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Environmental labeling of car tires—toxicity to *Daphnia magna* can be used as a screening method

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Abstract

Car tires contain several water-soluble compounds that can leach into water and have toxic effects on aquatic organisms. Due to tire wear, 10 000 tonnes of rubber particles end up along the Swedish roads every year. This leads to a diffuse input of emissions of several compounds. Emissions of polyaromatic hydrocarbons (PAHs) are of particular concern. PAHs are ingredients of the high aromatic oil (HA oil) that is used in the rubber as a softener and as a filler. The exclusion of HA oils from car tires has started, and an environmental labeling of tires could make HA oils obsolete. The toxicity to *Daphnia magna* from 12 randomly selected car tires was tested in this study. Rubber from the tread of the tires was grated into small pieces, to simulate material from tire wear, and the rubber was equilibrated with dilution water for 72 h before addition of test organisms. The 24-h EC_{50}s of the rubber pieces ranged from 0.29 to 32 g l^{-1}, and the 48-h EC_{50}s ranged from 0.0625 to 2.41 g l^{-1}. Summer tires were more toxic than winter tires. After the 48-h exposure, the daphnids were exposed to UV-light for 2 h, to determine if the tires contained compounds that were phototoxic. After UV-activation the EC_{50}s ranged from 0.0625 to 0.38 g l^{-1}. Four of the 12 tires had a very distinct photoactivation, with a toxicity increase of >10 times. This study has shown that the used method for toxicity testing with *Daphnia magna* according to ISO 6341 could be used as a basis for environmental labeling of car tires.

Keywords: Environmental; Labeling; Phototoxicity; Rubber; Tire; Toxicity

1. Introduction

A report from the Swedish National Chemical Inspectorate in 1994 initiated the discussion on environmental pollutants in automotive tires in Sweden. The report (Ahlbom and Duus, 1994) showed that oil containing large amounts of polyaromatic hydrocarbons (PAHs) is a major ingredient in most tires. PAHs are well known for their toxicity, carcinogenicity and mutagenicity (Rydén et al., 2003). The High Aromatic oils (HA oils) are residual products obtained from the refinement of base oils in, for example, lubricant oil manufacturing. HA oils are used as process oils in tire manufacturing, because they make the rubber easier to mould, and additional HA oils may also be added as fillers. Each tire contains about 1 kg of HA oil.

Approximately 60 000 tonnes of car tires are used in Sweden annually. Due to tire wear, this usage leaves around 10 000 tonnes of rubber particles along the Swedish roads every year (Ahlbom and Duus, 1994). Tires are designed to be durable and chemically stable, but nevertheless tires contain water-soluble components

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that leach out to water and are toxic to aquatic organisms (Day et al., 1993; Nelson et al., 1994; Ahlbom et al., 1996; Evans, 1997; Hartwell et al., 1998). Tire wear produce small rubber particles with a large surface area, from which toxic compounds can leach, and this is expected to result in higher toxicities compared to results from tests made with whole tires (Day et al., 1993; Nelson et al., 1994; Anthony et al., 1995; Evans, 1997; Hartwell et al., 2000).

Leakage of polyaromatic hydrocarbons (PAH) has been of most concern. Conflicting information, concerning the size of PAH emissions from tire wear has been presented in previous studies. For example, Ahlbom and Duus (1994) calculated the PAH contribution from tire wear in Sweden, to 10 tonnes per year, whereas Null (1999) suggested 1.7 tonnes per year based on the same figures. The inconsistency between different studies can be explained by the fact that calculations are based on different analytical methods, and also by the fact that different PAHs might have been measured. In any case, traffic is considered to be a significant source of PAH emissions, and tire wear contributes more to PAH emissions than the emissions from the engines of modern passenger cars. Tire wear gives a diffuse input to emissions, which is normally less apparent at once. Therefore, emissions from tires are more difficult to control than those from point sources. Baekken (1994) has shown that the PAH concentration in fish in a lake close to a highway was five times the concentrations in fish from a reference lake, and a major part of it may have originated from tire wear.

1.1. Rubber chemicals

Rubber for tires is made from a variety of chemicals. Several of these, apart from the earlier mentioned HA oil, are also of environmental concern. A summary of the different rubber constituents, their ingredients, functions and environmental aspects is given in Table 1.

1.2. Replacement of HA oils

Some low-aromatic oils, such as MES oils (mildly or medium extracted solvate oils), TDAE (treated distillate aromatic extracts), and NAP oils (naphtenic process oils), are being used as alternatives to HA oil in tire manufacturing (Null, 1999). The switch from HA oils has involved some technical challenges related to quality and safety (Ahlbom et al., 1996). Despite this, HA oils have now been replaced in the majority of the retreaded tires on the Swedish market. During the last couple of years, HA oils have also been replaced in most (75%) of the winter tires, but they are still used in most summer tires. A complete replacement of HA oils with the low-aromatic alternatives would reduce the PAH emission from tire wear by approximately 98% (Null, 1999).

1.3. Phototoxicity

Photochemical reactions take place when molecules absorb light photons. These reactions are of great importance in the atmosphere, but also in surface waters, for the chemical transformation and degradation of chemical compounds (Manahan, 1994). But photochemical reactions are not always environmentally beneficial. Some compounds, including some PAH species, may absorb the ultraviolet (UV) spectra of light, producing electronically excited forms that are more toxic than the original molecule. This phenomenon is called phototoxicity. Tires contain several PAH species that are phototoxic, for instance fluoranthene and pyrene (Ahlbom and Duus, 1994; Ankley et al., 1997).

1.4. Objectives

The primary objective of this study was to investigate differences in toxicity among different tires and if the differences were related to summer and winter type, especially with reference to HA oils. A secondary objective was to demonstrate if the toxicity test result could be used as a criterion for positive environmental labeling of tires.

2. Material and method

The tires were very kindly provided to us by NDF AB in Mölndal. Rubber from fresh tire treads was grated into small rubber pieces to simulate material from tire wear. All tests were performed according to the ISO standard (ISO, 1996) with *Daphnia magna* as the test organism. Twelve different car tires were studied; four summer tires and eight winter tires, and their origins are shown in Table 2.

2.1. Sample preparation

The grated rubber was weighed up in Petri dishes (50 ml). The samples were diluted, using dilution water according to ISO (1996), with hardness 250 mg $CaCO_3$/l and pH 8.0, to obtain seven concentrations (0.25, 0.5, 1, 2, 4, 8, 16 g l^{-1}) and a dilution water control (0 g l^{-1}). The rubber pieces did not dissolve completely in the water, and at the higher concentrations they tended to accumulate (float) on the surface. The Petri dishes with rubber-/water mixtures were allowed to equilibrate for 72 h at 20 ± 2 °C before addition of test organisms. The test is shown in Fig. 1 and an enlargement of the grated rubber material in Fig. 2.

2.2. Toxicity tests

Twenty 0–24 h old neonates of *Daphnia magna* were added after 72-h equilibration of grated rubber and