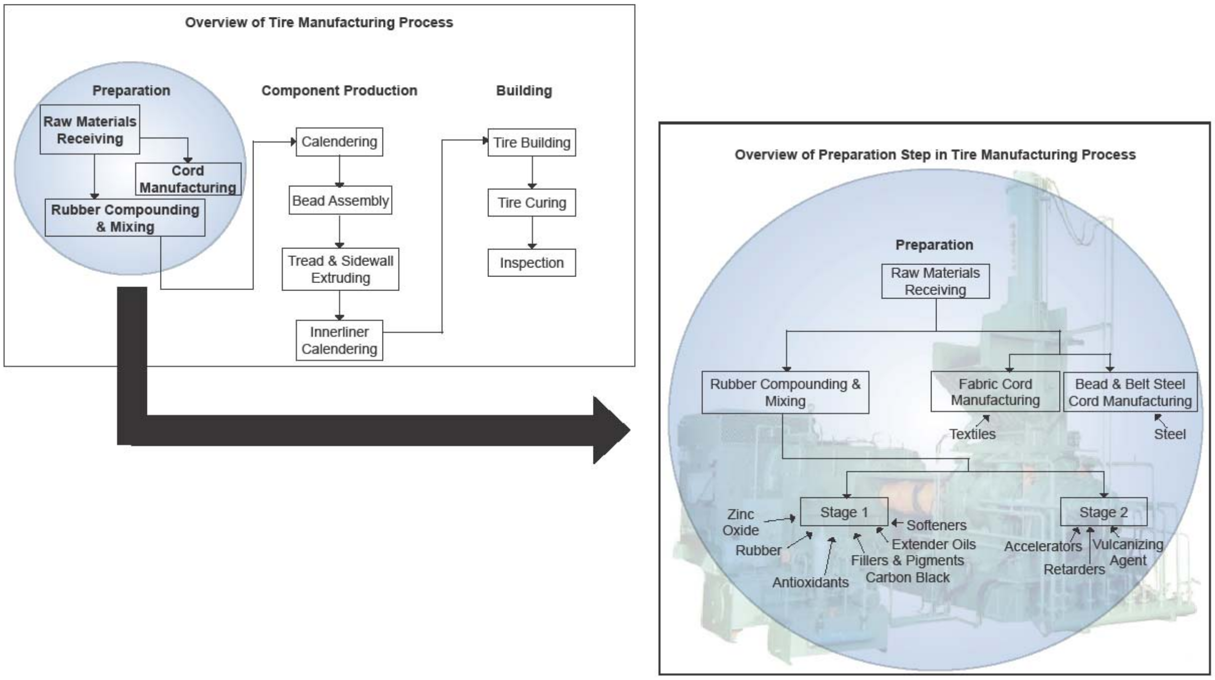


Figure 2. **Overview of the Tire Manufacturing Process**

The process temperature during mixing, extrusion and calendering ranges between approx 80 and 120 °C, while during vulcanization the temperature is higher ranging from approximately 150 to 180 °C. In vulcanization, the material changes from a viscous state to an elastic material by a cross-linking reaction between polymer, sulfur, accelerators and the activators stearic acid and zinc oxide.

There are hundreds of different tire formulations in existence and for the most part those formulations are proprietary to the individual tire companies. However, the TIPG agreed that the chemicals listed on Table 1-1 are common to all companies and are critical materials to the industry, such that use limitations or outright banning of one of the chemicals could have a serious impact on the industry's ability to manufacture tires. In addition to the critical tire materials, a variety of chemical impurities and byproducts were also evaluated. The impurities are a result of the manner in which the raw chemicals are manufactured and the byproducts are a result of the complex chemical reactions that occur during vulcanization. The tire materials including their impurities or reaction products were categorized into four groups: accelerators, antioxidants, oils, and miscellaneous. For each of the chemicals listed on Table 1-1, the toxicity, environmental exposure, and regulatory status were evaluated. The combination of these factors were evaluated to understand whether sufficient information was available to assess the potential for environmental health risks of each chemical associated with their use in the manufacture and use of tires.

Table 1-1 List of Critical Tire Materials

Material Family	Specific Chemicals and Subcategories	
Carbon black	Carbon Black, Furnace black, (single CB-types were not considered)	
Antioxidants	Heterocyclic compounds; such as, TMQ (2,2,4-Trimethyl-1,2-dihydroquinoline), TMDQ (Trimethyl-1,2-dihydroquinoline); Phenylene-diamine derivatives; such as, IPPD (N-Isopropyl-N'-phenyl-p-phenylendiamine), 6PPD (N-1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine), DTPD (N,N`-Ditolyl-p-phenylenediamine), DPPD (N,N'-Diphenyl-p-phenylenediamine), 77PD (N,N`-Bis(1,4-dimethylpentyl)p-phenylendiamine) ADPA (Acetone-diphenylamine condensation product), Phenolic stabilizers, such as BPH (2,2-Methylene-bis-(4-methyl-6-tert-butylphenol) and BHT (2,6-Di-tert-butyl-4-methylphenol)	
ZnO	ZnO	
Accelerators or Vulcanizing Agents	Sulphenamides	DCBS (N,N-Dicyclohexyl-2-benzothiazolesulfenamide), TBBS (N-tert-Butyl-2-benzothiazolesulfenamide), CBS (N-Cyclohexyl-2-benzothiazolesulfenamide), MBS (2-morpholinothio) benzothiazole)
	Guanidine derivatives	DPG (N,N'-Diphenylguanidine); DOTG (Di-ortho-tolyl-guanidine)
	Thiazoles	MBT (2-Mercaptobenzthiazole); MBTS (2,2'-Dithiobis(benzothiazole))
	Dithiophosphates	SDT (Di-(2-ethyl)hexylphosphorylpolysulfide)
	Thiurams	MPTD (Dimethyldiphenylthiuram disulfide)TBTD (tetrabutylthiuram disulfide); TMTD (Tetramethylthiuram disulfide); TMTM (tetramethylthiuram monosulfide),TBZTD (Tetrabenzylthiuram disulfide)
	Dithiocarbamates	ZDMC (Zn-dimethyldithiocarbamate); ZDEC (Zn-diethyldithiocarbamate);ZDBC (Zn-dibutyldithiocarbamate); ZBEC (Zn-Dibenzyldithiocarbamate)
	Thioureas	ETU (Ethylene thiourea); DETU (Diethylthiourea)
	Sulfur donors	DTDM (Dithiomorpholine); DPTT (Dipentamethylenethiuram tetrasulfide); CLD (Caprolactam disulfide); MBSS (2-Morpholinodithiobenzothiazole); OTOS (N-Oxydiethylenedithiocarbamyl-N`-oxydiethylenesulfenamide)
	Others	H or HEXA (Hexamethylenetetramine)
Oils	Aromatic oil	
	MES (special purified aromatic oil)	
	Naphthenic oil	
	TDAE (special purified aromatic oil)	
	Paraffinic oils	
Resorcinol	Resorcinol	
Formaldehyde	Formaldehyde.	

Of the many chemicals used by the TIPG in the manufacture of tires (or present as impurities or produced as reaction byproducts), 42 are considered high production volume (HPV) chemicals and therefore only this subset is used in appreciable quantities by the industry.

1.2 OVERVIEW OF TIRE WEAR PARTICLES IN THE ENVIRONMENT

Tire wear particles (TWP) are released from the tire tread during use of the tires. The particles are formed as a result of the tread abrasion from the road surface. Tire wear itself is a complex physio-chemical process which is driven by the frictional energy developed at the interface between the tread and the road pavement(2). The amount of wear that occurs during a tire's lifetime varies enormously depending on its type and how it is used. The factors affecting tire wear include:

- *Tire characteristics*
  - Size (radius/width/depth)
  - Tread depth
  - Construction
  - Tire pressure and temperature
  - Contact patch area
  - Chemical composition
  - Accumulated mileage
  - Alignment
- *Road surface characteristics*
  - Material: bitumen/concrete
  - Texture pattern
  - Texture wavelength -micro/macro/mega
  - Porosity
  - Condition, including rutting camber
  - Road surface wetness
  - Silt loading of road surface
  - Surface dressing
- *Vehicle operation*
  - Speed
  - Linear acceleration
  - Radial acceleration
  - Frequency and extent of braking and cornering
- *Vehicle characteristics*
  - Vehicle weight and distribution of load
  - Location of driving wheels
  - Engine power
  - Power/unassisted steering
  - Electronic braking systems
  - Suspension type and condition

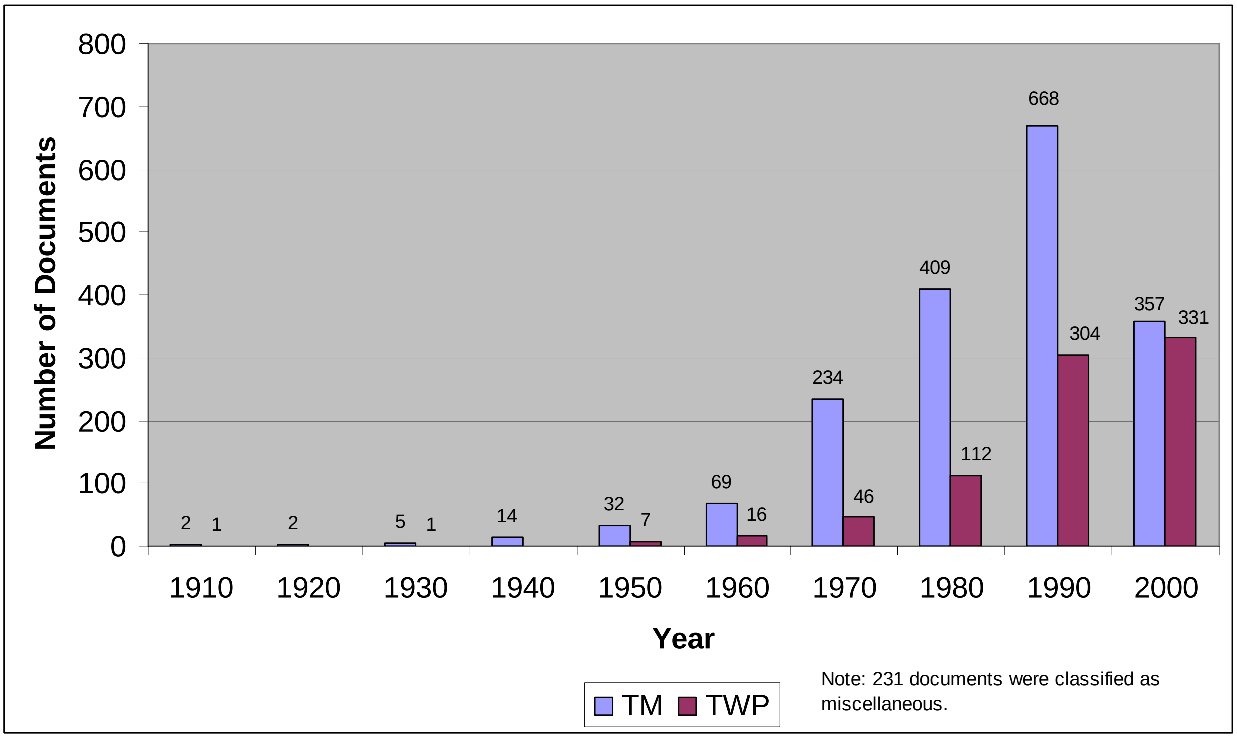
TWP consist of a complex mixture of rubber, asphalt, road dust, gravel, and other materials. TWP are released directly to the environment on both the road surface and suspended in the air. Subsequently the particles can be transported to the soil and surface water via roadway run-off and air deposition. During Phase I, data availability/usability for the assessment of potential human and ecological health risk was assessed including information on human and ecological exposure to tire wear particulate and the toxicity of tire wear particles.

2.0 GLOBAL LITERATURE SEARCH AND REVIEW

The published literature as well as the “gray literature,” which consists of information found in websites and unpublished papers and documents, were searched. The published literature was searched using a variety of publicly available electronic and library databases. The non-published or gray literature was searched using various internet search engines (i.e., Google, etc) and through contact with the international rubber trade associations (RMA, JATMA, KOTMA, and ETRMA – formerly known as BLIC), specific tire materials suppliers and their trade associations and various international government databases.

More than 2,800 scientific journal articles or non-peer reviewed publications were identified, with approximately 50% of the documents containing information directly relevant to the state of knowledge of tire materials and tire wear particulate. All directly relevant papers were reviewed and critiqued to ascertain the quality of the information provided in the paper and its level of relevance to the TIPG project objectives.

The oldest relevant publication that was identified in the search was published in 1895 and the most recent was published in 2007. When evaluated according to publication date, the majority of papers on tire materials were published in the 1990s. For tire wear particles the trend is increasing with more than 330 papers published since 2000 as compared to the total of 304 during the 1990s (See Figure 3).



Note: 231 documents were classified as miscellaneous.

Figure 3. Summary of Database Contents – By Publication Date

Additionally, in terms of publication language, the majority of the relevant publications were written in English, followed by German, and Japanese. In all, documents were retrieved in 14 different languages. Figure 4 provides an overview of the database contents by language. Non-English literature was read and interpreted by those fluent in the specific language.

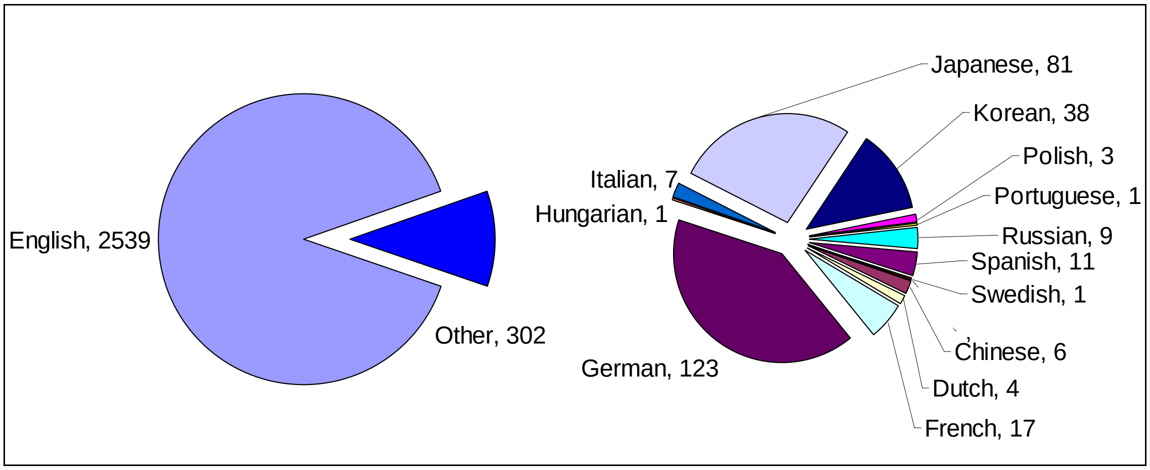


Figure 4. **Summary of Database Contents – by Language**

3.0 IDENTIFICATION OF INTERNATIONAL ENVIRONMENTAL REGULATORY POLICIES AND RESEARCH PLANS

International regulatory programs for chemicals in commerce and environmental protection were evaluated for their potential impact on the continued usage of the critical tire materials, as well as on TWP. With respect to the tire materials, international agreements [i.e., Stockholm Convention, Rotterdam Convention, Strategic Approach of International Chemicals Management (SAICM)], several ongoing industry voluntary programs (i.e., High Production Volume Chemicals), and one European regulatory program (i.e., REACH) were identified as having impact on tire materials. In each case, the focus of the various programs is on chemicals that are: high production volume (HPV) chemicals, persistent, bioaccumulative and toxic (PBT), very persistent/very bioaccumulative (vP/vB), carcinogenic, mutagenic, or reproductive toxicants (CMR), or as described in the REACH legislation “of equivalent concern” (e.g., endocrine disrupters).

In order to prioritize the tire materials in terms of potential for impact on the continued usage by the tire industry, each chemical was evaluated to determine whether it is or could be placed into one of the above mentioned categories. Internationally accepted definitions of each of the categories were used in the evaluation. For some categories, however, there was no generally accepted definition, therefore summary of the various chemical categories and how each were defined for this analysis is presented in Table 3-1.

Table 3-1 Summary of Categories used in Prioritization of Tire Materials

Category	Definition of Category
Carcinogen	Chemicals that may cause, promote, or aggravate cancer, based on IARC classification 1 or 2A
Mutagen	Chemicals that change the genetic information (usually DNA) of an organism based on EU Directive 67/548/EEC or information available in the published literature. For the purposes of this analysis, a chemical was considered mutagenic if it produced positive results in a majority of the mutagenicity models in which it was tested. In the instances in which the results were not predominantly positive or negative, the result of the mutagenicity tests *in vivo* were used to determine the potential for mutagenicity. If there were multiple and conflicting in vivo study results, results from the in vitro studies in mammalian cells were given priority because they are most close related to humans.
Reproductive Toxicant	Chemicals that impair the male and female reproductive functions or capacity based on EU classifications or information in the published literature.
Developmental Toxicant	Chemicals that interfere with normal development, both before and after birth. It should be noted that this effect is considered in conjunction with reproductive effects under EU guidance. However, for the purposes of this assessment, it was evaluated as a separate effect. Chemicals in this category are based on EU classifications or information in the published literature.
Potential Endocrine Disrupter	Chemicals that mimic natural hormones, block the effect of a hormone, or stimulate or inhibit the production of hormones. Although not used for regulatory purposes, the reference *Chemicals purported to be endocrine disrupters: A compilation of published lists. (Web Report W20) Leicester, UK MRC Institute for Environmental Health, available at http://www.le.ac.uk/ieh* was used for this evaluation. This report has not been subjected to scientific peer review and therefore the listing of a chemical in this document does not mean that the chemical is an endocrine disrupter. Rather, it means that at least one group believes that there is a potential for endocrine disruption based on other toxicity exhibited by the chemical.
PBT	Chemicals that do not degrade in the environment, accumulate in biological organisms, and are toxic. PBT definitions used by the USEPA, OECD and EU under the REACH program were used.

No specific environmental regulations are in place or have been proposed that directly target the release of tire wear particles to the environment. However, globally, environmental regulatory agencies have been actively involved in the regulation of ambient particulate matter (PM) in the air. The future regulation of PM in the environment is expected to center on control of the sources; thus, understanding the contribution of tire wear particles to PM_{10} and $PM_{2.5}$ is essential. Compared to the numerous studies performed on airborne PM, the non-airborne fraction of PM (or that which can only be suspended in the air for short periods of time) has received less scientific attention. However, there are many studies concerning the effects of chemical constituents of non-airborne PM that reach rivers, estuaries, or reside in soil.

4.0 STATE OF KNOWLEDGE OF TIRE MATERIALS

The literature search for the tire materials resulted in the identification of more than 1,700 potentially relevant documents. When analyzed by tire material category, the majority of the database consists of information regarding the accelerators/vulcanizing agents. In addition to the published literature, chemical-specific assessments prepared by various governmental agencies, and safety data sheets from chemical manufacturers and distributors were obtained and reviewed.

Each of the primary tire materials was evaluated for data gaps in toxicity. Additionally, the magnitude of the toxic effects, the potential for exposure through environmental media, any current regulatory concerns regarding the chemical, and specificity to the tire industry were also considered.

4.1 ACCELERATORS, VULCANIZING AGENTS, ANTIOXIDANTS AND CHEMICALS FOR ADHESIVE SYSTEMS

The HPV chemicals used by the industry had complete or nearly complete toxicity datasets, but published information regarding potential environmental exposure was lacking.

Table 4-1 is a listing of the HPV chemicals used as accelerators, vulcanizing agents, antioxidants and chemicals for adhesive systems in the manufacture of tires, along with the information available with regards to their CMR and aquatic toxicity status. Of the HPV chemicals used by the tire industry (or present as impurities or reaction byproducts, very few have been classified as carcinogens or mutagens. Currently, the European Union (EU) offers the only classification system for reproductive toxicants (i.e., Risk Phrase such as R-60 or R-62) and according to EU criteria very few of the HPV chemicals are designated as such.[1] However, several of the HPV chemicals have toxicity data indicating that they have the potential for reproductive effects based on effects in laboratory animals, despite the lack of a corresponding R-phrase. Evaluation of ecological toxicity data indicate that the majority of the chemicals are classified as toxic to the aquatic environment.

Because published environmental exposure information is lacking for most of the chemicals, additional data gathering will be necessary before determining whether the chemicals pose an environmental health risk due to their use in tire manufacturing. It should be noted that 17 of the HPV chemicals are accelerators/vulcanizing agents, which means that they are consumed or reacted in the curing process. As such, they are not expected to be released to the environment during the curing and are also not expected to be present in detectable quantities in a finished tire. While sulphenamides, guanidines and thiazoles are commonly used as accelerators in tire industry; use of zinc-dithiocarbamates (ZDMC, ZDEC, ZDBC) very limited because the curing rate of zinc-dithiocarbamates is too rapid for rubber components used in tires.

Additionally, resorcinol and formaldehyde are essential components of the adhesive systems used for bonding rubber to the textile fibers and for improving the adhesion between rubber and the brass plated steel belt. When used as raw materials in textile dipping, they are reacted into an adhesive resin which contains less than 0.1% of either chemical and therefore will have low potential for environmental release

---

[1] The European Union risk phrases are a method for communicating the potential for toxicity associated with chemicals. Definitions of the R-phrases and combinations can be found in the European Union Directive 67/548/EEC (Annex III)

Table 4-1 Summary of Select Toxicity Data for HPV Chemicals used in the Tire Industry as Accelerators/Vulcanizing agents, Antioxidants and other Chemicals

Family	Chemical	CAS#	Carcinogenicity[a]	Mutagenicity	Reproductive Toxicity [b]	Aquatic Toxicity [c]	Reference(s)
Accelerators/Vulcanizing Agents	***Sulphenamides***						
	DCBS	4979-32-2	Not listed	No	No	Yes*	(3, 4)
	TBBS	95-31-8	Not listed	No	No	Yes*	(5-7)
	CBS	95-33-0	Not listed	No	No	R50/53	(3, 5, 8)
	MBS	102-77-2	Not listed	No	No	R51/53	(3, 9)
	Guanidines						
	DOTG	97-39-2	Not listed	Unknown	Unknown	Yes*	(5)
	DPG	102-06-7	Not listed	No	R62	R51/53	(10-12)
	Thiazoles						
	MBT	149-30-4	Not listed	No	No	R50/53	(5, 13-18)
	MBTS	120-78-5	Not listed	No	Yes*	R50/53	(13, 19)
	Thiruams						
	TMTD	137-26-8	Not listed	No	Yes*	R50/53	(20-24)
	TMTM	97-74-5	Not listed	No	No	R51/53	(21-23, 25)
	Dithiocarbamates						
	ZDMC	137-30-4	Not listed	Yes	Yes*	R50/53	(21-24, 26-32)
	ZDEC	14324-55-1	Not listed	Yes	Unknown	R50/53	(21, 23, 24)
	ZBDC	136-23-2	Not listed	No	No	R50/53	(17, 33, 34)
	Sulfur Donors						
	DTDM	103-34-4	Not listed	No	Unknown	Yes*	(35)
	MBSS	95-32-9	Not listed	Unknown	Unknown	Yes*	(5)
	OTOS	13752-51-7	Not listed	Yes	No	No	(3, 36)
	Other						
	HMT	100-97-0	Not listed	Unknown	Unknown	No	(5)
Antioxidants	***Heterocyclics***						
	TMQ	26780-96-1	Not listed	No	No	Yes*	(37, 38)
	Phenolic Stabilizers						
	BPH	119-47-1	Not listed	No	Yes*	Yes*	(5, 39, 40)
	BHT	128-37-0	Not listed	No	No	Yes*	(5, 41, 42)
	Phenylenediamines						
	DPPD	74-31-7	Not listed	Unknown	Yes*	R52/53	(5)
	6PPD	793-24-8	Not listed	No	No	Yes*	(5, 43-46)
	IPPD	101-72-4	Not listed	No	Yes*	R50/53	(43, 47)
	7PPD	3081-14-9	Not listed	No	No	Yes*	(43)
Other Chemicals	***Other Chemicals***						
	Resorcinol	108-46-3	Not listed	No	No	R50	(75-80)
	Formaldehyde	50-0-0	IARC Group 1	Yes	Yes*	Yes*	(81-85)

Table 4-2 is a listing of impurities or by-products related to accelerators, vulcanizing agents and chemicals for adhesive systems, that are considered HPV chemicals. Although 11 impurities or byproducts listed in Table 4-2 are considered HPV chemicals, they are present at very low concentrations and therefore exposures or releases from tire manufacturing are likely to be insignificant.

Table 4-2 Summary of Select Toxicity Data for Impurities and Byproducts, Considered HPV Chemicals, Relating Accelerators/Vulcanizing Agents, Antioxidants and Other Chemicals

Chemical	CAS#	Carcinogenicity[a]	Mutagenicity	Reproductive Toxicity[b]	Aquatic Toxicity[c]	Reference
Aniline	62-53-3	Not listed	Yes	Yes*	R50	(5, 87)
Zn-MBT	155-04-4	Not listed	No	Unknown	Yes*	(13, 88)
Benzothiazole	95-16-9	Not listed	No	Unknown	Yes*	(13, 89)
Carbon Disulfide	75-15-0	Not listed	No	R62/63	Yes*	(22, 82, 90, 91)
Cyclohexylamine	108-91-8	Not listed	No	Yes*	Yes*	(5, 92)
Morpholine	110-91-8	Not listed	No	Unknown	R50/53	(5, 93-95)
Dicyclohexylamine	101-83-7	Not listed	No	Unknown	R50/53	(5, 96)
Methylisothiocyanate	556-61-6	Not listed	Yes	Unknown	R50/53	(97-99)
Isopropylacetone	108-10-1	Not listed	No	No	No	(94, 100-103)
Diphenylamine	122-39-4	Not listed	No	Yes*	R50/53	(5, 104)
Phenol	108-95-2	Not listed	Yes	Yes*	Yes*	(5, 105-110)

a. To be considered **listed** as a regulated carcinogen, a chemical must fall under IARC Group 1 or 2A. In some instances, no evaluation has been made for the chemical by IARC. For reference, see: http://monographs.iarc.fr/ENG/Classification/index.php

b. As per the EU definition, reproductive toxicity includes developmental toxicity, and both are considered in designation of the R-phrase[e].

c. In the absence of an EU designated R-phrase[e], aquatic toxicity was determined using the following criteria: the EC/LC50 of the chemical must be < 100 mg/L in one of three standard test species (119). Pesticide Profiles: Toxicity, Environmental Impact, and Fate. Lewis Publishers; Boca Raton, FL.)

d. Definitions of the R-phrases and combinations can be found in the European Union Directive 67/548/EEC (Annex III)

* Possible based on available literature, but not designated with regulatory phrase (R-phrase)

4.2 OILS

The mineral oils serve as plasticizers that are used to improve rubber properties such as tensile strength, elasticity, tear strength, hardness and elongation at break. Additionally, the oils aid the processing by affecting the viscosity of rubber mixtures. The extender oils used in the tire industry include those containing polycyclic aromatic hydrocarbons (PAH) and those that do not contain polycyclic aromatic hydrocarbons (non-PAH). The mineral oils are a complex mixture, with individual molecules containing various ratios of unsaturated aromatic rings, saturated rings (naphthenic rings) and paraffinic chains.

Toxicity information on the non-PAH oils indicates that the oils are of relatively low toxicity to humans and the aquatic environment. The PAH containing oils are of interest because they may contain carcinogenic compounds: benzo(a)pyrene (IARC Group 1), (benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, Indeno(1,2,3-cd)pyrene, naphthalene) (IARC Group 2B). In aquatic systems, these PAHs are toxic to algae, invertebrates and fish and are persistent and bioaccumulative.

Exposure to Polycyclic Aromatic Hydrocarbons in the Environment

PAHs are widespread contaminants in environmental media and can be measured in air, water, sediments, and soil. The sources of PAHs are both petrogenic – from crude and refined petroleum – and pyrogenic – from incomplete combustion of organic material, including fossil fuels. The contribution of PAHs to the aquatic environment from road dust including tire wear particulate has been evaluated by several groups (121-129). However, no study has been able to reliably quantify the contribution of PAHs from tire wear particulate.

High aromatic (HA) extender oils were considered because the EU has banned the use of HA oils in tire manufacturing due to a theoretical increased risk of cancer from exposure to PAHs in the environment released from tire wear particulate. While the EU concluded that tire wear particulate was not a significant of source of PAHs in the environment, it nevertheless ruled that the theoretical cancer risk was sufficient to ban the HA oils (130). EU Directive 76/769/EEC further stipulates that, as of January 2010, plasticizer oils for the manufacture of tires or tire components may no longer be put into circulation if they contain more than 1 mg/kg benzo(a)pyrene or a cumulative total of more than 10 mg/kg of eight polycyclic aromatic hydrocarbon substances cited. Also, after January 1, 2010 tires and tire treads for retreading purposes may not be put into circulation if they contain plasticizer oils that exceed the aforementioned limit values. The usage of these HA extender oils is scheduled to cease by 2010 in Japan and South Korea(131).

4.3 ZINC OXIDE

Zinc oxide primarily acts as an activator in sulfur vulcanization of tire compounds. The toxicities of zinc oxide, and its impurities and byproducts (cadmium, cadmium oxide, lead, lead oxide) were evaluated. None of the compounds are acutely toxic, except cadmium oxide which exhibits somewhat low acute toxicity. Zinc is generally considered as one of the least harmful of the metals and it is also one of the most prevalent in the environment. It occurs naturally in the environment at moderate levels and is an essential element for most life forms, including humans, animals and plants.

Zinc oxide is not carcinogenic, mutagenic or a developmental toxicant, although it has shown reproductive toxicity in animals. While zinc has been identified as a potential endocrine disrupter, zinc oxide has not been identified as such. In general, zinc and zinc compounds are highly toxic to aquatic systems, but the levels at which zinc is toxic to aquatic species varies by orders of magnitude depending on water chemistry parameters such as pH, hardness and dissolved organic carbon (DOC). Recently, studies of zinc aquatic toxicity have focused on the speciation of metals in the water and the binding of metals to biotic ligands. The biotic ligand models (BLM) are proposed as a tool to evaluate quantitatively the manner in which water chemistry affects the speciation and bioavailability of metals in aquatic systems.

In addition to naturally occurring zinc in the environment, there are numerous anthropogenic sources including local stationary sources such as zinc metal production, zinc galvanizing operations, brass production, alloy and die casting, production of rolled and wrought zinc, and the production of zinc compounds. Additionally, area wide sources may also contribute to zinc in the environment including agricultural operations, and galvanized structures (i.e., roofs, rain gutters, and crash barriers) that are vulnerable to atmospheric corrosion and run-off. Zinc concentrations from road traffic emissions have also been estimated including that from exhaust system corrosion, brake wear and tire wear. Many studies have been conducted in an effort to apportion zinc in the aquatic environment to these various sources. Tire wear particulate has been identified as one such source and the EU has concluded in their risk assessment of zinc that further work is necessary to quantify the zinc emissions to surface water and sediment from road sources, including tires and crash barriers(132).

Although not tire materials themselves, lead and cadmium compounds are found as impurities in the zinc oxide (i.e., <0.1%). Inorganic lead compounds and cadmium and cadmium compounds are mutagenic and regulated as carcinogens. Additionally, lead, cadmium and their respective compounds are reproductive and developmental toxicants. Like zinc, there are many anthropogenic sources of lead and cadmium in the environment. Given their low concentration, release of lead and cadmium from the use of zinc oxide in tire manufacturing is likely to be insignificant.

4.4 CARBON BLACK

Carbon black refers to a group of industrial products including thermal, furnace, channel and acetylene blacks. They essentially consist of elemental carbon and are obtained by the partial combustion or thermal decomposition of hydrocarbons. About 90% of the worldwide production of carbon black is used by the tire industry, where the carbon black enhances tear strength and improves modulus and wear characteristics of the tires.

Due to the source materials, the production methods, and their large surface areas and surface characteristics, carbon blacks typically contain varying quantities of adsorbed byproducts from the production process. In particular, these by-products consist of polynuclear aromatic hydrocarbons (PAHs)(120, 133). The specific chemicals detected in carbon black extracts and their relative quantities vary widely from sample to sample. Among the PAHs frequently found at the highest levels in carbon black extracts are benzo[*ghi*]perylene, coronene, cyclopenta[*cd*]pyrene, fluoranthene and pyrene.

Carbon black is not acutely toxic, but is a skin and eye irritant in humans. In studies of long-term exposure to carbon black, the respiratory and cardiovascular systems were impacted. *In vitro* mutagenicity studies on carbon black were generally negative and carcinogenicity studies utilizing various routes of exposure were negative in all mammalian species tested. Additionally, recent epidemiology studies of carbon black workers did not find a positive dose response between carbon black exposure and any type of cancer. The IARC classification for carbon black is “possibly carcinogenic to humans” (Group 2B), based on insufficient evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals.

The State of California lists carbon black – airborne, unbound, particles of respirable size, as “known to the State of California to cause cancer (http://www.oehha.org/prop65/prop65_list/files/hyphsinglelist082306.xls). However, the agency indicates that exposure to carbon black, per se, does not occur when it remains bound within a product matrix, such as rubber, ink or paint. Neither the U.S. National Toxicology Program (NTP), the U.S. Occupational Safety and Health Administration (OSHA) nor the EU have designated carbon black as a carcinogen.

Exposure to carbon black primarily occurs in industrial workplaces such as during the manufacturing of the product or during use of the material such as in tire manufacturing. However, because carbon black is bound as part of the elastomer complex, it is unlikely to be released from the tire as an unbound particle as a result of wear or abrasion. It should be noted that many studies of ambient air particulate quantify the amount of elemental carbon in the air, which is also called ‘black carbon.’ This term, however refers to carbon generated from industrial or motor vehicle combustion processes and is not synonymous with carbon black. In a recent study known as the “California Supersite”, diesel emissions were identified as the primary source of elemental carbon or black carbon in the ambient air(134).

4.5 SUMMARY OF TIRE MATERIALS STATE OF KNOWLEDGE EVALUATION

The toxicity data appears to be sufficient for most of the HPV chemicals and many of the lower production volume chemicals used by the tire industry. Where data gaps in the toxicity information were identified, the TIPG is committed to working with the materials suppliers to determine if any of the data gaps are data needs and to determine the best approach for obtaining the necessary information. Similarly, because the published literature did not contain sufficient information regarding environmental exposure to these chemicals, additional data gathering or exposure modeling will be necessary in order to determine whether any of the selected tire materials present a potential environmental health risk.

4.6 PRIORITIZATION

In order to assess the current regulatory status of each chemical, we determined the following for each chemical:

- Is it an HPV chemical?
- Is it listed as an OECD HPV but not yet sponsored?
- Is it harmful to the ozone?
- Is it a possible endocrine disrupter?
- Is it a reportable toxic substance (under TSCA/EINECS or other equivalent)?
- Is it subject to environmental release reporting (TRI/PRTR)
- Is it a Stockholm POP
- Is it a Rotterdam PIC?
- Is it a possible PBT?
- Is it regulated as carcinogen, mutagen or reproductive toxicant(under USEPA, IARC, EU Directive 67/549/EEC, California Prop 65)?
- Is it an aquatic toxicant?
- Do environmental standards already exist for the chemicals?
- Is it already severely banned or restricted (TSCA, EU Directive 76/769)?
- Is it unique to the tire industry?

Each of the above categories was then considered when determining the overall priority, with special consideration made for those chemicals that were identified as regulatory concerns (specifically HPVs, reportable toxic substances, regulated carcinogens, mutagens, reproductive toxicants and potential endocrine disrupters), or if data gaps prevented an adequate understanding of a chemical’s classification. The chemicals were prioritized by assigning them into priority groups (high, moderate to high, moderate and low priority) based on the number of positive responses for regulatory concerns or data gaps. A list of the primary tire materials by priority classification and the criteria (by the number of positive responses) for classification is provided in Table 4-3.

Table 4-3 Prioritization of Tire Chemicals by Number of Positive Responses in Regulatory Concerns or Data Gaps

Priority	Positive responses for regulatory concerns or data gaps	Primary Tire Materials
High	Seven or more	DOTG, MBT, TMTD, ZDMC, MBSS, IPPD, resorcinol, formaldehyde,
Moderate to High	Five or Six	MBS, DPG, ZDEC, BDC, DTDM, OTOS, TMQ, DPPD
Moderate	Three or Four	DCBS, CBS, TMTM, MBTS, ZBEC, DETU, HMT, BPH, BHT, 6PPD, 7PPD, ZnO, Carbon Black
Low	Two or fewer	TBBS, MPTD, TBTD, TBzTD, ADPA, DTPD

Note: Impurities and byproducts are not presented in Table 4 in order to simplify the explanation of prioritization. Further, exposures to those impurities and byproducts in the manufacturing and in-use portions of the tire life cycle are expected to be insignificant.

Usages of several chemicals in Table 4-3, such as DOTG, dithiocarbamates (ZDMC, etc), morpholine derivatives (MBSS, etc), etc. are limited in the tire industry. The TIPG has evaluated the high and moderate-high chemicals to determine which if any are commonly used among the representative companies. Based on this evaluation, the following chemicals were selected for focus in filling data gaps in toxicity, PBT status, and exposure for the manufacturing and in-use portion of the life cycle:

- TMTD
- MBT
- Resorcinol
- Formaldehyde
- DPG

5.0 STATE OF KNOWLEDGE OF TIRE WEAR PARTICLES

Tire wear particles (TWP) are included in the vehicle emission category called non-exhaust particulate matter, which in certain areas are a significant contributor to total PM emissions in the environment. For mobile sources, there are a number of non-exhaust processes, involving mechanical abrasion and corrosion, which can result in particulate matter being released directly to the atmosphere. The main abrasion processes leading to the direct emission of particulate matter are:

(i) Tire wear
(ii) Brake wear
(iii) Clutch wear
(iv) Road surface wear

Additionally, corrosion of chassis, bodywork, and other vehicle components, as well as corrosion of road structures such as signs, crash barriers and fencing can contribute to non-exhaust particulate in traffic areas.

The abrasion and corrosion processes can also lead to the deposition of particles on the road surface. The material previously deposited on the road surface, often referred to as ‘road dust’, may also contain exhaust particles, de-icing salt and grit originating from winter maintenance, and matter from a range of sources that are not related to road transport (e.g. crustal and vegetative material, and material from industrial/commercial/domestic activity). The residual road dust can be suspended or resuspended in the atmosphere as a result of tire wear, vehicle-generated turbulence, and wind dispersion. While non-exhaust emission sources may contribute significantly to atmospheric particle concentrations, the data relating to the emission rate, size, and composition of particles arising from such sources are not comprehensive.

Because many control devices, such as particulate filters for diesel engines, have been developed and are being installed on vehicles to minimize exhaust related particulate emissions, the importance of non-exhaust traffic related PM will grow in the future. In order to determine the relative importance of controlling the non-exhaust traffic related PM, the contribution of the major specific sources (tire abrasion, break wear, road wear) must be understood.

5.1 MEASUREMENT OF TIRE WEAR PARTICLES IN THE ENVIRONMENT

Currently, very little reliable and relevant quantitative data exist regarding TWP levels in the environment. The potential presence and significance of TWP in air, soil, and sediment compartments is an important focus for further study.

5.1.1 Estimates of Tire Wear Particles in Airborne Particulate Matter

The published literature contains several studies wherein estimates of the contribution of TWP to airborne particulate matter have been postulated. The quality of the studies is often variable and the methods used to make the contribution determination are not consistent. The determination of the levels of TWP in air requires validated sampling and analytical procedures. The methods that have been generally used to quantify TWP in the environment are based on tire wear rate and mass balance calculations, as well as the use of various chemical markers.

Table 5-1 presents a summary of studies on the relative contribution of tire wear to airborne particulate matter. These measurements were most often reported in high traffic areas, at tunnels or intersections in several countries.

Table 5-1 Contribution of Tire Wear Particles to Airborne Particulate Matter (in %)

Location	TSP	PM_{10}	$PM_{2.5}$	Reference
USA	2 – 10[a]	-	-	(135, 136)
	2 – 7	-	-	(137)
	< 5[a]	-	-	(138)
	7.2[b]	-	-	(139)
	1.6 - 3.5	-	-	(140)
	-	>1	-	(141)
	-	-	1	(142)
	-	-	1.3, 3[c]	(143)
Japan	5.2 ± 0.4	-	-	(144)
	1.3 – 3[d]	-	-	(145)
	5.6 ± 1.0	-	-	(146)
	0.5 - 1.5[e]	-	-	
	4.3[f]	-	-	(147)
	3.6 ± 4.7[g]			(148)
	3	-	-	(149)
	3 – 4[h]	-	-	(150)
	-	2.3	1.3	(150)
Europe	-	5	-	(151)
	16	10[i]	-	(152)
	-	8.6[i]	-	(153)
	-	5	-	(154)
	-	1 - 7.5	-	(155)
	5	-	-	(156)
	-	3 – 7	-	(157)
	-	6[j]	3[i]	(121)

[a] depending on driving conditions
[b] high traffic urban area, contribution to road dust
[c] marker high molecular weight alkanes
[d] winter conditions (Benzothiazole marker)
[e] spring conditions (Benzothiazole marker)
[f] heavy duty vehicles (specific marker)
[g] outside tunnel; specific marker
[h] specific marker (passenger car and truck); three size categories
[i] analytical procedure questionable
[j] averaged data
TSP: Total Suspended Particulate
PM_{10}: Particulate Matter with aerodynamic diameter <10 micrometers
$PM_{2.5}$: Particulate Matter with aerodynamic diameter <2.5 micrometers

A summary of the reported concentrations of TWP in ambient air is shown in Table 5-2. The average concentration of TWP in air for high traffic areas has been reported to range from 2 - 5 µg/m^3 in the size range of TSP and PM_{10} and from 0.2 to 2.2 µg/m^3 for $PM_{<3}$. One of the earliest studies on tire tread rubber in airborne PM was performed by Toyosawa et al.(144) at a tunnel in Tokyo, where the highest concentration of TWP was reported as 9.4 µg/m^3. Fukuzaki et al.(158) reported a maximum roadside TWP concentration of 24 µg/m^3 for PM smaller than 4.7 µm and other researchers have reported TWP TSP, PM_{10}, and $PM_{3.3}$ (i.e., particulate less than 3.3µm in size) levels of 7 µg/m^3, 2.2 µg/m^3, and 0.2 µg/m^3 respectively(159). In contrast to these concentrations Kumata et al.(160) observed a very low tire wear contribution (0.001 µg/m^3) to TSP concentrations in a forested area approximately 500 m from a suburban roadway in Tokyo. This result suggests that the transport of TWP from the roadway might be limited.

Table 5-2 Concentration of Tire Wear Particles in Air (µg/m³)

Sampling Location	TSP	Other Sizes	Reference
Roadway	1.2		(137)
Tunnel	9.6		
		1 - 4.9 (<7µm)	(135, 136)
Interstate highway	0.15	0.07 - 0.13 (PM$_{10}$)	(142)
Urban intersect		0.1 - 0.35 (PM$_{10}$)	
Highway tunnel		8.6 (PM$_{10}$)	(161)
		1 (<10µm)	(162)
Urban		2,2 (<3.3µm)	(159)
		0.22 (<10µm)	
Tunnel	9.4		(144)
		24 (4.7 µm)	(158)
Urban	6		(145)
Urban	7	2.2 (PM$_{10}$) 0.2 (PM$_{3.3}$)	(159)
Urban /summer		1.36 (< 10 µm)	(163)
Forest	0.001		(160)
Local-road/trucks	3.1 ± 1.6		(147)
Passenger-car	4.2 ± 1.3		
National road		0.51 - 2.3 (<7µm)	(150)
		0.20 - 0.91 (<7µm)	

TSP: Total Suspended Particulate
PM$_{10}$: Particulate Matter with aerodynamic diameter <10 micrometers
PM$_{3.3}$: Particulate Matter with aerodynamic diameter <3.3 micrometers
PM$_{2.5}$: Particulate Matter with aerodynamic diameter <2.5 micrometers

Based on these studies, it can be seen that the levels vary greatly and may be a result of factors such as:

- the methods of sampling and quantitative determination
- the use of markers with a large range of error in reference materials
- the variable amount of polymer in tire treads as well as in the samples
- the differences in types of roads, vehicles, driving behavior
- background concentrations and wind (direction and strength) between the sampling spots
- meteorological conditions, climate season etc.
-

There is no consensus in the literature about the TWP contribution to fine fraction (< 2.5 µm) or coarse fraction (>7 µm) of airborne PM. Some studies indicated that the PM$_{2.5}$ emissions from tire wear are important, (164)(165)(152), while other measurements do not confirm this (154, 153, 166). A summary of the results of the PM particle size research in the environment and the contribution of TWP to the fine and coarse size fraction is given in Table 5-3.

Table 5-3 Particle Size Fraction Found In Airborne Tire Wear Particles

Fine (< 3 µm)	Coarse (7 - 10 µm)	Reference
minor	dominant[a]	(167)
minor	dominant	(137)
minor	dominant	(168)
dominant	minor	(164, 165)b
minor	dominant	(169)
minor	dominant	(161)
dominant	minor	(154)c
minor	dominant	(150, 152)

Notes:

[a] Dominant means >50% of particles measured.

[b] 70% of the particles were classified as $PM_{2.5}$, 10% as PM_1 and 8% as $PM_{0.1}$

[c] 90% of the particles were classified as PM_1

Limitations to these studies include validity of the chemical markers, lack of standardization in the analytical technique used, methods to collect the air samples, and seasonal representativeness.

Early *indoor* investigations using actual emissions from a tire on a road surface showed that airborne TWP ranged in size from 0.01 µm to 30 µm (138). Dannis(170) found that the mean particle diameter decreases with increasing driving speed; this may be one of the factors contributing to differences in size and size distributions reported in the literature. Recently, *indoor* tests conducted in Sweden to evaluate pavement wear due to the use of studded tires and non-studded friction tires indicated PM_{10} concentrations of up to 5 mg/m^3 when using the studded tires and nearly non-detectable concentrations when using the non-studded friction tires(171). Within the PM_{10} fraction, there was a particle size mode at 4-5 µm and a peak at 7-8 µm, however the peak was artificial because the distribution was truncated at 10 µm by the PM_{10} inlet of the sampling device. Further, Gustaffson et al.(171), found that the studded tires generated more than 10-fold higher concentrations of particles than the friction tires and that the chemical analysis of the particles showed that they consist almost entirely of minerals from the pavement stone material. Ultra-fine particles (<0.1 µm) were also measured in the Swedish study and the number of particles per volume of air was found to increase with increasing speed(172).

Finally, it is important to note that not all worn tire material will be emitted as airborne PM or released as sedimentary PM. Some authors have argued that there might be at least two important wear mechanisms: 1) a purely mechanical process which produces particles from 10 to more than 300 µm and 2) a thermo-mechanical process which yields much smaller, perhaps partly oxidized, 'smoke'-like particles with diameters of a few tenths of microns. Some of the tire weight loss will be in the form of carbon dioxide and water vapor, although when Cadle and Williams(173) measured the gases emitted during continuous tire wear tests, no significant increases in CO_2 could be measured above the background levels. A fraction of the tire wear material also may adhere to vehicle surfaces, and some much coarser solid material, such as tire shreds, may also be deposited on the road.

5.2 ESTIMATES OF TIRE WEAR PARTICLES IN SOIL AND SEDIMENT

The potential environmental impact of coarse TWP has been largely attributed to leachates of metal ions (e.g. zinc), the extraction of water soluble organic compounds (e.g. by products from vulcanization accelerators, antioxidants, antiozonants) and the transport of PAHs into soil, sediment, and aquatic ecosystems. However, the extraction and leaching potential for chemicals has not been investigated in detail on actual TWP. Important factors such as the relevant particle size range, surface roughness, degree of ageing in terrestrial and aquatic systems and relevant environmental conditions of the leaching matrix have not been given proper consideration in the available studies. Thus, accurate estimates of potential risk to ecological receptors are not currently possible.

Camatini et al.(174) collected debris from the road of a tire proving ground, and found that tire debris agglomerated up to a few hundred micrometers in size. Such particles are not airborne and are of limited interest to air pollution, but they probably contribute the largest fraction by weight of total tire wear. Additional research indicates that the major part of the TWP can be distributed on the road itself and in soil near roadways(175-178). Due to partial biodegradation of the polymer phase or the susceptibility of markers to post depositional decomposition under aerobic conditions, the quantification of sedimentary TWP is a challenging task.

5.3 MARKERS FOR TIRE WEAR PARTICLES

In order to accurately quantify the relative contribution of different sources including tire wear to the total suspended particulate matter, chemical markers for TWP are required. Since neither the fraction of airborne TWP nor the content of TWP in soil or sediment can be determined from measured or theoretically derived tire wear rates; the only feasible way to quantify TWP concentrations in the environment is through the use of specific markers.

Since TWP were first detected in sedimentary matter at a parking garage(179) the search for adequate markers has proceeded in two different directions. One effort pursued a more physical approach by trying to identify a characteristic shape and morphology of individual particles(161, 180-182). However, such procedures have not lead to reliable methodologies for detecting TWP. The chemical approach, believed to be the more robust methodology however, tries to identify specific chemical species that are significantly related to one or more of the characteristic tire tread ingredients. A review of the TWP publications ranging from the early 1970s to 2006 indicated four discrete groups of markers that have been considered:

Polymer based markers - Because passenger tire treads are composed mainly of SBR and BR and truck tire treads contain mainly NR, a potential tire specific marker related to the polymers or specific thermolysis products of the polymers may be possible. In addition, there are nearly no interfering sources for these groups of markers among the exhaust and other non-exhaust PM. Two experimental routes have been used for polymer based markers including: 1) the quantification of the polymer phase(137, 138, 183-185); and 2) the quantification of the type of polymer by using one or a combination of tire tread-specific pyrolysis products(135, 144, 146, 150, 168). Currently, the pyrolysis markers, isoprene, butadiene, and various thiophenes appear to be the most promising.

Accelerator based markers - The most widely used group of accelerators in the tire industry are derivates from benzothiazole (BT). BT was proposed as a potential marker to trace tire wear debris in the urban atmosphere and intensively investigated(142, 145, 186). However, due to different recipes of the compounds, the vulcanization history and the analytical procedure the BT content varies in the range of ± 50%. Therefore, it may be very difficult to identify a reference BT content for a representative tire. Also, there is conflicting information in the literature about other environmental confounders for BT(186, 187), and BT that is not linked to the polymer can be leached out in aquatic or humid terrestrial environments. Thus, BT does not adequately fulfill the marker requirements for a tire wear particles.

Two researchers have investigated the use of 2-(4-Morpholinyl)-benzothiazole (24MoBT), present as an impurity in 2-Morpholino-benzothiazole in the accelerators MBS or MBSS, as marker for TWP(160, 188, 189). However, since the early 1990s, MBS/MBSS was replaced by CBS, TBBS and other compounds as accelerators of choice for tire tread manufacturing. Thus, 24MoBT is no longer a reliable marker for airborne TWP. However, the temporal change in the use of MBS vs. CBS have been observed in sediment, therefore, 24MoBT may still be useful as a potential geomarker(188).

Recently Kumata et al.(188, 190) investigated N-Cyclohexyl-2-benzothiazolamine (NCBA), which appears as an impurity of N-Cyclohexyl-2-benzothiazolesulfenamide (CBS), one of the most frequently used accelerators in the modern tire industry worldwide. Although the analytical methods are complex, there is reasonably good reproducibility. In a Swiss study, the two marker compounds 24MoBT and NCBA were identified from PM_{10} filters(191). In an urban area the contribution of TWP in PM_{10} was reported to be 7.5% by using NCBA as a marker.

<u>Zinc based markers</u> - After Pierson and Brachaczek(137) established a correlation between traffic activity and elemental zinc concentrations in airborne PM as well as in roadside soil samples, zinc was proposed as a marker for TWP. However, other sources of zinc from exhaust and non-exhaust emissions such as corrosion of crash barriers and brake wear that can confound results were not considered in the studies. Because the use of elemental zinc lacks specificity to TWP, Fauser et al.(154, 192) have proposed to use extractable organic zinc (zinc-mercaptobenzothiazole) as a marker because tires are, with the exception of engine oil, the only significant contributors to extractable organic zinc in airborne particulates. The determination of the elemental zinc content in the organic extract is performed by atomic absorption spectrometry (FAAS) and the assessment of TWP content is completed by using IR-spectroscopic determination of styrene. Based on analyses from soil samples the zinc content from tires comprises approximately one percent of the total elemental zinc(156). It is important to note that the interference from additives used in engine oils (zinc-dithiophosphates) which are widely used in Europe creates some uncertainties for determinations of TWP in soil samples using organic zinc as the marker.

<u>High boiling additives</u> - High molecular weight alkanes (Carbon number > 35) and alkanoic acids have been proposed as discriminative markers for TWP because of their low volatility, good solubility in the polymer matrix and their substantial amount in tire compounds(140, 143, 193). However, the research has revealed predominantly n-alkanes which are not totally characteristic for aromatic extender or processing oil. Hydrocarbon acids (alkanoic) have been identified in the second highest amounts. Fatty acids and resin acids, are present in SBR after emulsion polymerization and electrolyte coagulation in an amount of approximately 4 - 7% of the total polymer. Therefore, this group of high boiling substances does not consist of compounding ingredients but rather impurities of E-SBR. Consequently, these substances can be used as a marker for TWP from E-SBR only. Taking into account that E-SBR is replaced or partly substituted by S-SBR in passenger tire treads the value of this type of marker is questionable. Lastly, hydrogenated resin acids, which do not occur in nature, have received some limited attention as potential marker in areas that were highly impacted by vehicle traffic(194). However, this potential marker has not been further developed.

In summary, the markers which appear to have the greatest potential for future use are likely to be the pyrolysis markers from the polymer and the organic zinc.

5.4 TOXICITY PROFILE OF TIRE WEAR PARTICLES

Although numerous studies have been conducted on the toxicity of leachates from tire materials and road particles, there is no information available regarding the human and ecological toxicity potential of real world TWP. Studies have shown that some of the chemicals that can leach out of tire components (such as zinc oxide, diphenylamine, 2-mercaptobenzothiazole, and PAHs) exhibit toxicity to aquatic organisms in laboratory tests; however, no studies have specifically evaluated the toxicity of the TWP under realistic environmental or biological conditions.

Several aquatic studies were identified that implicated TWP as a toxicant in the environment because of potential for acute toxicity, endocrine disruption, and teratogenicity(157, 195-198). Wik and Dave(196) exposed *Daphnia magna* to 0.25 – 16 g/L of grated fresh rubber treads generated from 12 types of tires and observed toxicity at a wide range of concentrations. Additionally, the authors indicated that UV photo-activation increased the toxicity by a factor of 10-fold. One of the most important limitations to this study is that the test concentrations used by the investigators are likely to far exceed actual environmental levels and therefore the relevance of these findings are questionable. Also, the test material was derived from new tires in the laboratory and not actual TWP.

Gualtieri et al.(157) exposed daphnids to eluates from 50 g/L tire tread diluted 1, 10 and 50%. The daphnids were killed by day 5 from exposure to the 10% dilution and algae growth was also inhibited. The authors also observed significant malformations at all dilutions in frog embryos. While this study's findings of toxicity were significant, the tire tread was extracted using organic chemicals that are clearly not representative of environmental conditions and thus under real-world environmental conditions this toxicity is unlikely to be observed. Wik(199) also evaluated toxicity to daphnids from different rubber formulations in order to attempt to identify the most toxic tire leachate components, and also introduced UV treatment as a variable. The resulting EC50 values were in grams per liter which suggests a very low potential for acute aquatic toxicity in the actual environment.

Henkelmann(195) reported that polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are in the "tire soot" and may be extractable in the environment. The author extracted 10 different milled tread samples from used tires and found PCDD/Fs and PCBs in every sample. Although the author believes that the total contribution of PCDD/Fs and PCBs in the environment from TWP would be low, it is unclear whether the PCCD/Fs and PCBs are actually tire related or present because the used tires could have entrained particles containing the compounds while they were in use. Zheng et al.(198) performed a study similar to that of Henkelmann(195) and concluded that TWP exhibited significant anti-estrogenic activity, and therefore that TWP was a form of endocrine disrupter. Further Zheng et al.(198) hypothesized that this effect was a result of the presence of PCCD/Fs and PCBs in the TWP.

Beyond these leaching studies, a significant amount of research has been focused on zinc in aquatic environments. Zinc is very toxic to aquatic organisms and has been shown to leach from tire tread. Smolders and Degryse(200) observed elemental zinc concentrations in tire debris (< 100 µm) of 11.4 mg/g for car tires and 24.1 mg/g for truck tires. Councell et al.(201) reported a range for the measured zinc content of tire tread of 0.04% to 1.66% by weight, based on a review of 13 separate studies. Bioavailability and chronic toxicity (EC10) of elemental and organic zinc can vary widely between aquatic life forms such as algae, crustaceans, and fish algae and crustacean(202). Based on acute toxicity criteria, zinc dithiocarbamates are substantially more toxic to Daphnids than zinc oxide(22, 23, 28, 30, 49, 203, 204).

Only one study was identified that evaluated the mammalian toxicity of tire tread materials (205). In this study, the investigators used tire tread generated from studded tires (<10m) and exposed rats via inhalation using a whole body inhalation chamber. Four groups of animals were exposed to four different doses of tire tread; namely 0 µg/m^3 (N=40); 100 µg/m^3 (N=30); 300 µg/m^3 (N=30); and 1000 µg/m^3 (N=40) and were sacrificed after either 1 year or 1.5 years. The study showed that tire tread particles accumulated in the lungs and in the lymph node in all dose groups and the degree of accumulation was related to the exposure concentration. Analysis of the lung tissues showed that the amounts of silica and aluminum increased according to the dust concentration in the lungs. No dose response relationship between concentrations, duration of exposure, and animal survival numbers was found. Mild fibrosis was found in the lungs in the 1000 µg/m^3 dose group, but not in the controls or at 100 µg/m^3 or 300 µg/m^3. Further, no exposure related tumors were identified. Based on the results of the study, the no observed adverse effect level (NOAEL) was 300 µg/m^3. There are several limitations to this study including lack of systemic toxicity evaluation, and use of tire tread particles generated only from snow tires.

In vitro studies of human cell lines by Gualtieri et al.(157) investigated the effects of organic extracts of tire tread materials. Particulate from laboratory wear tests was extracted using dichloromethane. A549 cells were exposed to extract at concentrations of 10, 50, 60, and 75 µg/ml, which the authors report corresponds to potential human exposure. Cytotoxicity, as measured by the MTT assay, was dose and time dependent, as was cell viability. DNA strand breaks were measured using the Comet Assay and were also dose and time dependent. Cell cycle and morphology were also affected by RP extract, particularly at the high dose. However, this study has significant limitations including extraction of the tread materials in organic solvent and application of DMSO to enhance absorption across the cell membrane; as such its relevance to human biology is unclear.

Karlsson et al.(206) reported that particles from tire–road wear collected using a road simulator were genotoxic and able to induce cytokines, however significant uncertainty is associated with the findings because of improper use of statistics, insufficient controls, low sample size, and design flaws to reasonably link potential exposure with effect.

Beretta(207) looked at solvent extracts of tire debris and potential impacts on human lung epithelial cells. Mantecca et al.(208) report on organic solvent extracts of tire debris and potential impacts in a frog development assay. These studies have significant limitations and relevance because they do not use TWP generated under real conditions, and the extraction in organic solvent is not relevant to biological conditions. Furthermore, delivery of TWP extract in DMSO may cause more uptake of chemicals into cells than would be possible under real-life conditions, and finally, the relatively high ppm doses applied are not environmentally realistic.

In summary, the available tire tread materials and TWP toxicity data are limited both for humans and ecological receptors. These data gaps hinder current abilities to conduct a rigorous risk assessment of TWP.

6.0 CONCLUSIONS

The current state of knowledge indicates that there are data gaps which significantly limit a scientifically robust analysis of the potential environmental health risks associated with the selected tire materials and TWP. Thus additional data collection has been recommended.

For the tire materials, the TIPG has evaluated the high and moderate-high chemicals to determine which if any are commonly used among the representative companies. Based on this evaluation, the following chemicals were selected for focus in filling data gaps;

- TMTD
- MBT
- Resorcinol
- Formaldehyde
- DPG

It is recommended that the following research be conducted in order to conduct environmental health risk assessments:

- Where toxicity data gaps exist, request specific toxicity information from tire material manufacturers;
- Determine persistence, bioaccumulation, and toxicity (PBT) status for high volume chemicals; and,
- Conduct exposure assessments of chemicals for the manufacturing and in-use portions of the life cycle.

After a thorough analysis of the available literature regarding TWP, it was concluded that the most significant data gaps are: 1) lack of understanding of the chemical composition of TWP, 2) lack of understanding of the levels of TWP in the environment (air, soil, and sediments) and their potential associated health risks; and 3) lack of understanding of the potential for TWP to leach chemicals into the environment. As such is it recommended that the following research be conducted to allow for environmental health risk assessment of TWP:

- Chemical composition analysis of TWP generated under representative driving conditions;
- Acute aquatic toxicity studies of TWP;
- Characterization of TWP leachate under simulated environmental/biological conditions;
- Development of chemical marker for TWP in environmental media; and,
- Measurement of TWP in air, soil, water and sediment to determine representative exposure concentrations.

7.0 REFERENCES

1 **Mark, J., T. Erman, and B. Eirich (Eds.):** *Science and Technology of Rubber* San Diego: Academic Press, 1994.

2 **Veith, A.G.:** Tyre tread wear – the joint influence of compound properties and environmental factors. *Tyre Sci Technol* 23: 212-237 (1995).

3 **American Chemistry Council:** "Sulfenamide Accelerators: Category justification and testing rationale, Rubber and Plastics Additive Panel", pp. 1-13. 2001.

4 **European Chemicals Bureau:** "Dataset for N-N-dicyclohexylbenzothiazole-2-sulphenamide (CAS# 4979-32-2)". In *International Uniform Chemical Information Database (IUCLID)*, pp. 1-21. European Commission, 2000.

5 **Chemical Management Center:** National Institute of Technology and Evaluation. In Accessed August 2006: http://www.safe.nite.go/jp/english/dbi.html. Tokyo, Japan, 2006.

6 **European Chemicals Bureau:** "Dataset for N-tert-butylbenzothiazole-2-sulphenamide (CAS# 05-31-8)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

7 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for N-tertbutylbenzothiazole-2-sulphenamide (CAS# 95-31-8)". In *Series Information Data Set (SIDS)*. 2003.

8 **European Chemicals Bureau:** "Dataset for N-cyclohexylbenzothiazole-2-sulphenamide (CAS# 95-33-0)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

9 **European Chemicals Bureau:** "Dataset for 2-morpholinothio-benzothiazole (CAS# 102-77-2)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

10 **European Chemicals Bureau:** "Dataset for 1,3-diphenylguanidine (CAS# 102-06-7)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

11 **National Toxicology Program (NTP):** "NTP Technical Report on Toxicity Studies of 1,3-diphenylguanidine." Department of Health and Human Services, 1995.

12 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for 1,3-diphenylguanidine ". In *Series Information Data Set (SIDS)*. 2004.

13 **American Chemistry Council:** "Benzothiazole- and Morpholine-based Thiazoles: Category justification and testing rationale." pp. 1-12. Rubber and Plastic Additives Panel, 2003.

14 **Bayer:** "2-Mercaptobenzothiazol (2-3H)-benzothiazolthion) uns Salze herausgegeben", pp. 1-104. New York: Beratergremium fuer umweltrelevante Altstoffe (BUA), 1991.

15 **Brewster, D.W., K.J. Mirly, A.G. Wilson, and J.W. Barnett, Jr.:** Lack of in vivo DNA binding of mercaptobenzothiazole to selected tissues of the rat. *Biochem Biophys Res Commun* 165(1): 342-348 (1989).

16 **European Chemicals Bureau:** "Dataset for benzothiazole-2-thiol (CAS# 149-30-4)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

17 **Matsuoka, Isama, and Tsuchiya:** In vitro induction of polyploidy and chromatid exchanges by culture medium extracts of natural rubbers compounded with 2-mercaptobenzothiazole as a positive control candidate for genotoxicity tests. *J Biomed Mat Res* 75(2): 439-444 (2005).

18 **Whittaker, M.H., A.M. Gebhart, T.C. Miller, and F. Hammer:** Human health risk assessment of 2-mercaptobenzothiazole in drinking water. *Toxicol Ind Health* 20(6-10): 149-163 (2004).

19 **European Chemicals Bureau:** "Dataset for di(benzothiazol-2-yl)disulphide (CAS# 120-78-5)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

20 **European Chemicals Bureau:** "Dataset for thiram (CAS# 137-26-8)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

21 **Hedenstedt, A., U. Rannug, C. Ramel, and C.A. Wachtmeister:** Mutagenicity and metabolism studies on 12 thiuram and dithiocarbamate compounds used as accelerators in the Swedish rubber industry. *Mut Res* 68(4): 313-325 (1979).

22 **Van Leeuwen, C., J. Maas-Diepeveen, G. Niebeek, W. Vergouw, P. Griffioen, and M. Luijken:** Aquatic toxicological aspects of dithiocarbamates and related compounds. I. Short-term toxicity tests. *Aqua Tox* 7(3): 145-164 (1985).

23 **Van Leeuwen, C., F. Moberts, and G. Niebeek:** Aquatic toxicological aspects of dithicarbamates and related compounds. II. Effects on survival, reproduction and growth of Daphnia magna. *Aqua Tox* 7(3): 165-175 (1985).

24 **Yamaguchi, T., H. Yamazaki, A. Yamauchi, and Y. Kakiuchi:** Mutagenicity of rubber additives in tire. *Jap J Toxicol Environ Health* 37: 6-13 (1991).

25 **European Chemicals Bureau:** "Dataset for tetramethylthiuram monosulphide (CAS# 97-74-5)". In *International Uniform Chemical Information Database (IUCLID)*, pp. 1-21. European Commission, 2000.

26 **European Chemicals Bureau:** "Dataset for ziram (CAS# 137-30-4)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

27 **Henry, Grant, Klopman, and Rosenkranz:** Induction of forward mutations at the thymidine kinase locus of mouse lymphoma cells: evidence for electrophilic and non-electrophilic mechanisms. *Mut Res* 397: 313-335 (1998).

28 **Maloney, T., and C. Palmer:** Toxicity of six chemical compounds to thirty cultures of algae. *Water & Sewage Works* 103: 509-513 (1956).

29 **Office of Pesticide Programs:** "Pesticide ecotoxicity database [Formerly: Environmental Effects Database (EEDB)]". In *Environmental Rate and Effects Divisions*. Washington, DC: USEPA, 2000.

30 **Pickering, Q.H., and C. Henderson:** The Acute Toxicity of Some Pesticides to Fish. *Ohio Journal of Science* 66(5): 508-513 (1966).

31 **Staub, R.E., S.E. Sparks, G.B. Quistad, and J.E. Casida:** S-methylation as a bioactivation mechanism for mono- and dithiocarbamate pesticides as aldehyde dehydrogenase inhibitors. *Chem Res Toxicol* 8(8): 1063-1069 (1995).

32 **World Health Organization (WHO):** "Occupational exposure in insecticide application, and some pesticides: Summary of data reported and evaluation,". In *53*, pp. 1-48. International Agency for Research on Cancer (IARC), 1999.

33 **American Chemistry Council:** "Robust summaries for HPV challenge program submission: CAS# 136-23-2, Zinc bis(dibutylcarbimodithioato-S,S)." Rubber and Plastic Additives Panel, 2003.

34 **European Chemicals Bureau:** "Dataset for zinc bisdibutyldithiocarbamate (CAS# 136-23-2)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

35 **Flexsys:** "Material Safety Data Sheet for Sulfasan$^{(R)}$ (DTDM)". 2003.

36 **American Chemistry Council:** "N-oxydiethylenethiocarbamyl-N-oxydiethylenesulfenamide (OTOS Accelerator)", pp. 1-6. Rubber and Plastics Additive Panel, 2006.

37 **Flexsys:** "Material Safety Data Sheet for Flectol$^{(R)}$ (TMQ)". 2004.

38 **Healy, C.:** "Toxicology Profile for Flectol Pastilles, Flectol H, Flectol Flakes". 1993.

39 **European Chemicals Bureau:** "Dataset for 6,6'-di-tert-butyl-2,2-methylendi-p-cresol (CAS# 119-47-1)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

40 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for 6,6-di-tert-butyl-2,2-methylenedi-p-cresol (CAS# 119-47-1)". In *Series Information Data Set (SIDS)*. 2000.

41 **European Chemicals Bureau:** "Dataset for 2,6-di-tert-butyl-p-cresol (CAS# 128-37-0)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

42 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for 2,6-di-tert-butyl-4-methyl-phenol (CAS# 128-37-0)". In *Series Information Data Set (SIDS)*. 2002.

43 **American Chemistry Council:** "Substituted diphenylamines: Category Justification and Testing Rationale", pp. 1-30. Rubber and Plastics Additive Panel, 2001.

44 **European Chemicals Bureau:** "Dataset for N-1,3-dimethylbutyl-N-phenyl-phenylendiamine (CAS# 793-24-8)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

45 **Flexsys:** "Material Safety Data Sheet for Santogard(R) (6PPD)". 2006.

46 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine (CAS# 793-24-8)". In *Series Information Data Set (SIDS)*. 2004.

47 **European Chemicals Bureau:** "Dataset for N-isopropyl-N-phenyl-p-phenylendiamine (CAS# 101-72-4)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

48 **European Chemicals Bureau:** Zinc oxide (CAS# 1314-13-2). In Risk Assessment Report: Institute for Health and Consumer Protection, European Chemicals Bureau, 2004.

49 **Gale, N., B. Wixson, and M. Erten:** An evaluation of the acute toxicity of lead, zinc, and cadmium in Missouri Ozark Groundwater. *Trace Subst. Envrion. Health* 25: 169-183 (1992).

50 **Abernethy, S., A. Bobra, W. Shiu, P. Wells, and D. Mackay:** Acute lethal toxicity of hydrocarbons and chlorinated hydrocarbons to two planktonic crustaceans: The key role of organism-water partitioning. *Aqua Tox* 8(3): 163-174 (1986).

51 **Agency for Toxic Substances and Disease Registry (ATSDR):** "Toxicological profile for polycyclic aromatic hydrocarbons". Department of Health and Human Services, 1995.

52 **Atienzar, F., M. Conradi, A. Evenden, A. Jha, and M. Depledge:** Qualitative assessment of genotoxicity using random amplified polymorphic DNA: Comparison of genomic template stability with key fitness parameters in Daphnia magna exposed to benzo(a)pyrene. *Environ Toxicol Chem* 18(10): 2275-2282 (1999).

53 **Battalora, M.S., W.E. Hawkins, W.W. Walker, and R.M. Overstreet:** Occurrence of thymic lymphoma in carcinogenesis bioassay specimens of the Japanese medaka (Oryzias latipes). *Cancer Res* 50(17 Suppl): 5675S-5678S (1990).

54 **Brooke, L.T.:** "Conducting toxicity tests with freshwater organisms exposed to dieldrin, fluoranthene and phenanthrene", R.L. Spehar (ed.) Contract No. 68-C1-0034, Work Assignment No. 5, pp. 18. Duluth, MN: United States Environmental Protection Agency, 1993.

55 **Casserly, D., E. Davis, T. Downs, and R. Guthrie:** Sorption of organics by Selenastrum capricornutum. *Water Res.* 17(11): 1591-1594 (1983).

56 **Finger, S.E., E.F. Little, M.G. Henry, J.F. Fairchild, and T.P. Boyle:** Comparison of Laboratory and Field Assessment of Fluorene - Part 1: Effects of Fluorene on the Survival, Growth, Reproduction, and Behavior. In *Validation and Predictability of Laboratory Methods for Assessing the Fate and Effects of Contaminants in Aquatic Ecosystems, 1st Symposium*, T.P.Boyle (ed.), 120-133. Philadelphia, PA: ASTM STP 865, 1985.

57 **Foran, J., L. Holst, and J. Giesy:** Effects of photoenhanced toxicity of anthracene on ecological and genetic fitness of Daphnia magna: A reappraisal. *Environ Toxicol Chem* 10(3): 425-427 (1991).

58 **Gala, W., and J. Giesy:** Flow cytometric determination of the photoinduced toxicity of anthracene to the green alga Selenastrum capricornutum. *Environ Toxicol Chem* 13(5): 831-840 (1994).

59 **Gaur, J.P.:** Toxicity of Some Oil Constituents to Selenastrum capricornutum. *Acta Hydrochim Hydrobiol* 16(6): 617-620 (1988).

60 **Hall, A., and J. Oris:** Anthracene reduces reproductive potential and is maternally transferred during long-term exposure in fathead minnows. *Aqua Tox* 19(3): 249-264 (1991).

61 **Halling-Sorensen, B., N. Nyholm, and A. Baun:** Algal toxicity tests with volatile and hazardous compounds in air-tight test flasks with CO2 enriched headspace. *Chemosphere* 32(8): 1513-1526 (1996).

62 **Holst, L., and J. Giesy:** Chronic effects of the photoenhanced toxicity of anthracene on Daphnia magna reproduction. *Environ Toxicol Chem* 8(10): 933-942 (1989).

63 **International Programme on Chemical Safety:** International Chemical Safety Card (ICSC) for Indeno(1,2,3-cd)pyrene (CAS# 193-39-5): Chemical Safety Information from Intergovernmental Organizations (INCHEM), 1999.

64 **LeBlanc, G.A.:** Acute toxicity of priority pollutants to water flea (Daphnia magna). *Bull Environ Contam Toxicol* 24(5): 684-691 (1980).

65 **Munoz, M.J., and J.V. Tarazona:** Synergistic effect of two- and four-component combinations of the polycyclic aromatic hydrocarbons: phenanthrene, anthracene, naphthalene and acenaphthene on Daphnia magna. *Bull Environ Contam Toxicol* 50(3): 363-368 (1993).

66 **Newsted, J., and J. Giesy:** Predictive models for photoinduced acute toxicity of polycyclic aromatic hydrocarbons to Daphnia magna, Strauss (Cladocera, Crustacea). *Environ Toxicol Chem* 6(6): 445-461 (1987).

67 **Oris, J.:** The photo-induced toxicity of polycyclic aromatic hydrocarbons to larvae of the fathead minnow (Pimephales promelas). *Chemosphere* 16(7): 1395-1404 (1987).

68 **Schoeny, R., T. Cody, D. Warshawsky, and M. Radike:** Metabolism of mutagenic polycyclic aromatic hydrocarbons by photosynthetic algal species. *Mutat Res* 197(2): 289-302 (1988).

69 **Spehar, R.L., S. Poucher, L.T. Brooke, D.J. Hansen, D. Champlin, and D.A. Cox:** Comparative toxicity of fluoranthene to freshwater and saltwater species under fluorescent and ultraviolet light. *Arch Environ Contam Toxicol* 37(4): 496-502 (1999).

70 **Suedel, B.C., and J.H. Rodgers, Jr.:** Toxicity of fluoranthene to Daphnia magna, Hyalella azteca, Chironomus tentans, and Stylaria lacustris in water-only and whole sediment exposures. *Bull Environ Contam Toxicol* 57(1): 132-138 (1996).

71 **Trucco, R., F. Englehardt, and B. Stacey:** Toxicity, accumulation and clearance of aromatic hydrocarbons in Daphnia pulex. *Environ Pollut Ser A* 31(3): 191-202 (1983).

72 **United States Environmental Protection Agency (USEPA):** "In-Depth Studies on Health and Environmental Impacts of Selected Water Pollutants “Contract No. 68-01-4646. Duluth, MN: USEPA, 1978.

73 **Warshawsky, D., T. Cody, M. Radike, R. Reilman, B. Schumann, K. LaDow et al.:** Biotransformation of benzo[a]pyrene and other polycyclic aromatic hydrocarbons and heterocyclic analogs by several green algae and other algal species under gold and white light. *Chem Biol Interact* 97(2): 131-148 (1995).

74 **Wernersson, A., and G. Dave:** Phototoxicity identification by solid phase extraction and photoinduced toxicity to Daphnia magna. *Arch Environ Contam Toxicol* 32(3): 268-273 (1997).

75 **Calamari, D., R.D. Gasso, S. Galassi, A. Provini, and M. Vighi:** Biodegradation and toxicity of selected amines on aquatic organisms *Chemosphere* 9(12): 753-762 (1980).

76 **Curtis, M., T. Copeland, and C. Ward:** Aquatic toxicity of substances proposed for spill prevention regulation. In Proc. Natl. Conf. Control of Hazardous Material Spills, 93-103. Miami Beach, FL, 1978.

77 **Curtis, M., T. Copeland, and C. Ward:** Acute toxicity of 12 industrial chemicals to freshwater and saltwater organisms. *Water Res.* 13(2): 137-141 (1979).

78 **European Chemicals Bureau:** "Dataset for resorcinol (CAS# 108-46-3)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

79 **Ewell, W.S., J.W. Gorsuch, R.O. Kringle, K.A. Robillard, and R.C. Spiegel:** Simultaneous evaluation of the acute effects of chemicals on seven aquatic species. *Environ Contam Tox* 5: 831-840 (1986).

80 **Stom, D.I., and L.D. Zubareva:** Comparative Resistance of Daphnia and Epischura to Toxic Substances in Acute Exposure. *Hydrobiol J 30(3):35-38 (1994) / Gidrobiol J 29(2):31-34* (1993).

81 **Agency for Toxic Substances and Disease Registry (ATSDR):** "Toxicological profile for formaldehyde". Department of Health and Human Services, 1999.

82 **Bengtsson, B.E., and M. Tarkpea:** The Acute Aquatic Toxicity of Some Substances Carried by Ships. *Marine Pollution Bulletin* 14(6): 213-214 (1983).

83 **International Programme on Chemical Safety:** Environmental health criteria 89: Formaldehyde: Chemical Safety Information from Intergovernmental Organizations (INCHEM), 1989.

84 **Organization for Economic Cooperation and Development (OECD):** "SIDS Initial Assessment Report for formaldehyde (CAS# 50-0-0)". In *Series Information Data Set (SIDS)*. 2002.

85 **United States Environmental Protection Agency (USEPA):** "Toxicological review of formaldehyde (CAS# 50-0-0)", Integrated Risk Information System (IRIS) (ed.). 1991.

86 **European Chemicals Bureau:** "Dataset for carbon black (CAS# 1333-86-4)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

87 **European Union:** Aniline (CAS# 62-53-3). In Risk Assessment Report: Institute for Health and Consumer Protection, European Chemicals Bureau, 2004.

88 **Mohanan, P.V., R. Joseph, P. Ramesh, and K. Rathinam:** Assessment of in vivo chromosomal aberrations--potency of zinc mercapto benzo thiazole. *J Biomater Appl* 14(3): 224-228 (2000).

89 **European Chemicals Bureau:** "Dataset for benzothiazole (CAS# 95-16-9)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

90 **European Chemicals Bureau:** "Dataset for carbon disulphide (CAS# 75-15-0)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

91 **Korhonen, A., K. Hemminki, and H. Vainio:** Embryotoxicity of industrial chemicals on the chicken embryo: thiourea derivatives. *Acta Pharmacol Toxicol (Copenh)* 51(1): 38-44 (1982).

92 **European Chemicals Bureau:** "Dataset for cyclohexylamine (CAS# 108-91-8)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

93 **Bayer:** "Report on Morpholine", pp. 1-196. New York: Beratergremium fuer umweltrelevante Altstoffe (BUA), 1990.

94 **Bringmann, G., and R. Kuhn:** The effects of water pollutants on Daphnia magna. *Z. Wasser-Abwasser-Forsch* 10(5): 161-166 (1977).

95 **European Chemicals Bureau:** "Dataset for morpholine (CAS# 110-91-8)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

96 **European Chemicals Bureau:** "Dataset for dicyclohexylamine (CAS# 101-83-7)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

97 **Alexeeff, G.V., D.J. Shusterman, R.A. Howd, and R.J. Jackson:** Dose-response assessment of airborne methyl isothiocyanate (MITC) following a metam sodium spill. *Risk Anal* 14(2): 191-198 (1994).

98 **Birch, W.X., and K.V. Prahlad:** Effects of nabam on developing Xenopus laevis embryos: Minimum concentration, biological stability and degradative products. *Arch Environ Contam Toxicol* 15: 637-645 (1986).

99 **Pesticide Action Network of North America:** Pesticide Database, 2006.

100 **Broderius, S., and M. Kahl:** Acute toxicity of organic chemical mixtures to the fathead minnow. *Aqua Toxico* 6: 302-322 (Author communication used) (1986).

101 **Brooke, L., D. Call, D. Geiger, and C. Northcott:** "Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales promelas)", pp. 414. Superior, WI: Center for Lake Superior Environmental Studies, University of Wisconsin-Superior, 1984.

102 **European Chemicals Bureau:** "Dataset for 4-methylpentan-2-one (CAS# 108-10-1)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

103 **International Programme on Chemical Safety:** Environmental health criteria 117: Methyl isobutyl ketone: Chemical Safety Information from Intergovernmental Organizations (INCHEM), 1990.

104 **European Chemicals Bureau:** "Dataset for diphenylamine (CAS# 122-39-4)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

105 **Agency for Toxic Substances and Disease Registry (ATSDR):** "Toxicological profile for phenol". Department of Health and Human Services, 1998.

106 **European Chemicals Bureau:** "Dataset for phenol (CAS# 108-95-2)". In *International Uniform Chemical Information Database (IUCLID)*, pp. 1-21. European Commission, 2000.

107 **European Union:** Phenol (CAS# 108-95-2). In Risk Assessment Report: Institute for Health and Consumer Protection, European Chemicals Bureau, 2006.

108 **International Programme on Chemical Safety:** Environmental health criteria 161: Phenol: Chemical Safety Information from Intergovernmental Organizations (INCHEM), 1994.

109 **McGregor, D.B., A. Brown, P. Cattanach, I. Edwards, D. McBride, C. Riach et al.:** Responses of the L5178Y tk+/tk- mouse lymphoma cell forward mutation assay: III. 72 coded chemicals. *Environ Mol Mutagen* 12(1): 85-154 (1988).

110 **World Health Organization (WHO):** "Re-evaluation of some organic chemicals, hydrazine and hydrogen peroxide: Summary of data reported and evaluation". In *71*, pp. 1-171. International Agency for Research on Cancer (IARC), 1999.

111 **Agency for Toxic Substances and Disease Registry (ATSDR):** "Toxicological profile for cadmium". Department of Health and Human Services, 1999.

112 **European Chemicals Bureau:** "Dataset for cadmium (CAS# 7440-43-9)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

113 **European Chemicals Bureau:** "Dataset for cadmium oxide (CAS# 1306-19-0)". In *International Uniform Chemical Information Database (IUCLID)*. European Commission, 2000.

114 **Agency for Toxic Substances and Disease Registry (ATSDR):** "Toxicological profile for lead". Department of Health and Human Services, 2005.

115 **European Chemicals Bureau:** "Dataset for lead (CAS# 7439-92-1)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

116 **European Chemicals Bureau:** "Dataset for lead monoxide (CAS# 1317-36-8)". In *International Uniform Chemical Information Dataset (IUCLID)*. European Commission, 2000.

117 **International Programme on Chemical Safety:** International Chemical Safety Card (ICSC) for Lead monoxide (CAS# 1317-36-8): Chemical Safety Information from Intergovernmental Organizations (INCHEM), 2002.

118 **Mount, D., and T. Norberg:** A seven-day life cycle cladoceran toxicity test. *Environ. Toxicol. Chem.* 3(3): 425-434 (Author communication used) (1984).

119 **Kamrin, M.A.:** Environmental risk harmonization: federal/state approaches to risk assessment and management. *Regul Toxicol Pharmacol* 25(2): 158-165 (1997).

120 **Nutt, A.:** *Toxic Hazards of Rubber Chemicals.* New York: Elsevier Science Ltd 1984.

121 **BLIC:** "BLIC Annual Report 2004-2005". Brussels, 2005.

122 **Budzinski, H., I. Jones, J. Bellocq, C. Piérard, and P. Garrigues:** Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary *Marine Chemistry* 58(1-2): 85-97 (1997).

123 **Caricchia, A.M., S. Chiavarini, C. Cremisini, F. Martini, and R. Morabito:** PAHs, PCBs, and DDE in the northern Adriatic Sea. *Marine Poll Bull* 26(10): 581-583 (1993).

124 **KEMI:** "HA oils in automotive tyres – prospects of a national ban"360760. Stockholm, Sweden: Swedish National Chemicals Inspectorate, 2003.

125 **Macias-Zamora, J.V., E. Mendoza-Vega, and J.A. Villaescusa-Celaya:** PAHs composition of surface marine sediments: a comparison to potential local sources in Todos Santos Bay, B.C., Mexico. *Chemosphere* 46(3): 459-468 (2002).

126 **Sanders, M., S. Sivertsen, and G. Scott:** Origin and distribution of polycyclic aromatic hydrocarbons in surficial sediments from the Savannah River *Arch Environ Contam Toxicol* 43(4): 438-448 (2002).

127 **Takada, H., T. Onda, and N. Ogura:** Determination of Polycyclic Aromatic Hydrocarbons in Urban Street Dusts and Their Source Materials by Capillary Gas Chromatography. *Environ Sci Technol* 24(8): 1179-1186 (1990).

128 **Van Dolah, R.F., G.H.M. Riekerk, M.V.L.G.I. Scott, M.H. Fulton, D.B.S. Sivertsen, K.W. Chung et al.:** An Evaluation of Polycyclic Aromatic Hydrocarbon (PAH) Runoff from Highways Into Estuarine Wetlands of South Carolina *Arch Environ Contam Toxicol* 49(3): 362-370 (2005).

129 **Zakaria, M.P., H. Takada, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno et al.:** Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs. *Environ Sci Technol* 36(9): 1907-1918 (2002).

130 **European Commission:** "Directive 2005/69/EC of the European Parliament and of the Council". In *Official Journal of the European Union* OJ L323, pp. 51-54. http://eurlex.europa.eu/LexUriServ/site/en/oj/2005/l_323/l_32320051209en00510054.pdf ; Strasbourg: The European Parliament and The Council of the European Union, 2005.

131 **Trimbach, J.:** Oil in the rubber - new oils for an old product. In German Rubber Conference. Nuremberg, Germany, 2006.

132 **Bodar, C.W., M.E. Pronk, and D.T. Sijm:** The European Union risk assessment on zinc and zinc compounds: the process and the facts. *Integr Environ Assess Manag* 1(4): 301-319 (2005).

133 **Donnet J. Ed.:** *Carbon Black: Science and Technology.* New York: Marcel Dekker, Inc., 1993.

134 **Sioutas, C., J. Viterbi, and J.R. Froines:** "Southern California Supersite - Final Report"CR-82805901. EPA, 2005.

135 **Cardina, J.A.:** The Determination of Rubber in Atmospheric Dusts. *Rubber Chem Technol* 46(232-241)(1973).

136 **Cardina, J.A.:** Particle Size Determination of Tire Tread Rubber in Atmospheric Dusts. *Rubber Chem Technol* 47(271-283)(1974).

137 **Pierson, W., and W. Brachaczek:** Airborne particulate debris from rubber tyres. *Rubber Chem Technol* 47: 1275-1299 (1974).

138 **Williams, R.L., and S.H. Cadle:** Characterization of Tire Emissions Using an Indoor Test Facility. *Rubber Chem Technol* 51(1): 7-25 (1978).

139 **Hopke, P.K., R.E. Lamb, and D.F.S. Natusch:** Multielemental characterization of urban roadway dust. *Environ Sci Technol* 14: 164-172 (1980).

140 **Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass, and B.R.T. Simoneit:** Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environ Sci Technol* 27: 1892-1904 (1993).

141 **Pollard, I.:** M. Res. Dissertation. In Department of Civil Engineering. Leeds: University of Leeds, 1997.

142 **Fishman, R., and J. Turner:** "Tyre wear contributions to ambient particulate matter"Air Quality Laboratory Report No. WUAQL-0399-03. St. Louis: Washington University, 1999.

143 **Schauer, J.J., M.P. Fraser, G.R. Cass, and B.R. Simoneit:** Source reconciliation of atmospheric gas-phase and particle-phase pollutants during a severe photochemical smog episode. *Environ Sci Technol* 36(17): 3806-3814 (2002).

144 **Toyosawa, S., Y. Umezawa, Y. Ikoma, and Y. Kameyama:** Analysis of tire tread rubber in airborne particulate matter by pyrolysis-gas chromatography. *Anal. Chem. of Japan (Bunseki Kagaku)* 26(38)(1977).

145 **Kim, M.G., K. Yagawa, H. Inoue, Y. Lee, and T. Shirai:** Measurement of tyre tread in urban air by pyrolysis-gas chromatography with flame photometric detection. *Atmos Environ* 24A: 1417-1422 (1990).

146 **Yamaguchi, T., H. Yamazaki, A. Yamauchi, and Y. Kakiuchi:** Analysis of tire tread rubber particles and rubber additives in airborne-particulates at a roadside. *Jap. J. Toxicol. Environ. Health* 41(2): 155-162 (1995).

147 **Sakamoto, K., Y. Hirota, T. Nezu, M. Tsubota, K. Kimijima, and M. Okuyama:** Contribution of Rubber Dust Generated from Tire-Dust by Travelling of Heavy-Duty and Passenger Vehicles on the Road to Atmospheric Particulate Matter. *J Aerosol Res* 14(3): 242-247 (1999).

148 **Kumata, H., H. Takada, and N. Ogura:** 2-(4-Morpholinyl)benzothiazole (24MoBT) as an indicator of tire wear particles and road dust in the urban environment. In *Environmental Geochemistry*, Eganhouse (ed.), ACS Symposium Series 671 R.P. pp. 291-305. Washington D.C: American Chemical Society, 1997.

149 **Doki, S., H. Kunimi, and K. Takahasi:** Estimation of tire emission factors by roadside observation – Japan Clean Air Program (JCAP II). In 43rd Annual Meeting of Japan Society for Atmospheric Environment. Japan, 2002.

150 **Japan Automobile Tire Manufacturers Association (JATMA)**(2001).

151 **Annema, J., H. Booij, J. Hesse, A. van der Meulen, and W.e. Slooff:** "Integrated Criteria Document Fine Particulate Matter "RIVM Rapport 601014015 pp. 102. Bilthoven - the Netherlands RIVM, 1996.

152 **Israël, G.W., M. Pesch, and C. Schlums:** Bedeutung des Reifenabriebs für die Rußemission des Kfz-Verkehrs. *Staub - Reinhaltung der Luft; Springer-Verlag.* 54: 423-430 (1994).

153 **Rauterberg-Wulff, A.:** Beitrag des Reifen- und Bremsenabriebs für Rußemissionen an Straßen. In Dissertation am Fachgebiet Luftreinhaltung der Technischen Universität Berlin, 1998.

154 **Fauser, P.:** "Particulate Air Pollution with Emphasis on Traffic Generated Aerosols"Risø-R-1053(EN). Roskilde, Denmark: Risø National Laboratory, 1999.

155 **Hüglin, C.:** "Anteil des Strassenver-kehrs an den PM_{10}- und $PM_{2.5}$-Immissionen". Dübendorf: EMPA Dübendorf Abt. Luftfremdstoffe, 2000.

156 **Fauser, P., J.C. Tjell, H. Mosbaek, and K. Pilegaard:** Tire-tread and bitumen particle concentrations in aerosol and soil samples. *Petro Sci Tech* 20(1&2): 127-141 (2002).

157 **Gualtieri, M., M. Andrioletti, P. Mantecca, C. Vismara, and M. Camatini:** Impact of tire debris on in vitro and in vivo systems. *Part Fibre Toxicol* 2(1): 1 (2005).

158 **Fukuzaki, N., T. Yanaka, and U. Y.:** Effects of Studded Tires on Roadside Airborne Dust Pollution in Nigata, Japan. *Atmos Environ* 20(2): 377-386 (1986).

159 **Lee, Y.-K., M.G. Kim, and K.-J. Whang:** Simultaneous determination of natural and styrene-butadiene rubber tire tread particles in atmospheric dusts by pyrolysis-gas chromatography. *J Anal Appl Pyrolysis* 16(1): 49-55 (1989).

160 **Kumata, H., H. Takada, and N. Ogura:** Determination of 2-(4-morpholinyl)benzothiazole in environmental samples by a gas chromatograph equipped with a flame photometric detector. *Anal Chem* 68(11): 1976-1981 (1996).

161 **Rauterberg-Wulff, A.:** Determination of Emission Factors for Tire Wear Particles by Tunnel Measurements. In 8th International Symposium "Transport and Air Pollution". Graz, Austria, 1999.

162 **Miguel, A., G. Cass, J. Weiss, and M. Glovsky:** Latex allergens in tire dust and airborne particles. *Environ Health Perspect* 104(11): 1180-1186 (1996).

163 **Kim, M.G., K. Yagawa, T. Shimozato, H. Inoue, and T. Shirai:** Diurnal variations of tire tread concentration in particulate matter *Nippon kagaku kaishi* 6: 826-830 (1991).

164 **United States Environmental Protection Agency (USEPA)**. USEPA, 1995.

165 **Berdowski, J.J.M., W. Mulder, C. Veldt, A.J.H. Visschedijk, and P.Y.J. Zandveld:** "Particulate matter emissions (PM_{10} - $PM_{2.5}$ - $PM_{0.1}$) in Europe in 1990 and 1993"TNO-MEP report. R96/472. Apeldoorn, The Netherlands: TNO Institute of Environmental Sciences, Energy and Process Innovation 1997.

166 **Weingartner, E., C. Keller, W.A. Stahel, H. Burtscher, and U. Baltensperger:** Aerosol emission in a road tunnel. *Atmospheric Environment* 31(3): 451-462 (1997).

167 **Toyosawa, S., and et al.:** Size distribution of rubber particles in highway atmosphere. *J Chem Soc Japan* 7(124): 124 (1978).

168 **Cadle, S.H., and R.L. Williams:** Environmental degradation of tire wear particles. *J Air Pollut Control Assoc* 53(7): 903-914 (1980).

169 **Moosmuller, H., J.A. Gillies, C.F. Rogers, D.W. DuBois, J.C. Chow, J.G. Watson et al.:** Particulate emission rates for unpaved shoulders along a paved road. *J Air Waste Manag Assoc* 48(5): 398-407 (1998).

170 **Dannis, M.:** Rubber dust from the normal wear of tires. *Rubber Chem Technol* 47: 1011-1037 (1974).

171 **Gustafsson, M.:** "Non-exhaust particles in the road environment. A literature review." In *VTI meddelande 910*0347-6049. http://www.vti.se/EPiBrowser/Publikationer/M910.pdf; Linkoping Sweden: Swedish National Road and Transport Research Institute, 2001.

172 **Dahl, A., A. Gharibi, E. Swietlicki, A. Gudmundsson, M. Bohgard, A. Ljungman et al.:** Traffic-generated emissions of ultrafine particles from pavement–tire interface. *Atmospheric Environment* 40: 1314-1323 (2006).

173 **Cadle, S.H., and R.L. Williams:** Gas and particle emissions from automobile tires in laboratory and field studies. *Rubber Chem Technol* 52(1): 146-158 (1979).

174 **Camatini, M., G.F. Crosta, T. Dolukhanyan, C. Sung, G. Giuliani, G.M. Corbetta et al.:** Microcharacterization and identification of tire debris in heterogeneous laboratory and environmental specimens *Mat Charact* 46(4): 271-283 (2001).

175 **BLIC:** Personal Communication with Patrick Lepercq, Michelin, 2006.

176 **Lagerwerff, J., and A. Specht:** Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. *Environ Sci Technol* 4(7): 583-586 (1970).

177 **Ward, N.L.:** Multi-element contamination of British motorway environments. *Sci Tot Environ* 39: 393-401 (1990).

178 **Warren, R.S., and P. Birch:** Heavy metal levels in atmospheric particulates, roadside dust and soil along a major urban highway. *Sci Tot Environ* 59: 253-256 (1987).

179 **Thompson, R.N., C.A. Nau, and C.H. Lawrence:** Identification of vehicle tire rubber in roadway dust. *Am Ind Hyg Assoc J* 27(6): 488-495 (1966).

180 **Adachi, K., and Y. Tainosho:** Characterization of heavy metal particles embedded in tire dust. *Environ Int* 30(8): 1009-1017 (2004).

181 **Adachi, K., and Y. Tainosho:** Single Particle Characterization of Size-Fractionated Road Sediments. *Applied Geochemistry* 20: 849-859 (2005).

182 **Luhana, L., R. Sokhi, L. Warner, H. Mao, P. Boulter, I. McCrae et al.:** "Non-exhaust particulate measurements: Results". Deliverable 8 of European Commission DG TrEn 5th Framework PARTICULATES Project, 2004.

183 **Myslinski, T.:** Exploration of major gaseous products from rubber tire tread wear. Cincinnati, OH: University of Cincinnati, 1970.

184 **Raybold, R., and R. Byerly:** "Investigation of products of tire wear". Gaithersburg, MD: National Bureau of Standards, 1972.

185 **Subramani, J.:** Particulate air pollution from automobile tire tread wear, Dissertation Abstracts 32:3936B. Cincinnati: University of Cincinnati, 1972.

186 **Kim, M.G., K. Yagawa, H. Inoue, and T. Shirai:** Determination of Tire Tread in Urban Airborne Particulate Matter by Pyrolysis-GC with Flame Photometric Detection. *Jap Anal* 38(5): 233-238 (1989).

187 **Sakamoto, K., Y. Hirota, T. Nezu, M. Tsubota, K. Kimijima, and M. Okuyama:** Determination of tire tread pyrolyzates, thiophenes in suspended particulate matter. *J Jap Soc Air Poll* 29(9)(1994).

188 **Kumata, H., Y. Sanada, H. Takada, and T. Ueno:** Historical Trends of N-Cyclohexyl-2-benzothiazolamine, 2-(4-Morpholinyl)benzothiazole, and Other Anthropogenic Contaminants in the Urban Reservoir Sediment Core *Environ Sci Technol* 34(2): 246-253 (2000).

189 **Spies, R., B. Andresen, and DW Rice Jr:** Benzothiazoles in estuarine sediments as indicators of street runoff. *Nature* 327: 697-699 (1987).

190 **Kumata, H., J. Yamada, K. Masuda, H. Takada, Y. Sato, T. Sakural et al.:** Benzothiazolamines as tire-derived molecular markers: sorptive behavior in street runoff and application to source apportioning. *Environ Sci Technol* 36(4): 702-708 (2002).

191 **Schmid, P.:** EMPA, Personal Communication. Switzerland, 2000.

192 **Fauser, P., J.C. Tjell, H. Mosbaek, and K. Pilegaard:** Quantification of tire-tread particles using extractable organic zinc as tracer. *Rubber Chem Technol* 72(5): 969-977 (1999).

193 **Hildemann, L.M., G.R. Markowski, and G.R. Cas:** Chemical Composition of Emissions from Urban Sources of Fine Organic Aerosol. *Environ Sci Technol* 25(4): 744-759 (1991).

194 **Nolte, C.G., J.J. Schauer, G.R. Cass, and B.R. Simoneit:** Trimethylsilyl derivatives of organic compounds in source samples and in atmospheric fine particulate matter. *Environ Sci Technol* 36(20): 4273-4281 (2002).

195 **Henkelmann, B., T. Wottgen, J. Kotalik, A. Kettrup, and K.-W. Schramm:** Concentrations of polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in tyres. *Organ Com* 50: 363-365 (2001).

196 **Wik, A., and G. Dave:** Environmental labeling of car tires--toxicity to Daphnia magna can be used as a screening method. *Chemosphere* 58(5): 645-651 (2005).

197 **Wik, A., and G. Dave:** Acute toxicity of leachates of tire wear material to Daphnia magna--variability and toxic components. *Chemosphere* 64(10): 1777-1784 (2006).

198 **Zheng, M., G.R. Cass, J.J. Schauer, and E.S. Edgerton:** Source Apportionment of PM2.5 in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers. *Environ Sci Technol* 36(11): 2361-2371 (2002).

199 **Wik, A.:** Toxic components leaching from tire rubber. *Bull Environ Contam Toxicol* 79(1): 114-119 (2007).

200 **Smolders, E., and F. Degryse:** Fate and effect of zinc from tire debris in soil. *Environ Sci Technol* 36(17): 3706-3710 (2002).

201 **Councell, T.B., K.U. Duckenfield, E.R. Landa, and E. Callender:** Tire-wear particles as a source of zinc to the environment. *Environ Sci Technol* 38(15): 4206-4214 (2004).

202 **De Schamphelaere, K.A., S. Lofts, and C.R. Janssen:** Bioavailability models for predicting acute and chronic toxicity of zinc to algae, daphnids, and fish in natural surface waters. *Environ Toxicol Chem* 24(5): 1190-1197 (2005).

203 **Gale, G.R., A.B. Smith, M.M. Jones, and P.K. Singh:** Evidence of active transport of cadmium complexing dithiocarbamates into renal and hepatic cells in vivo. *Pharmacol Toxicol* 71(6): 452-456 (1992).

204 **Pickering, Q.H., and C. Henderson:** The acute toxicity of some heavy metals to different species of warmwater fishes. *Air Water Pollut* 10(6): 453-463 (1966).

205 **Masano, I.:** Report of the health influence of dusts by studded tires - experiment of long-term exposure to dusts in rats. *National Environmental Protection Department, Special Pollution Research Information* 23(5): 35-42 (1988).

206 **Karlsson, H.L., A.G. Ljungman, J. Lindbom, and L. Moller:** Comparison of genotoxic and inflammatory effects of particles generated by wood combustion, a road simulator and collected from street and subway. *Tox Letters* 165: 203-211 (2006).

207 **Beretta, E., M. Gualtieri, L. Botto, P. Palestini, G. Miserocchi, and M. Camatini:** Organic extract of tire debris causes localized damage in the plasma membrane of human lung epithelial cells. *Tox Letters* 173: 191-200 (2007).

208 **Mantecca, P., M. Gualtieri, M. Andrioletti, R. Bacchetta, C. Vismara, G. Vailati et al.:** Tire debris organic extract affects Xenopus development. *Environ Int* 33(5): 642-648 (2007).