NanoDialogue
of the German Government

Use of Nanomaterials in Tires – Environmental Relevance and Emissions

Topical report related to the ExpertDialogue “Opportunities and Risks of the Use of Nanotechnologies in the Automotive Sector” which took place on September 26 to 27, 2017

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1 Background

Since 2006, the German Ministry of the Environment, Nature Protection and Nuclear Safety has organised the German Government's NanoDialogue. This dialogue supports information exchange about the opportunities and risks of using nanomaterials among stakeholders from enterprises and industry, science, ministries and authorities as well as civil society organisations.

The ExpertDialogue "Opportunities and Risks of the Use of Nanotechnologies in the Automotive Sector took place in the 5th phase of the NanoDialogue[1]. The discussions focussed on the societal contextualisation of this particular application area.

The discussions showed that the production of vehicles heavily relies on the use of nanotechnologies and nanomaterials. However, modern material science develops different approaches to overcome current challenges and hence, nanotechnologies are only one technology among many. They are mainly used to achieve improvements in the areas of safety, convenience, fuel use (batteries), to reduce emissions of pollutants as well as to improve the optical performance of vehicles. Therefore, nanomaterials can be found in any car part and fulfil various functions.

The use of "free", i.e. non-matrix bound, nanoparticles is limited to a few applications, such as additives in fuels or in lubricants. As the majority of uses involves a firm binding to a matrix, it is reasonable to assume low emissions and hence low (eco-)toxicological risks for humans and the environment in the use phase of vehicles.

Generally, nanomaterials may reach the environment from disposal processes as well as via abrasion and aging of materials. If small material pieces are emitted into the environment, they may degrade more rapidly than the nanomaterials they contain. Consequently, the nano particles may persist as agglomerates or as aggregates in the environment. Very little information is available about the type and extent of potential risks from these exposure pathways.

This report complements the discussions at the ExpertDialogue by providing detailed information on the use of nanomaterials in tires and related potential exposures of humans and the environment. The application area "tires" is particularly relevant, as large amounts of nano silica are used as filler and are abraded with the tread rubber. The report presents the various environmental aspects of tread rubber abrasion; it presents recent data from national emission reporting and describes ongoing research projects.

[1] The documentation of this and the previous events in the context of the NanoDialogue can be accessed via the web-pages of the Ministry of the Environment http://www.bmub.bund.de/themen/gesundheit-chemikalien/nanotechnologie/nanodialog/

1.1 Use of Nanomaterials in Vehicles

Nanomaterials and nano structures enable new material characteristics and functionalities. In vehicles, nanomaterials are used for example as a component in the chassis, engine, tires, electrical and electronic components and in used fluids. The aims of the nanomaterial application in vehicles are among others:

- Reduced fuel need and lower emissions by reducing the friction (engine, tires) or increasing incineration efficiency (fuel additives, catalysts);
- Prolonged life-times via more stable materials (composite plastics, coatings);
- Reduced wear and tear (lubricants);
- Improved cleaning performance of materials (air filters, easy-to-clean surfaces);
- Increased driving safety through sensors and electronic control systems;
- Improved convenience, optics, haptics and equipment of the interior in general.

Electronics are an increasingly important application area. Here, nanomaterials support and enable a large variety of different new functionalities.

During the use phase of the vehicles, most of these uses are unlikely to create direct exposures to humans and the environment; however, it should be mentioned that there are unanswered questions regarding disposal, such as where nanomaterials partition to within the treatment process and after disposal. This is particularly relevant with a view to the high share of exported end-of-life vehicles (app. 2/3 of all deregistered vehicles are exported).

1.2 Use of Nanomaterials in Tires

Tires mainly consist of synthetic or natural rubber, to which additives are added to achieve or enhance particular material properties. The main additive used is a combination of carbon black and nano silica (SiO_2).

The use of nano silica as a tire additive may reduce the roll resistance by 20 %, increase adhesion to the pavement by 12 % and shorten the breaking distance by 10 % (European Parliament 2008 in (OECD 2014)). Hence, the use of nano silica may decrease environmental burdens by saving fuel as well as increase driving safety. The potential reduction in environmental burdens is estimated at 5 – 10 % over the life cycle of tires.

In (OECD 2014), the concentration of nano silica in tires on the European market is given as 11.4 % and that of carbon black as 17.5 %. Wigger et al. (2018) state a typical share of nano silica of 5-15 %. Table 1 gives an overview of the tire composition on the European market as well as in the United States and China based on an OECD study. The composition includes the tread rubber, which is relevant for the abrasion (c.f. next section), and the tire layers below it.

Table 1: Shares of different components in an “average tire“ in various regions (OECD 2014)

Share Component	**EU**	**US**	**China**
Synthetic rubber	24.3%	25.0%	24.4%
Natural rubber	16.6%	17.0%	16.7%
Carbon black	17.5%	19.1%	17.5%
Nano silica	**11.4%**	**9.1%**	**11.4%**
Steel	11.7%	10.4%	11.7%
Softeners	6.6%	6.8%	6.6%
Other	11.9%	12.6%	11.8%

2 Materials abraded from tire

The amount and composition of abraded rubber from tires depend on the material properties of the tire (used rubber, hardness, resistance against aging), the construction of the tire and the interplay between the vehicle and the tire (Hillenbrand et al. 2005). Finally, the driving style also influences the extent of tire abrasion.

Information on the amount of abraded rubber varies depending on the source. An evaluation made for the German UBA (Hillenbrand et al. 2005) determined an average amount of abraded rubber for passenger cars of 90 mg per driven kilometre (mg/PCkm) with a range of 53-200 mg/PCkm. For delivery vans/trailer trucks, the average values are much higher, i.e. between 700 mg/PCkm and 1.200 mg/PCkm. Other sources estimate the share of rubber that is abraded from tires to 10-11% of the total tire mass (Giese et al. 2018; Wang et al. 2016) or alternatively 10-20 % (Wigger et al. 2018). The per capita emission of abraded rubber from tires are estimated to be between 0.23 and 4.7 kg/a with a global average of 0.81 kg/a (Kole et al. 2017). In a study by the German UBA from 2015, the per capita emissions are described as 0.75 to 1.38 kg/a (Essel et al. 2015). A comparison between the abraded rubber from tires (= 100 %) and abraded materials from breaks (8 %) and street markings (5 %) underlines the high relevance of emissions from tires (Kole et al. 2017).

Particles abraded from tires mainly stem from the tread rubber and therefore their composition is not identical to the “average tire composition”. The inner tire layers are made to contain air inside the tire and to prevent the inner components from oxidation, which necessitates a different material composition (OECD 2014). In addition, the composition also differs because tires are contaminated with other substances during their use phase and some tire constituents degrade over time.

The composition of abraded tire rubber was analysed in various studies (Dave 2013; Wik and Dave 2009; Krömer et al. 1999a; Degussa 2007; Okel and Rueby 2016; Kocher 2010). The results of these studies are summarised in Table 2. The share of included nanomaterials (nano silica and carbon black) ranges between 20 and 40 % with three studies unanimously specifying the percentage at 34 % (Okel and Rueby 2016; Krömer et al. 1999a; Degussa 2007).

Table 2: Composition of abraded tire rubber

Material	**(Dave 2013; Wik and Dave 2009)**	**(Kocher 2010)**	**(Krömer et al. 1999a)**	**Degussa (2007) in (Kocher 2010)**	**(Okel and Rueby 2016)**
Synthetic or natural rubber	40-60%	39%	42%	53.6%	No data
Carbon black / SiO2	**20-35%**	**34%**	**34%**	**34%**	**22-40 %**
Mineral oil	15-20%	No data	17.1%	4.3%	No data
Sulphur	1%	No data	No data	2.1%	1-4%
Zink oxide	1.5%	1.1%	0.5%	1.3%	1%
Stearin acid	1%	No data	No data	0.9%	No data
Sulfen amide or thiazoles	0.5%	No data	No data	2.7%	No data
Other/not further specified	1.2%	24.5%	6.4%	1.1%	55-76 %

2.1 Fate and Behaviour in the Environment

The abraded rubber from tires is either swirled into the air or remains on the pavement, e.g. if streets are wet. The rubber particles are transported with the (rain) water and air and may deposit onto soils (c.f. Hillenbrand et al. 2005) or surface waters (c.f. Sundt et al. 2014; Wik und Dave 2009). Up to now, scientific assessments on abraded tires and their environmental relevance have primarily focussed on:

- Dust and fine dust emissions
- Emissions of heavy metals
- Discharge of plastics into the environment.

The discharge of nanomaterials from tires into the environment has been discussed as an individual issue in only a very few cases. Figure 1 illustrates fate and behaviour of particles abraded from tires in the environment.

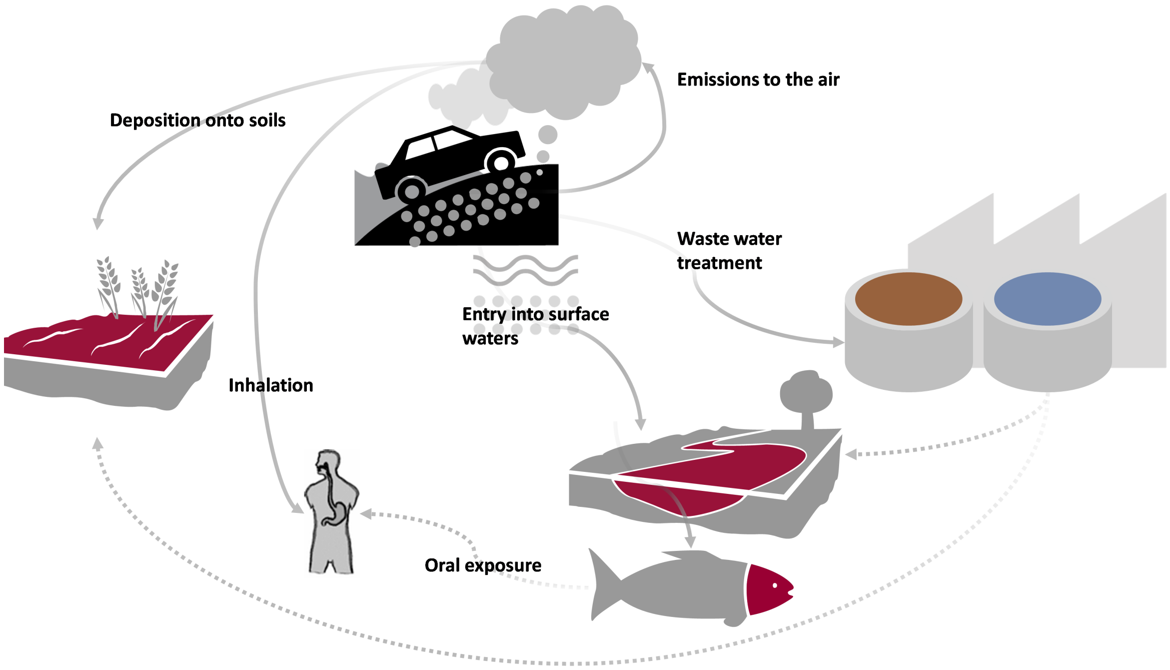

Figure 1: Possible behaviour and environmental sinks of particles abraded from tires (Graph: Ökopol)

The organic components of the abraded rubber slowly degrade in the environment[2] while the other components, despite their low concentration in the tire rubber may accumulate in soils, e.g. heavy metals (Kocher 2010). This means that inorganic nano particles may be released into the environment from the rubber matrix of abraded tires.

2.2 Relevance of Particles Abraded from Tires for Health and the Environment

In terms of amounts, abraded materials from tire are one of the largest sources of dust emissions from street traffic. Dust from street traffic consists mainly of sedimentable but to a smaller extent, also of fine dusts. Kocher (2010) identifies the relation between sedimentable dust and fine dust as 14:1. The share of fine dusts emitted as particles from abraded tires is estimated at 1 to 7 % of the total abraded rubber from tires (Kocher 2010). The share of abraded tire rubber in the total fine particle dust in the air (PM 2.5) is estimated at 3-7 % (Kole et al. 2017). Hence, the contribution of

[2] Krömer et al. 1999b calculated an equilibrium between input to and degradation of abraded tires in soil at 16 g per m³.

abraded tire materials to air pollution with potential impacts on human health can be regarded as relevant.

Analyses of traffic-based soot emissions show that abraded tires constitute a major share of all soot emissions, besides soot particles from vehicle exhaust gas. The contribution of abraded tires to the soot load from street traffic is estimated to be between 7 and 25 % (Kocher 2010).

2.2.1 Input of Nano Silica into the Environment

In the recent years, a few scientific studies considered the discharge of nano silica into the environment. For example, Wang et al. (2016) created an emission and exposure model for any of nano silica's use with a geographical focus on the EU and Switzerland. Giese et al. (2018) conducted a similar work for Germany. Wigger et al. (2018) focused on improving the data basis on production volumes of nanomaterials, which was the reason for the high uncertainty of the data in the other two studies.

Material Flows and Environmental Releases of Nano Silica in the EU according to Wang et al.

Wang et al. probabilistically modelled material flows and environmental risks from nano silica (Wang et al. 2016). Starting from the total production volume, their assessment not only covers the use in tires but any known application area. An overview of these uses and their relevance is provided in Figure 2. An annual production volume in the EU of 5,800 t of nano silica is used as median, with a considerably large range of values due to the variety of different data sources.

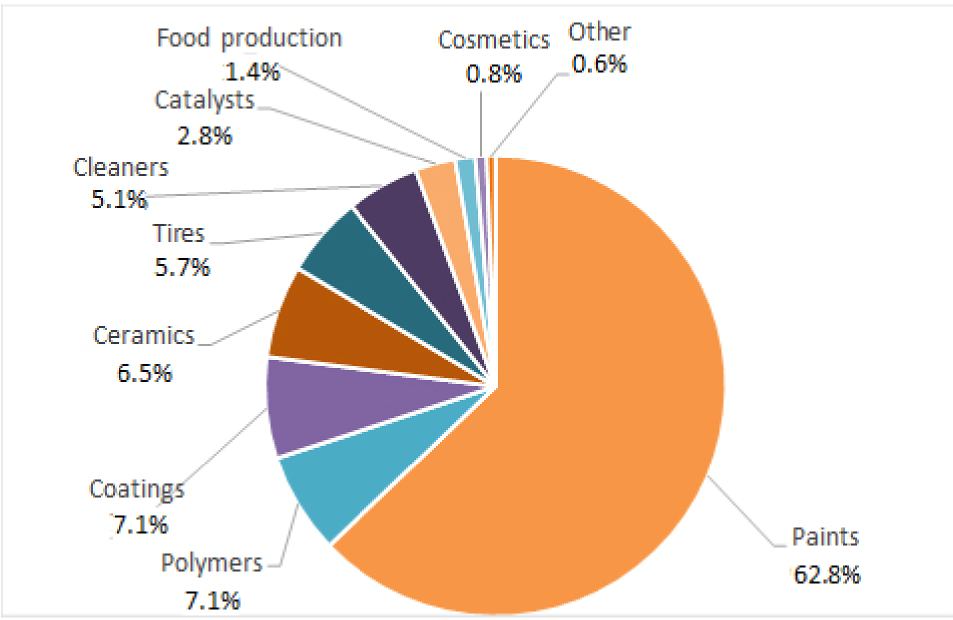

Figure 2: Applications of nano silica in the EU according to (Wang et al. 2016)

The discharge from these uses into the environment is modelled. It is assumed that from the use of nano silica in paints and polymers, which are the main application areas, no releases take place during use and in the waste treatment processes (landfilling of ashes from thermal treatment with an assumed lack of emissions to the environment). From the other uses, relevant emissions occur into water and soils. According to this study, the resulting environmental concentration (PEC) of nano silica in surface water is predicted to be between 0.053 and 3.3 µg/l in the EU.

Material Flows and Environmental Inputs of Nano Silica in Germany according to Giese et al.

Similarly, Giese et al. (2018) modelled the material flows and resulting potential environmental risks from nano silica based on the production volumes. Apart from SiO_2, also nano-scale CeO_2 and silver are assessed. The geographical area is Germany. The environmental concentrations were identified using a dynamic model covering the period from 1950 until 2050.

The production volumes were identified with similarly large ranges as provided by Wang et al. With 18-19 %, the share of all applications that is used in tires is assumed to be slightly higher. The resulting surface water PECs modelled by Giese et al. resemble those estimated by Wang et al.

“Correction” of production volumes and impact on the material flow analysis by Wigger et al.

Wigger et al. (2018) worked on the available information on production volumes of nanomaterials, among others SiO_2. A central approach to reduce the related uncertainties was to specify the partly “fuzzy” demarcation of nanomaterials and bulk materials. Their study showed that almost the entire SiO_2 is produced at nano scale. Hence, the European production volume is determined to be 459,000 tonnes. Using this information as input to the exposure models, they estimate that app. 9.3 % of this amount reach soils and persist there. The following table lists the PECs for the year 2013, together with the values of Giese et al. to facilitate the identification of the impacts of the changed production volume.

Table 3: PECs of nano silica in the EU in 2013 with (Wigger et al. 2018) and without corrected input figures (Giese et al. 2018)

Environmental compartment	Median of PECs 2013 (Wigger et al. 2018)	Median of PECs 2017 (Giese et al. 2018)	Unit
Surface waters	8.6	5.34	µg/l
Wastewater from treatment plant	240	44.37	µg/l
Sewage sludge	5,200	-	mg/kg
Soils fertilized with sewage sludge	27,000	3,085-78,272 (depends on degradation)	µg/kg
Soils	83	63	µg/kg
Sediments	30	32	mg/kg

The figures reflect that nano silica in particles abraded from tread rubber reaches wastewater treatment plants, may accumulate in sewage sludge and reaches soils if that sludge is used to fertilize soils. The PEC of sludge-treated soils is significantly higher than that of non-treated soils. The correction of production volumes caused a significant increase of the predicted environmental concentrations in almost all environmental compartments.

3 National Emission Reporting

Abraded tires are considered in national emission reporting with regard to the emissions of dust (PM2.5 and PM10), carbon black and heavy metals (Cr, Ni, Zn)[3]. Each year, the emitted amounts are modelled and reported based on specific emission factors and the annual driving performance provided by the Federal Office for Motor Traffic. Abraded materials from tires and brakes are reported together. For 2017, the following emissions were reported.

Table 4: Emissions from abraded tires and brake, Germany 2017, all data in t/a

PM2.5	PM10	Carbon black	Pb	Cd	Hg	As	Cr	Cu	Ni	Se
7.3	13.5	1.8	89.8	0.3	0.1	0.4	24.4	2192	4.1	2.3

[3] C.f. https://iir-de.wikidot.com/1-a-3-b-vi-emissions-from-tyre-and-brake-wear

Currently, the method for considering abraded tires in national emission reports is under revision and an implementation using the model TREMOD is being assessed[4], which is the basis for emission reporting in the traffic sector in Germany.

4 Abraded Tires in Current Research Projects

4.1 UBA-Project: „Plastics in the Environment“

In the frame of the UFOPLAN-project "Plastics in the Environment", the annually emitted amount of plastics from their various (more than 60 different) uses is estimated, including releases from tire abrasion. The calculated amount of app. 140,000 t would result in an equivalent amount of 14,000 t of SiO_2 if its share is assumed to be 10 %.

4.2 BMBF Project: "Abraded Tires in the Environment"

The project "Abraded Tires in the Environment" is led by the Technical University of Berlin (Prof. Barjenbruch) and supported by the German Research Ministry's (BMBF) funding programme in the focal area of "Plastics in the Environment – Sources, Sinks and Solutions". It analyses the released particles and the release mechanisms in more detail. Emphasis is placed on:

- Empirical analyses of the fate in the use phase;
- Analytical studies of abraded tires in the environment;
- In-situ observation of rain events in street water run-off;
- Simulation and evaluation of particles abraded from tires and input into the environment.

Various further projects in the BMBF's same funding area include assessments of the entry pathways of plastics into the environment and related risk assessments. However, none of them includes an assessment of abraded tires at a comparable level of detail.

5 Conclusions

Nano silica is used in tires in significant amounts. It may reach the environment in a matrix-bound form via abrasion. After degradation of the rubber matrix, it may persist as individual particle in the environment.

[4] C.f. https://www.ifeu.de/methoden/modelle/tremod/

Abraded particles from tires are a source of fine dust emissions and hence contribute to the overall health burden. To what extent environmental exposure to nano silica abraded with particles from tires pose risks to the aquatic environment cannot be determined due to a number of uncertainties in the available data basis and models. However, there are indications from model calculations that in the mid-term environmental concentrations could be reached which may cause damage to aquatic ecosystems, in particular burdened environmental compartments.

Emissions from abraded tires pertain to the national emission reporting. Several research projects assess the environmental relevance of (emissions from) abraded tires. However, impacts stemming particularly from nanomaterials in these abraded tires are currently not systematically analysed.

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