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For the Degree of Doctor of Philosophy in
Applied Environmental Science

When the Rubber Meets the Road

Ecotoxicological Hazard and Risk Assessment of Tire Wear Particles

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Abstract

Large amounts of rubber particles are dispersed into the environment due to tire wear. The rubber contains a wide range of chemicals, including several of environmental concern. The purpose of this thesis, which is based on six papers [I–VI], was to assess the ecotoxicological hazard and risk associated with tire wear particles, with a main focus on the aquatic environment. A method was developed that enables rapid screening of the toxicity of tire particle leachates [I]. Acute and chronic toxicity of tire particle leachates to aquatic organisms was found to occur at concentrations ranging from 10 to >10 000 mg/l [I–IV]. The toxicity of wear material from different tires was found to vary with more than two orders of magnitude [I–II]. Toxicity identification studies (TIEs) identified organic compounds [II–IV] and Zn [IV] as the toxic components of tire particle leachates. Zn was also identified as the contaminant in the sediments of detention ponds, receiving road runoff, posing the highest threat to surrounding water bodies, and tire wear particles are a main source of this Zn contamination [V].

The Predicted No Effect Concentration (PNEC) was calculated, according to European chemical risk assessment guidelines, based on long term tests with the cladoceran *Ceriodaphnia dubia* and the microalgae *Pseudokirchneriella subcapitata* [IV]. The PNECs are 3.9 mg/l and 0.3 g/kg dw for water and sediments, respectively [VI]. A literature review of markers for tire wear in the environment showed tire particles to be present in surface waters, soils/sediments, air, and biota [VI]. Most of the tire particles are deposited on or close to the road surface and are then further transported by runoff water to receiving waters and sediments. The maximum Predicted Environmental Concentrations (PECs) of tire wear particles in surface water range from 0.03 to 56 mg/l, and the maximum PECs in sediments range from 0.3 to 155 g/kg dw [VI]. Thus, the upper range for PEC/PNEC ratios exceeds unity in both surface waters and sediments, meaning that tire wear particles constitute potential risks for aquatic organisms. The risk for the terrestrial environment is suggested to be restricted to the immediate road surroundings, and it is suggested that more research should be directed towards evaluating the health aspects associated with the inhalation of airborne tire particles [VI].

To conclude, the work presented in this thesis has shown that the contamination from tire wear particles needs to be reduced in order to protect receiving surface waters. This could be achieved by developing tires with more environmentally friendly constituents. Road runoff detention ponds are primary recipients of tire wear particles, and, therefore it is important that construction, environmental monitoring and management of such ponds receive increased attention.

Keywords: tire wear, tire particles, rubber, leaching tests, ecotoxicity tests, *Daphnia magna*, *Ceriodaphnia dubia*, *Pseudokirchneriella subcapitata*, *Danio rerio*, toxicity identification evaluation, road runoff, detention ponds, hazard assessment, risk assessment.

Sammanfattning

Stora mängder gummipartiklar sprids till miljön till följd av däckslitage. Däckgummi innehåller ett flertal olika ämnen varav flera är miljöfarliga. Syftet med denna avhandling, som baseras på sex artiklar [I–VI], var att bedöma den ekotoxikologiska faran och risken med däckpartiklar, med huvudsakligt fokus på den akvatiska miljön. En metod utvecklades som möjliggör en snabb testning av toxiciteten hos lakvatten från däckpartiklar [I]. Den akuta och kroniska toxiciteten för akvatiska organismer av lakvatten från däckpartiklar visade sig ligga mellan 10 och >10 000 mg/l [I–IV]. Toxiciteten av slitagematerial från olika däck visade sig variera med mer än två tiopotenser [I–II]. Toxicitetsidentifieringar visade att det är organiska föreningar [II–IV] och Zn [IV] som orsakar toxiciteten hos lakvatten från däckpartiklar. Zn identifierades också som den förorening i sediment i vägdagvattendammar som utgör störst risk för omkringliggande vattendrag och däckpartiklar är en huvudkälla till denna zinkkontamination [V].

Den koncentration under vilken skadliga effekter i miljön inte väntas uppstå (PNEC-värdet) beräknades, enligt riktlinjerna för europeisk kemikalieriskbedömning, baserat på långtidsstudier med hinnkräftan *Ceriodaphnia dubia* och mikroalgen *Pseudokirchneriella subcapitata* [IV]. PNEC-värdena är 3.9 mg/l för vatten och 0.3 g/kg torrvikt för sediment [VI]. En litteraturöversikt av markörer för däckpartiklar i miljön visade att dessa sprids till ytvatten, jord/sediment, luft och biota [VI]. Den största andelen däckpartiklar deponeras på eller intill vägen och sprids sedan vidare med avrinningsvattnet till kringliggande vattendrag och sediment. Den maximala förväntade koncentrationen (PEC-värdet) av däckpartiklar varierar mellan 0.03 och 56 mg/l i ytvatten och mellan 0.3 och 155 g/kg torrvikt i sediment [VI]. Därmed överstiger de övre PEC/PNEC kvoterna 1 både i vatten och i sediment, vilket innebär att däckpartiklar utgör en potentiell risk för vattenlevande organismer. Riskerna för den terrestra miljön bedöms vara begränsade till den direkta vägmiljön och mer forskning föreslås för att bedöma hälsoriskerna med inandningsbara däckpartiklar [VI].

Sammanfattningsvis presenterar den här avhandlingen resultat som visar att spridningen av toxiska föroreningar från däckslitage måste minskas för att skydda recipienterna. Detta kan uppnås genom att nya däck, med mer miljövänliga beståndsdelar, utvecklas. Vägdagvattendammar är huvudrecipienter för däckpartiklar och därför är det viktigt att ökad uppmärksamhet riktas mot deras konstruktion, miljöfunktion och skötsel.

Nyckelord: däckslitage, däckpartiklar, gummi, laktester, ekotoxicitetstester, *Daphnia magna*, *Ceriodaphnia dubia*, *Pseudokirchneriella subcapitata*, *Danio rerio*, toxicitetsidentifiering, vägdagvatten, sedimentationsdammar, farobedömning, riskbedömning.

List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. The papers are appended at the end of the thesis.

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

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

III. Wik A. 2007. Toxic components leaching from tire rubber. *Bulletin of Environmental Contamination and Toxicology* 79(1):114–119.

IV. Wik A, Nilsson E, Källqvist T, Tobiesen A, Dave G. 2008. Toxicity assessment of sequential leachates of tire powder using a battery of toxicity tests and toxicity identification evaluations. *Journal of Environmental Science and Health, Part A (in press).*

V. Wik A, Lycken J, Dave G. 2008. Sediment quality assessment of road runoff detention systems in Sweden and the potential contribution of tire wear. *Water, Air & Soil Pollution (in press).*

VI. Wik A, Dave G. 2008. Occurrence and effects of tire wear particles in the environment – a critical review and an initial risk assessment. (Manuscript submitted).

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CONTENTS

1. Introduction

1.1 Background

More than 100 000 different chemical substances are currently in use (ECB, 2008), and the annual global chemical production has increased from 7 to 400 million tonnes during the last half-century (European Commission, 2001). While the use of chemicals increases, the society also aims to reduce the chemical pollution of the environment. According to the Swedish environmental quality objective “A Non-Toxic Environment”, the levels of foreign substances in the environment should, by 2020, be reduced to close to zero, and the levels of naturally occurring substances should be reduced to close to background levels (KemI, 2008). The European Water Framework Directive aims to achieve good chemical and ecological status in all water bodies by 2015, and the emissions of hazardous substances to water should be progressively reduced (European Commission, 2000). Whereas previous pollution was dominated by point source inputs (e.g. from industries and sewage treatment plants), most of the pollution today comes from non-point sources. The pollution has moved from the production phase to the consumer phase of products, at least in western countries (Rydén and Migula, 2003). This diffuse pollution is hard to control, and therefore there is a need to prevent hazardous substances from being included in products.

Estimates show that highway runoff contributes to more than 10% of the total receiving water pollutant budget (Ellis and Mitchell, 2006). During the 40 000 km lifespan of the average tire, some thirty percent of its tread rubber is being worn off (Dannis, 1974). Based on the annual global consumption of about one billion tires, it can be estimated that more than $2*10^6$ tonnes of tread rubber are discharged into the global environment each year. Tire rubber contains a wide range of compounds, including several of environmental concern. Previous studies have shown that tire rubber leaches compounds that are toxic to aquatic organisms (e.g. Evans, 1997). Currently, very limited information is available regarding the effects that tire wear particles might have on the environment and on human health.

Tire tread rubber composition and tire wear

The tread is the part of the tire which comes in contact with the road surface. Tread components generally consist of blends of styrene-butadiene rubber (SBR), polybutadiene (PBD), and natural rubber (NR) compounded with carbon black or silica (as reinforcing agent/filler), oils (as softeners and extenders), and vulcanisation chemicals (Kovac and Rodgers, 1994). During the vulcanisation process cross-links, generally sulphur bridges, are formed between adjacent polymer chains to give the rubber its elastic properties. The vulcanisation system requires accelerators to both increase the rate of cross-linking and the density of cross-links, and activators to "activate" the accelerators. Antidegradants are added to prevent the rubber from degradation by e.g. oxygen, ozone, and heat (Ahlbom and Duus, 1994; Barbin and Rodgers, 1994). Table 1 shows a typical tire tread composition with approximate percentages of different ingredients. However, it must be kept in mind that a wide range of different chemicals may be used as protective agents and processing aids, so the composition of different tires varies.

Tread wear rates reported in the literature range between 0.006 and 0.09 g per km and tire (Rogge et al., 1993). The wear rate is dependent on a range of factors such as driving style, weather, and tire and road characteristics (Environment agency news, 1999). The wear rate is considerably higher during urban driving than during motorway driving, due to increased acceleration, braking, and cornering in cities (Stalnaker et al., 1996). The following annual figures on the emissions of tire wear particles to the environment have been reported for different countries; Great Britain $57*10^6$ kg (Environment agency news, 1999), Germany $60*10^6$ kg (Baumann and Ismeier, 1998), Italy $50*10^6$ kg (Milani et al., 2004), Sweden $10*10^6$ kg (KemI, 2003), Denmark $7.3*10^6$ kg (Fauser et al., 2002), and USA $500*10^6$ kg (Cadle and Williams, 1978; Councell et al., 2004). Most of the abraded rubber is released in the form of relatively large particles that will deposit on or close to the road (Pierson and Brachaczek, 1974; Cadle and Williams, 1978; Fauser, 1999). Less than 5% of the tire wear particles are airborne (Pierson and Brachaczek, 1974; Cadle and Williams, 1978), and less than 1% of the abraded rubber is released in the form of gaseous (hydrocarbons and sulphur compounds) emissions (Cadle and Williams, 1978).

Table 1. Example of a standard rubber composition for tire treads (modified from [VI]).

Component/additive	**Ingredients**	**Content (wt-%)**
Rubber polymer	Synthetic and natural rubbers	40–60
Reinforcing agent (filler)	Carbon black and silica	20–35
Process-/extender oils	Mineral oils[a]	15–20
Vulcanisation system		
-vulcanisation agent	Sulphur	1
-vulcanisation activators	Zinc oxide	1.5
	Stearic acid	1
-vulcanisation accelerators	e.g. Sulphenamides and thiazoles	0.5
Protective agents	Antioxidants and antiozonants e.g. Diamines and waxes	1
Processing aids	Peptizers, plasticizers, and softeners	<1

[a] High aromatic oils (HA-oils), with a high content of polyaromatic hydrocarbons (PAHs), have been the types generally used. However, as from January 2010, tires sold within the European Union will be prohibited from containing these kinds of oils.

Toxicity of tire leachates and components of particular concern

Tire rubber leaches compounds that are toxic to aquatic organisms (e.g. Evans, 1997). The first studies that were conducted on tire leachate toxicity aimed to assess the risks associated with the use of tires as artificial reefs (Stone et al., 1975; Kellough, 1991; Goudey and Barton, 1992; Nelson et al., 1994; Hartwell et al., 1998; Collins et al., 2002). Others have focused on the potential environmental problems related to the use of tire shreds as fill material (Humphrey and Katz, 2000; Sheehan et al., 2006). Some recent studies have called attention to the hazards associated with tire wear particles (Draper and Robinson, 2001; Benevento and Draper, 2005; Gualtieri et al., 2005a; Mantecca et al., 2007). The risks associated with tire wear particles will differ substantially from the risks associated with the use of tire rubber in other applications due to the different shapes and sizes of the rubber material (whole/shredded tires vs tire tread particles), that lead to different leaching potentials of compounds from the material. The exposure routes are obviously also very different.

Tire wear particles are a major source of Zn in the urban environment (Davis et al., 2001; Councell et al., 2004; Hjortenkrans et al., 2007), of phthalates to highway stormwater (Hwang and Young, 2004), and of polyaromatic hydrocarbons (PAHs) to urban waters (Boonyatumanond et al., 2007; Kose et al., 2008). A study evaluating the environmental risks associated with run-off from artificial turf (made from ground tires) pitches predicted that alkylphenols would exceed effect levels (Källqvist, 2005). Latex allergens from airborne tire wear particles have been suggested to play an important role for some of the health effects that have previously been associated with air particulates (Williams et al., 1995; Miguel et al., 1996; Dorsey et al., 2006). A few laboratory studies have been conducted on the human toxicity of tire particles (Gualtieri et al., 2005b; 2008; Gerlofs-Nijland et al., 2007). This study has not dealt with human toxicity, but it is clearly an area that needs further research.

Hazard and risk assessment of chemicals

Risk can be defined as the likeliness (probability) for a given undesirable event (hazard) to occur. An ecological risk assessment determines the likeliness that a chemical (or a mixture of chemicals) will cause harm to ecosystems or their components. The prevailing paradigm for the ecotoxicological risk assessment of chemicals involves two components: (1) knowledge of the inherent toxicological properties of the chemical and the determination of the Predicted No Effect Concentration (PNEC); and (2) knowledge of the environmental fate of the chemical and the Predictions or Measurements of Environmental Concentrations (PECs or MECs) (Suter, 1993). The PEC/PNEC ratio, also called the risk characterisation ratio (RCR), is often used as a numerical estimate of the environmental risk for chemicals. When this ratio is >1 there is, in principle, a reason for concern. The confidence in the predicted environmental concentration and the predicted no effect concentration increases as more tiers of testing and measurements are completed (see Fig. 1). The use of a sequential testing approach, thus, results in a more accurate risk assessment. The lower tier tests in a hazard evaluation are laboratory tests. At the first tiers, test organisms are exposed to high concentrations of the chemical(s) during a short period of time (acute tests) and the endpoint most commonly measured is mortality. In the next tiers, test organisms are exposed to lower concentrations for a longer period of time (chronic tests) and sublethal endpoints, like growth or reproduction, are measured. Most commonly, these

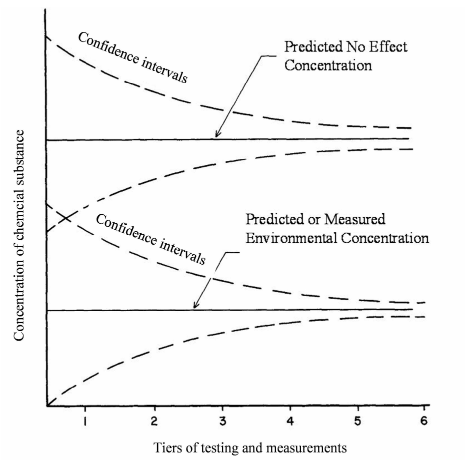

Fig. 1. The risk assessment paradigm (modified from Cairns et al., 1979).

lower tier tests are single species tests. The higher tier tests include tests with endpoints at a higher level of biological organisation such as community or ecosystem levels.

Safety factors (uncertainty factors) are often used to handle uncertainties in risk assessments. These are arbitrary factors that are applied to the concentration causing some biological effect in order to estimate a safe level for a substance in the environment. The prevailing guidance for the risk assessment of chemicals within the European Union does, for example, recommend a factor (here called assessment factor) of 1000 to be used to derive a PNEC if short-term toxicity data is available for at least three species from three trophic levels. If one long-term no effect concentration (NOEC) is available a factor of 100 is recommended, and if long-term NOECs from at least three species from three trophic levels are available, a factor of 10 should be used (ECB, 2003).

Another approach to determine PNECs is by the use of species sensitivity distribution (SSD) methods. SSD is a statistical distribution describing the variation among a set of species in toxicity of a certain chemical or mixture of chemicals. The distribution is used to predict Hazardous Concentrations affecting a certain percentage (HC_ps) of species in a community. The fifth percentile of a chronic toxicity distribution is often chosen (HC_5), i.e. in order to protect 95% of the species (Posthuma et al., 2002). It is generally assumed that the SSD should be based on at least ten NOECs (preferably fifteen) to generate reliable estimates (ECB, 2003). It is important to realize that the sizes of the safety factors (assessment factors) as well as the values of $_p$s in HC_ps are policy decisions rather than science.

Toxicity testing of consumer products

REACH, the new European regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals, aims at ensuring a high level of protection of human health and the environment (European Parliament and Council, 2006). The requirements for substances in articles (e.g. in textiles, plastics, or tires) are, however, not as far-reaching as the requirements for substances existing on their own or in preparations/mixtures. In addition, no tests of the finished product are required. This means that substances formed during the production process, or as breakdown products, will be ignored. Neither is the combined effect of the ingoing components taken into account. Considering the substantial (diffuse) pollution from consumer products (Rydén and Migula, 2003), there is a need for methods that enable an efficient hazard assessment of substances that might be released from products during their use or disposal phases. The Environmental Choice Program of Environment Canada categorises products, in order to help consumers to identify those products that are less harmful to the environment. One of the elements considered in the rating process is toxicity tests of the product (e.g. general purpose cleaners) or of the waste from making it (e.g. pulp and paper) (Scroggins, 1999). Toxicity testing of products enables an assessment of the total toxicity of all ingredients in a mixture. Toxicity testing of products reported in the literature includes for example tests with: anti-fouling paints (Karlsson et al., 2006), detergent and softener products (Pettersson et al., 2000), and plastics (Lithner et al., unpublished).

The ecological relevance of toxicity tests on products at very high concentrations, that are unlikely to occur in the environment, has rightly been questioned (Scroggins, 1999). Toxicity testing of products should only be used for the purpose of ranking of similar products; e.g. as one element of an environmental labelling. Moreover, for toxicity testing to be a relevant part on an environmental labelling there need to be some intended or unintended release of the product (or of components from the product) during its use- or disposal phase. If the purpose is to assess the ecotoxicological impacts of a product, toxicity testing is not enough; but a thorough risk assessment, which considers environmental concentrations as well as ecotoxicological effects, is needed.

1.2 Research objectives

The main purpose of this work was to assess the ecotoxicological hazard and risk of tire wear particles released into the environment, with special focus on the aquatic environment. A secondary objective was to develop a method for screening of tire tread rubber toxicity that would enable ranking of tires in terms of their ecotoxicological hazard potentials. The specific objectives of the studies presented in papers [I–VI] were to:

- develop a screening method for toxicity testing of tire tread particles [I]
- evaluate acute and chronic toxicity to aquatic organisms [I–IV]
- investigate differences in toxicity among tires/rubber recipes [I–III]
- identify the toxic components of tread rubber [II–IV]
- evaluate the long term leachability of toxic compounds from tire wear material [IV]
- assess pollution induced degradation in waters receiving road runoff and investigate the possible contribution from tire wear [V]
- make an initial risk assessment of tire wear particles in the environment [VI]

2. Methods

Most methodological aspects have been described in detail in the different papers. Therefore, only some general aspects are presented and discussed here.

2.1 Determination of effect concentrations

The impacts of chemical mixtures on aquatic environments can be assessed by determining the levels of single contaminants in the mixture, and then evaluating the hazards associated with these specific contaminants. Another approach, that is often used for wastewaters, is to assess the hazards resulting from the combined impact of the contaminants present in the mixture by the use of biological tests. This latter approach is particularly useful when the mixtures are complex and the most toxic constituents are unknown. Since tire leachates are very complex mixtures, and there is a scarcity of information on the chemical composition of tire leachates (especially of leachates of tire wear particles), this approach was considered to be the most suitable for the hazard assessment of tire wear particles.

Production of tire particle leachates

Rubber was abraded from the treads of the tires using a rasp. The size distribution of the obtained tire particles was determined by sieving them through two sieves that were put on a mechanical shaker for 24 h. On a weight percentage basis, 44% of the particles were >500 µm, 46% were between 180 and 500 µm, and 8% were <180 µm. The determined size distribution is, however, precarious, since the fractionation was complicated by the tackiness of the particles that caused them to aggregate. Fig. 2 shows a magnification of the tested tire tread particles. The tire particles were then leached for 72 h [I–III] or between 5–20 d [IV], and the leachates were then either filtered [II, IV] or not filtered [I, III] before the test organisms were added. Fig. 3 shows a photo of the testing setup used in [I].

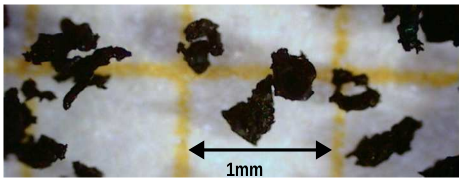

Fig. 2. Magnification of the tire tread particles as tested in [I, II, IV].

Fig. 3. Photo of the testing setup used in study [I].

Toxicity tests

Toxicity tests were, as far as possible, conducted according to standard protocols. Since tire wear particles are released worldwide and to many types of ecosystems, all species were considered “relevant” and test species were chosen in order to represent different trophical levels and also based on their availability. Algae contribute substantially to the primary production in most aquatic habitats. The freshwater green microalgae *Pseudokirchneriella subcapitata* is widely used for toxicity testing, and was used to determine the toxicity of tire leachates in [IV]. Algal tests are multigeneration studies, and it is generally assumed that a 72-h NOEC value can be considered as a long-term result (ECB, 2003). The cladocerans (*Daphnia magna* and *Ceriodaphnia dubia*) are important primary consumers in pelagic freshwater habitats. Due to its known sensitivity to a broad range of contaminants (Von der Ohe and Liess, 2004) and to the convenience of the test, the *D. magna* acute immobility test was chosen for the initial screening tests of tire particle leachates [I, II]. The *C. dubia* 9-day survival and reproduction test was used to determine the chronic toxicity of tire leachates in [IV]. *D. magna* and *C. dubia* were also used to determine the toxicity of sediment elutriates in [V]. Sediment tests in [V] also included tests with the amphipod *Hyalella azteca*, a benthic primary consumer common in freshwater and widely used for sediment toxicity testing. Tire leachates in [IV] were also tested for toxicity using zebrafish (*Danio rerio*) eggs. This test enables determinations of both lethal and sublethal endpoints after short exposure times (48-h).

Toxicity identification evaluations

Toxicity Identification Evaluation (TIE) manipulations were conducted in order to characterise the toxic components of tire particle leachates [II, IV] and of sediments and waters contaminated with road runoff [V]. Manipulations of the toxic sample before repeating the toxicity test give information on the characteristics of the toxic compound(s). Manipulations that were undertaken included sodium thiosulphate (STS) addition, that will reduce the toxicity of oxidants (e.g. chlorine and some electrophile organic chemicals) and of some cationic metals (e.g. Cd, Cu, Ag and Hg), EDTA (ethylenediaminetetraacetic acid) addition, that will reduce the toxicity of several divalent cationic metals, C18 solid phase (SPE) extraction, that will reduce the toxicity of nonpolar organic compounds, and ion exchange extractions through CM- and QMA columns, that will reduce the toxicity due to cations (e.g. metals) and anions, respectively (Norberg-King et al., 2005). The TIE experiments were conducted with *D. magna* as the test organism throughout this study.

2.2 Sediment quality triad assessment of road runoff detention ponds

Road runoff detention ponds (see Fig. 4 for an example) are constructed in order to balance water flow and to improve water quality. As primary recipients of road runoff they were subjects for a sediment quality triad assessment [V]. In the sediment quality triad approach, data on sediment chemistry, sediment toxicity and benthic faunal structure are linked, in order to establish a weight-of-evidence for pollution induced degradation (Chapman et al., 1987). The study [V] was performed in order to screen and assess the potential risks of contamination from road runoff and to estimate the contribution from tire wear particles to any observed effects.

Fig. 4. Road runoff detention pond in the western part of Sweden.

2.3 Determination of exposure concentrations

Several tire components have been used as markers for tire wear particles in the environment. The concentration of tire material in different environmental matrices can be estimated based on the content of these marker chemicals in the environmental matrix and in tire rubber. Styrene butadiene rubber (SBR) is the most commonly used rubber polymer in passenger car tires and has been used as a marker for tire wear particles by several investigators (Pierson and Brachaczek, 1974; Cadle and Williams, 1978; 1980; Lee et al., 1989; Saito, 1989; Fauser, 1999). Over 70% of the SBR produced globally is used in tire manufacturing (ICIS, 2008), which means that the contribution from other sources is small. The tire industry also accounts for 75% of the global consumption of natural rubber (NR), which is especially used in truck tires (Barbin and Rodgers, 1994). Benzothiazoles (benzothiazole and its derivates), hereinafter referred to as BTs, have also been used as tire markers (Spies et al., 1987; Kim et al., 1990; Kumata et al., 1997; 2000; 2002). Although BTs have wide uses as corrosion inhibitors in antifreeze products, as pesticides, and as photosensitizers in photography, the largest amount is used as vulcanisation accelerators (Brownlee et al., 1992). The BTs that are discussed in this thesis are 24MoBT (2-(4-morpholinyl) benzothiazole), BT (benzothiazole), HOBT (2-hydroxybenzothiazole), and NCBA (N-cyclohexyl-2-benzothiazolamine). Fauser (1999) developed a method to analyse extractable organic zinc (zinc vulcanisation accelerator complexes) as a marker for tire wear material. Spill of engine oil is supposed to be the only interfering source of extractable organic zinc. Scrap tires used in different geotechnical applications may, in addition to tire wear particles, be important sources of some of the above mentioned chemical markers at certain locations.

A literature review of the available data on tire markers in the environment was performed [VI]. A meta-analysis was conducted to determine the corresponding environmental concentrations of tire wear material based on these reports on tire markers in the environment and in tire rubber.

2.4 Risk assessment of tire wear particles

The ratios between the predicted or measured environmental concentrations (PECs or MECs) derived from the meta-analysis, and the derived PNECs were calculated in order to obtain numerical estimates of the environmental risk (RCRs) for tire particles in various environmental matrices [VI]. This general approach with established safety factors was considered more appropriate than one using chemical-specific safety factors based on species sensitivity distributions, considering the scarcity of data. Fig. 5 shows an illustration of the approach used in this study for the risk assessment of tire wear particles.

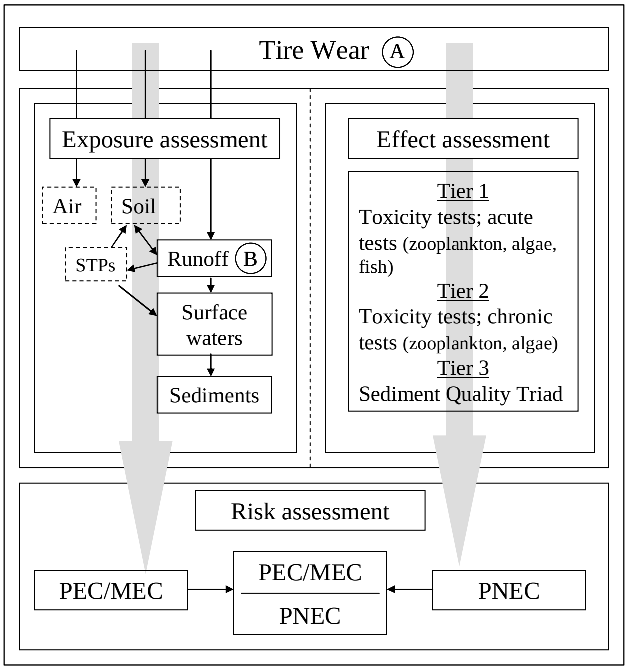

Fig. 5. Illustration of the approach used in this study for the risk assessment of tire wear particles. The focus of the risk assessment has been on the aquatic environment (solid-lined boxes in the exposure assessment box). Two options to reduce the environmental impacts by tire wear particles are also suggested (in circles); rubber formulation (A) and road runoff treatment (B).

PEC = Predicted Environmental Concentration
MEC = Measured Environmental Concentration
PNEC = Predicted No Effect Concentration
STPs = Sewage Treatment Plants

3. Results and Discussion

The most important findings from the studies presented in papers I–VI are summarized in the section below, and discussed in relation to available information in the literature.

3.1 Acute and chronic toxicity

A pilot study was conducted prior to studies [I–IV] in order to confirm that the test organisms were affected by toxicants that leached from the rubber and not physically damaged by the tire particles per se. In beakers, containing unfiltered leachate water, the same number of daphnids was exposed either directly to the leachate or in a cage that prevented the daphnids from coming into direct contact with the particles. There were no significant differences in toxicity between the two exposure routes, so it was concluded that the daphnids were affected by toxic components that leached from the rubber.

A method was developed that enables rapid screening of the toxicity of tire particle leachates [I]. The toxicity to *D. magna* of leachates from 12 [I] and 25 [II] tires was found to vary between 0.29 and >10 g/l after 24-h exposure, and between 0.06 and >10 g/l after 48-h exposure. UV-exposure (UVA) of the leachates (and exposed daphnids) increased the toxicity between 1 and 39 times [I]. The large variation in toxicity observed among tires shows that a change in tire rubber composition and choice of appropriate and more environmentally friendly chemical additives is of great importance in order to reduce the environmental impact of tire wear particles. Furthermore, the method described in [I] can be used to rank tires in terms of their ecotoxicological hazard potential.

Variations in results, due to differences induced by the test design, are inevitable in toxicity testing, and especially the testing of “difficult compounds”, i.e. poorly water-soluble, volatile, and unstable compounds, often results in quite large differences between laboratories. The toxicity of tire leachates is influenced by several factors. The size and shape of the tested rubber influences the leachability of components from the rubber material, as mentioned above. The procedure by which the leachate is prepared is also of importance. At higher concentrations, the toxicity is influenced by the weight to volume proportions of tire particles and dilution water. Dilutions produced from 50 g/l tire particle leachates were more toxic than dilutions prepared from 100 g/l tire particle leachates, due to particle aggregation (Gualtieri et al., 2005a). The toxicity of concentration series prepared at lower concentrations (≤16 g/l) was, however, found to be concentration dependent [I, III, IV]. The procedure for leachate preparation was also found to influence the photo-enhanced toxicity of tire particle leachates, but it was not concluded whether the observed differences were due to the use of different leaching temperatures, to the filtering or not filtering of leachates, or to the use of different test vessels [II]. Moreover, the type of leaching solution influences the leachability of different compounds, as well as their toxicity. For example, more Zn was leached at lower pH (when tested in the pH range of 2–11) (Abernethy et al., 1996; Gualtieri et al., 2005a), and more organic compounds were leached at pH 2 and 11 than at pH 8 (Abernethy et al., 1996).

Tire wear material from three different tires was leached for six sequential leachings in order to investigate how much leachable toxic substances were present in the material [IV]. The toxicity of all three tires, to all species tested (*D. magna*, *P. subcapitata*, *C. dubia*, and *D. rerio*), was successively reduced during the six sequential leachings. The toxicity of the most toxic tire, to the most sensitive endpoint tested (*C. dubia* reproduction) was, however, still 140 mg/l after the sixth consecutive leaching. These results are in agreement with results obtained by Hartwell et al. (1998), who showed that three sequential 7-d periods of leaching reduced the toxicity of tire chips (1 cm^3), and with results obtained by Abernethy et al. (1996), who showed that nine sequential leachings reduced the toxicity of granulated rubber (0.4–0.5 mm). Only a slight reduction in toxicity was, however, observed for leachates of tire pieces (5–10 cm) after 52 d of daily renewals of test solutions (Goudey and Barton, 1992). It is plausible that the size and shape of the leached rubber material have an impact on the leachability of toxicants, with a more rapid leaching from smaller particles with a greater surface area. Study [IV] also showed that the toxicity varied significantly with respect to the tested species and endpoints, with the order of the most sensitive to the least sensitive being; 9-d reproduction of *C. dubia* > 9-d survival of *C. dubia* > 72-h growth inhibition of *P. subcapitata* = 48-h immobility of *C. dubia* > 48-h immobility of *D. magna* > 48-h lethality to *D. rerio* eggs.

The chronic effect concentrations determined for *C. dubia* 9-day reproduction and survival range from 10 to 1800 mg/l and from 50 to 3600 mg/l, respectively [IV]. The corresponding acute values for *C. dubia* range from 550 to 5000 mg/l, and the acute-to-chronic ratio is around 10. The acute and chronic effect concentrations of leachates of tire wear particles, found in this study and reported in the literature, range from 10 to 100 000 mg/l [VI]. These results are summarized in Table 2.

Table 2. Toxicity of tire particle leachates to aquatic organisms (modified from [VI]).

Test species	Effect concentration (EC/LC50 in mg/l)	Comment	Reference
Green algae *P. subcapitata*	470; 1640	Diluted leachate from two leachate concentrations, 72-h EC50	Gualtieri et al., 2005a
	50–2800	Sequential leachates from three tires, 72-h EC50	[IV]
Water flea *D. magna*	26 750; 53 300	Diluted leachate from two leachate concentrations, 48-h EC50	Gualtieri et al., 2005a
	100–2400	Leachates from 12 tires, 48-h EC50	[I]
	60–400	Leachates from 12 tires, 48 h + 2 h UV light EC50s	
	300– >10 000	Diluted leachates from 25 tires, 48-h EC50	[II]
	370–7500	Sequential leachates from three tires, 48-h EC50	[IV]
Water flea *C. dubia*	550–5000 50–3600 10–1800	48-h EC50 9-d LC50 9-d young/female EC50	
Zebrafish eggs *D. rerio*	550– >10 000	48-h LC50	
Frog embryo *X. laevis*	50 000–100 000	27–80% mortality & 80–98% malformed larvae after 120-h exposure	Gualtieri et al., 2005a
Overall range	10–100 000	1–9 d exposure to standard organisms	All references above

A few studies have evaluated sublethal effects of tire particle leachates. These have shown that tire particles leach compounds that have mutagenic (Benevento and Draper, 2005), teratogenic (Gualtieri et al., 2005a; Mantecca et al., 2007), and estrogenic (Zhang et al., 2002; Li et al., 2006) activities.

The long-term tests with *C. dubia* and *P. subcapitata* [IV] were used to derive a $PNEC_{water}$. By applying a safety factor of 50 to the lowest of these NOECs (on average 194 mg/l for *C. dubia* reproduction), a $PNEC_{water}$ for tire wear particles of 3.9 mg/l was derived [VI]. The $PNEC_{sediment}$ was estimated from the $PNEC_{water}$ using the equilibrium method since no effect studies on sediment living organisms have been conducted. This gave a $PNEC_{sediment}$ of 273 mg/kg dw [VI].

3.2 Toxicity identification evaluation

The TIE-study of leachates from 25 (new) tires indicated that the toxicity was caused mainly by organic compounds [II]. By passing the leachates through C18 SPE columns, the immobility of *D. magna* was, in all cases, reduced by more than 70%. Loaded columns extracted with a methanol/water gradient revealed that the toxicity was recovered in some of the methanol fractions, further reinforcing the conclusion that organic toxicants were present. The toxicity of the leachates from the three (used) tires tested in [IV] was reduced both by passing the samples through C18 SPE columns and through CM columns. Thus, the toxicity in this case was probably caused by both metals and organic compounds. Furthermore, a regression between the toxicity and the Zn concentrations in the leachates showed that this was the metal causing the toxicity. The Zn concentrations in the leachates (10 g rubber/liter leaching water) from study [IV] ranged from 0.5 to 5 mg/l, whereas the leachates in [II] contained between 0.1 and 0.6 mg/l Zn. The two studies used different leaching waters, reconstituted hard water [II] and deionised water [IV], respectively, and this probably caused the differences in TIE-results and Zn levels between the two studies. It is also possible that used tires leach more Zn and less organic compounds compared to new tires.

Consistently, Zn and/or organic compounds have been identified as the toxic components of tire particle leachates also in other studies. Zn and organic compounds were identified as the main toxicants to *D. magna* and *C. dubia* in tire leachates prepared from granulated tire rubber (Abernethy et al., 1996). Metals and organic compounds were suggested to be the toxicants responsible for the growth reduction of *R. subcapitata* exposed to tire particle leachates (Gualtieri et al., 2005a). The attempts to identify the organic toxicants in tire particle leachates are complicated by the fact that so many different chemicals are used by the rubber industry. A wide range of potentially toxic organic compounds are present in tire particle leachates. Sarasa et al. (2006) identified the following main organic constituents in tire powder leachates; benzothiazole derivates, phthalates, phenolic derivates, hydrocarbons, and fatty acids. Abernethy et al. (1996) detected more than hundred different organic compounds in the leachates with granulated rubber, mentioned above, and total phenols, aromatic amines, and resin acids were present at high concentrations.

A different approach to identify the toxic tire components were used in [III], in which specially manufactured tread rubber samples with different compositions were tested. Rubbers containing antidegradants of phenylenediamine types, benzothiazolic accelerators, and certain process oils, all leached compounds that were toxic to

D. magna. Photo-enhanced toxicity was found to be caused by both the antidegradent DTPD (chemical composition mixture of diaryl-p-phenylenediamine) and the high aromatic process oil [III].

3.3 Sediment quality triad assessment

High levels of contaminants were detected in several of the eighteen road runoff detention devices studied in [V]. Zn exceeded the Predicted Effect Level (PEL) at eight of the sites, and, thus, was the contaminant exceeding this level at most sites. Furthermore, Zn has, together with Cd, been shown to be the most mobile metal in detention pond sediments (Durand et al., 2004). Hence, Zn is probably the contaminant posing the highest threat to surrounding water bodies. As mentioned above, tire wear is a major source of Zn emissions in urban areas. This is supported by the strong correlation between tire wear particles (extractable organic Zn) and Zn found in this study [V]. Two other contaminants showing a strong correlation with tire particles were Cu, with brake linings as the most probable source (Hjortenkrans et al., 2007), and W (tungsten), a common component in tire studs (Bäckström et al., 2003).

The sediment concentrations of tire particles varied between <0.15 and 11 g/kg dw among the studied sites. The highest concentrations were found in two ponds receiving runoff from a bridge with an Annual Average Daily Traffic (AADT) of 12 500 vehicles per day, and in two manholes receiving road runoff from a road with an AADT of 100 000 vehicles per day. The high concentrations observed at the bridge sites were presumably caused by the steep road gradient leading up to the bridge causing an increased wear rate at these sites. Thus, tire particle concentrations >11 g/kg dw are likely to occur at locations with high traffic loads and where the driving pattern causes an increased wear rate.

Chemical contamination, sediment toxicity and *in situ* benthic fauna were found to correlate only poorly. The inconsistency between probable exposure and observed effects was probably related to a reduced bioavailability. Results from the literature have shown sediments contaminated by road runoff to be toxic in many cases (Maltby et al., 1995a; Wenholz and Crunkilton, 1995; Marsalek et al., 1999; Lee et al., 2004; Christensen et al., 2006), but not in all (Karouna-Renier and Sparling, 1997). Effects on the benthic fauna in streams receiving highway runoff have also been somewhat inconsistent between studies; effects were shown by Shutes (1984) and by Maltby et al. (1995b), whereas no effects were observed by Grapentine et al. (2004), and no or only slight effects were observed by Perdikaki and Mason (1999) and by Smith and Kaster (1983). No significant relationships between contaminant concentrations and effects on benthic fauna communities were found in five highway runoff detention ponds studied by Scher (2005). In this case, the observed differences in macroinvertebrate assemblages between ponds were attributed to differences in pond habitat characteristics rather than to contamination. These results are in agreement with study [V] that showed that the differences in benthic fauna communities among ponds are related to differences in nutrient supply rather than to contamination. Most of the ponds studied in [V] were dominated by tolerant (opportunistic) taxa like *Chironomidae* or *Oligochaeta*.

In order to further assess the environmental impact of road runoff and the possible contribution from tire wear, more ecotoxicological research should be directed towards road runoff recipients using appropriate chemical markers and a sediment quality triad approach, preferably combined with *in situ* bioassays and TIE. *In situ* approaches provide more realistic exposure scenarios than laboratory tests, and this would be of great importance given the inconsistent exposures from road runoff (pulse exposures) (Crane et al., 2007). Furthermore, since road runoff detention ponds were found to be dominated by pollution-tolerant organisms [V], that would be present regardless of the presence or absence of pollutants, *in situ* approaches would probably provide more sensitive endpoints than benthic fauna studies (Crane et al., 2007).

3.4 Environmental concentrations

Table 3 summarizes the results from the meta-analysis of published data on tire markers in different environmental matrices [VI]. The results show that tire material is present in all environmental compartments, including air, water, soils/sediments, and biota. The largest amount of tire wear particles accumulate on the road surface and its vicinity and are then further transported by runoff water. The concentrations in road runoff and receiving waters are particularly high at the beginning of storm events (Kumata et al., 1997; 2000). The maximum predicted concentrations in surface waters range between 0.03 and 17.9 mg/l [VI]. Sediments, and at certain locations also sewage sludge, are the probable final deposition sites for tire wear particles. Sediment concentrations as high as 155 g tire wear particles/kg dw have been reported at locations were runoffs from highly trafficked roads are directly discharged to receiving waters without prior infiltration (Spies et al., 1987; Voparil et al., 2004). The concentrations in soil decrease rapidly with distance from the road, and concentration reductions of >80% have been reported at 30 m distance from roads (Cadle and Williams, 1978; Fauser, 1999). More than 90% of the airborne particles have been reported to be <1 µm, and are, thus, inhalable (Fauser, 1999). The concentration of tire particles smaller than 1 µm where 40–50% higher at 18 m distance from a road compared to at 3 m from a road (Fauser et al., 2002). The concentration of larger particles was, however, found to decrease with the distance from the road. The concentrations of tire particles at 86 m height above a road were about 30% of the concentrations of airborne tire particles just above the road (Kim et al., 1990). These studies, thus, suggest that airborne tire particles can be transported over relatively long distances.

Table 3. Estimated and reported maximum concentrations of tire wear particles in various environmental matrices based on different chemical markers as reported in the literature (modified from [VI]).

Matrix	Concentration range	Marker(s)	References
Soil	0.6–117 g/kg dw	SBR, 24MoBT, Extr. Org. Zn	Pierson and Brachaczek, 1974; Cadle and Williams, 1978; Spies et al., 1987; Fauser, 1999
Snow	563 mg/l	BT	Baumann and Ismeier, 1998
Road runoff	12–179 mg/l	HOBT, 24MoBT, BT	Kumata et al., 1997; 2000; 2002; Reddy and Quinn, 1997; Baumann and Ismeier, 1998; Zeng et al., 2004
Surface water	0.5–6.4 mg/l	24MoBT, NCBA, 24MoBT, HOBT	Reddy and Quinn, 1997; Kumata et al., 2000; Ni et al., 2008
Sewage sludge	43 g/kg dw	Zn	[VI]
Sediment	0.4–155 g/kg dw	24MoBT, HOBT, Extr. Org. Zn	Spies et al., 1987; Reddy and Quinn, 1997; [V]
Air	0.5–11 $\mu g/m^3$	SBR/NR, BT, NCBA, Extr. Org. Zn	Cardina, 1974; Pierson and Brachaczek, 1974; Cadle and Williams, 1978; Lee et al., 1989; Kim et al., 1990; Fauser et al., 1999; Kumata et al., 2000

Abbreviations for chemical markers; styrene-butadiene rubber (SBR), natural rubber (NR), benzothiazole (BT), 2-hydroxybenzothiazole (HOBT), 2-(4-morpholinyl)benzothiazole (24MoBT), N-cyclohexyl-2-benzothiazolamine (NCBA), and extractable organic zinc (Extr. Org. Zn).

3.5 Risk characterisation

The risk characterisation ratios (RCRs) for tire particles in various environmental matrices that were calculated in [VI] are summarized in Table 4. The RCRs indicate potential risks from tire wear particles to aquatic organisms in surface waters and sediments. The risk to pelagic organisms is mainly related to first flush runoff, which means that runoff detention devices are important in protecting surface waters from toxicity caused by tire wear particles. The risk to sediment living organisms is particularly high at certain locations, such as downstream of highly trafficated bridges, where the runoff is directly discharged to the receiving water without prior infiltration, which means that runoff treatment devices are especially important at these locations. More research is, however, needed to evaluate the performance of runoff treatment systems and to improve their performance. For instance, the reduction of contaminant concentrations by ponds and ditches is often difficult to control due to fluctuations in water flow.

Studies on terrestrial organisms are very sparse. Given the limited dispersion of tire wear particles in soil, the risks are, however, probably restricted to the immediate road surroundings. At some locations tire particles might, however, be important as a source for the contamination of sewage sludge making it unsuitable as a soil fertilizer [VI]. Risks associated with the airborne fraction of tire particles are mainly related to the unknown effects on human health, which need to be further assessed.

Table 4. Summary of risk characterisation ratios (RCRs) for various environmental matrices (modified from [VI]).

Matrix	RCR range	Comment
Surface water	0.008–4.6	Potential risk to aquatic organisms
	14.4	Risk associated with peak runoff concentrations during snow melting periods
Sediment	1.3–40.3	Potential risk to sediment living organisms
	568	Risk to sediment living organisms at certain locations with heavy traffic and with no infiltration of the road runoff before discharge to receiving waters
Soil	?	Studies on terrestrial organisms are very sparse but risks are probably restricted to the immediate road surroundings
Air	?	More research is needed to evaluate the risks to human health related to the inhalation of airborne tire particles

3.6 Uncertainty/variability in the risk assessment

Uncertainty is an inherent part of risk assessments. The sources of uncertainty include both lack of understanding/lack of data and variability in the inherent properties of ecosystems and their components. The uncertainties involved in the extrapolations, from observed effects in a few species in laboratory tests to effects on natural ecosystems, are large and dealt with by the application of “safety” factors, as described above. As was also mentioned, these factors are arbitrary factors and there is vague scientific evidence that the application of these factors really lead to safe concentrations in the environment (without being too conservative). A set of sources of variability specifically associated with the risk assessment of tire wear particles have been identified [VI]. These sources and their magnitudes are summarized in Table 5.

Table 5. Variability associated with various components related to the hazard and risk assessments of tire wear particles (modified from [VI]).

Source of variation	**Min–max**[a]	**Comment**
Exposure assessment		
Road runoff conc.	0.3–179 mg/l	600-fold range, from 6 studies
Surface water conc.	0.5–6.4 mg/l	13-fold range, from 3 studies
Sediment conc.	0.3–155 g/kg dw	517-fold range, from 4 studies
Soil conc.		
road adjacent	0.6–117 g/kg dw	195-fold range, from 4 studies
30 m from road	0–≤0.1 g/kg dw	100-fold range, from 2 studies
Air conc.	0.4–11.0 µg/m^3	28-fold range, from 7 studies
Effect assessment		
Overall toxicity	10–100 000 mg/l	10 000-fold range, from 4 studies
Tire composition	100–2400 mg/l	>100-fold range, among 12 to 25 tires
Species and endpoints	10–>10 000 mg/l	>1000-fold range, among 4 species and 6 endpoints
Leaching procedure	630–53 300 mg/l	85-fold range, from 2 studies

[a] From Tables 2 and 3.

The variability associated with the estimates of environmental concentrations may be related to the use of different analytical methods and different chemical markers. Most of the variability is, however, probably due to “true variability” reflecting different concentrations at different places, e.g. at various distances from roads. The variability associated with the estimates of toxic effect concentrations is related to different tires (rubber formulations) tested, interspecies variability, and to test induced differences like leachate production, as discussed above.

4. Concluding remarks

Tire wear particles accumulate on the road surface and its vicinity and are then further transported by runoff water. Sediments, and at certain locations also sewage sludge, are the probable final deposition sites. The initial risk assessment indicates potential risks for aquatic organisms in surface waters and sediments, which means that further risk assessment is needed. The maximum risk characterisation ratios occur on a local scale, close to the road. In countries with well-developed road networks, a significant part of the land area is, however, affected by roads. Figures from the USA show, for example, that 20% of the total land area is within 127 m from a road (Riitters and Wickham, 2003). Thus, any effects occurring close to roads are probably also important on a regional scale. The effects of tire wear particles on the ecosystems are, however, probably of minor importance compared to the total ecological impact of roads, including impacts on the abiotic components of ecosystems such as, e.g., the hydrology, microclimate, and water and air chemistry, as well as impacts on the biotic components such as, e.g., barriers to movement, behaviour modification, and mortality (Coffin, 2007). Nevertheless, the release of toxic components from tire wear particles needs to be reduced in order to protect receiving surface waters and to reach the established environmental quality objectives on chemical pollution and water quality, and thereby achieve an ecologically sustainable development. The most efficient way to achieve this is probably by developing new tires with more environmentally friendly constituents.

4.1 Summarized conclusions

- Simple standardized aquatic toxicity tests, e.g. the acute *Daphnia magna* immobilization test, using grated tread rubber equilibrated with reconstituted test water, can be used as a screening method for ranking of tires in terms of their ecotoxicological hazard potential [I].

- Acute and chronic toxicity of tire particle leachates to aquatic organisms occurs at concentrations ranging from 10 to 100 000 mg/l [VI].

- The toxicity of wear material from different tires varies by >2 orders of magnitude [I–II].

- The toxicity of tire particle leachates is mainly caused by zinc and organic compounds [II–IV].

- The toxicity of tire particles is reduced over time (by sequential leachings) [IV].

- Detention ponds, receiving road runoff, are primary recipients of tire wear particles. The levels of tire material in Swedish pond sediments correlate with the levels of tungsten (from tire studs) and of copper (from brake linings) [V].

- Zinc is the contaminant in detention pond sediments posing the greatest threat to surrounding water bodies and tire wear is a main source of this metal [V].

- Tire wear particles are also present in surface waters, soils/sediments, air and biota [VI].

- Risk characterisation ratios (RCRs) for exposure of aquatic organisms in surface waters and sediments exceed unity, showing a need for further risk assessment [VI].

- Two options are recommended to reduce the environmental impact by tire wear particles; the development of tires with more environmentally friendly constituents and improved road runoff treatment [VI].

4.2 Proposals for future research

The $PNEC_{sediment}$ used in this risk assessment was estimated from the $PNEC_{water}$ using the equilibrium model. The bioavailability of the tire particles may, however, differ from what the model assumes. Future ecotoxicological research should, therefore, be focused on the sediment toxicity of tire particles.

Tire rubber is known to be an efficient adsorbent of metals and organic compounds, and tire particles may, therefore, alter the bioavailability of these contaminants in the environment. Tire particles were, for example, shown to increase the bioavailability of PAHs in sediments (Voparil et al., 2004). It is, therefore, important to further investigate the role that tire particles might play in altering the bioavailability of other contaminants.

Field studies on the toxic effects of tire wear particles in the aquatic environment are very rare. Road runoff detention ponds are primary recipients of tire wear particles, and, therefore, construction, environmental monitoring and management of such ponds should receive increased attention. More ecotoxicological research should be directed towards these ponds preferably using *in situ* bioassays and TIE, and appropriate chemical markers.

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