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Dissipation of tungsten and environmental release of nanoparticles from tire studs: A Swedish case study

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Abstract
Tire studs, with pins made of cemented tungsten carbide with cobalt (WC-Co), are used in many countries during winter. Tungsten, the main content of the pins, is geochemically scarce and a critical raw material. In addition, analytical studies have identified WC-Co nanoparticles in the environment, which are worn off during the use of studded tires. The aims of this study are to assess (i) the dissipation rate and functional recycling related to the use of tungsten in tire studs as well as (ii) the magnitude of the WC-Co nanoparticle release in Sweden. Tungsten mass flows related to WC-Co in tire studs were estimated throughout the product chain, from mining to waste management, using material flow analysis. This study shows that 100% of the tungsten in Swedish tire studs is presently dissipated (67% as release during use) and there is no functional recycling. This can be compared with the estimated average global dissipation rate of >60% and functional recycling rate of 10–25% after use for tungsten. Recovery of tungsten during waste management and alternative solutions to WC-Co in tire studs are discussed as possible remedies. Furthermore, the estimated release of nano-sized WC-Co particles is in the same order of magnitude as the modeled release of some engineered nanomaterials in Sweden and higher than for e.g. nano-silver.

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1. Introduction
In order to improve the gripping power on slippery roads, studded tires are used in a number of countries, including Canada, Russia, Sweden, Norway, Finland, and more than forty states in the United States (US). The use of studded tires varies between places and over time but is extensive in many regions. For example, 88% of the passenger cars in Finland used studded tires in 2009–2010 (Malmivuo et al., 2017), 66% of the passenger cars in Sweden in 2015 (Swedish Transport Administration, 2015), 49% in Alaska in 1990 (Zubeck et al., 2004) and 24% in Oregon in 1994–1995 (Brunette and Lundy, 1996). The first modern tire studs, having approximately the same lifetime as that of the tire, were made by a cemented carbide pin, containing tungsten carbide and cobalt (WC-Co), fitted into a steel body (Rietz, 1969). Today, the steel body is substituted by aluminum while the tire stud pin that increases the friction between the tire and the road is still made of WC-Co (Vogler, 2016) (Fig. 1).

The tire stud pin contains mainly tungsten carbide (80–92%) and cobalt (6–10%) but also some minor amounts of titanium carbide, tantalum carbide and niobium carbide (Vogler, 2016). In this study, for reasons of simplicity, the pin is assumed to contain only WC-Co. WC-Co can be referred to as either of the two synonymous terms cemented carbide and hard metal (Ettmayer et al., 2014). Tungsten, the main material in the pin, offers an appealing combination of properties, including high hardness and melting point, which explains its use in a wide range of applications beyond tire studs (Brown and Pitfield, 2014). Tungsten is also a geochemically scarce element with a crustal content of only 1 ppm (Wedepohl, 1995). Due to its estimated supply risk and economic importance, tungsten has been identified as a critical raw material for the European Union (EU) (European Commission, 2017). The ascribed supply risk is related to the fact that China is dominating the tungsten production worldwide, being responsible for approximately 73 000 tonnes (82%) of the global tungsten mine production in 2015 (USGS, 2017). On average, 10–25% of tungsten is functionally recycled after use globally and >60% is being dissipated between manufacturing and waste management (Graedel et al., 2011; Zimmermann and Gößling-Reisemann, 2013). Dissipation implies that a resource is lost, for example as release, in a way that makes it...
technically or economically unfeasible to recycle. Furthermore, minerals containing tungsten are categorized as conflict minerals since their mining and trade are financing civil wars and violent conflicts in the Democratic Republic of the Congo (Coghlan et al., 2006; Young, 2015). Although only about 2% of the global tungsten production originate from the Democratic Republic of the Congo, revenues from illegal mineral trade is in the order of hundreds of million dollars and constitute an essential part in the financing of violence in this region (Young, 2015). Cobalt is also identified as a critical raw material for the EU but is not the focus of this study.

Up to this point in time, three material flow studies have covered US and global societal flows of tungsten (Harper and Graedel, 2008; Leal-Ayala et al., 2015; Wang et al., 2018). None of these studies focus on specific products containing tungsten. Thus, the societal fate of tungsten in specific applications, such as tire studs, has so far not been detailed. To complement the material-generic flow studies of tungsten previously conducted, there is a need for studies with higher resolution, focusing on specific tungsten products, since the dissipation of a specific product may differ notably from the material average. Such studies are needed in order to identify and implement product-specific measures for reducing dissipative losses (Zimmermann, 2015, 2016).

In addition to these resource-related issues for tungsten, a number of studies have reported elevated levels of tungsten-rich particles in road dust, road run-off and roadside soils and related these findings to the wear of tire studs (Bäckström et al., 2003, 2004; Bourcier et al., 1980; Bucko et al., 2011, 2013; Peltola and Wikström, 2006; Tuoriniemi, 2013). As much as 10% of the released particles could be in the form of nanoparticles (Tuoriniemi, 2013), meaning that they are approximately in the 1–100 nm size range in at least one dimension (ISO, 2015). Studies evaluating the ecotoxicity of WC-Co nanoparticles are very limited (Kühnel et al., 2014), but existing data indicate that WC-Co nanoparticles could cause adverse effects to rainbow trout gill cells (Kühnel et al., 2009). Release of WC-Co nanoparticles from tire studs have thus been confirmed, but the quantity and significance of this release have not been assessed and previous studies estimating release of nanoparticles have not included WC-Co (e.g. Keller and Lazareva, 2014; Sun et al., 2016).

There are thus both problematic resource and environmental issues related to the use of tungsten in tire studs. Consequently, the first aim of this study is to assess resource implications related to the use of tungsten in tire studs by quantifying its dissipation rate and functional recycling. The second aim is to assess the magnitude and relative significance of WC-Co nanoparticle release worn from the pins.

2. Materials and methods

Mass-based flows in the product chain of tungsten in tire studs were estimated using the environmental systems analysis tool of material flow analysis (Bringezu and Moriguchi, 2002; Brunner and Rechberger, 2004; Finnveden and Moberg, 2005). A steady-state mass-balance flow model, applying a product chain perspective from mining over production and use to waste management, was employed for assessing the societal flows of tungsten related to the use of tire studs in Sweden (within the system boundary shown in Fig. S1 in the Supplementary Material (SM)). The assumption of steady state was based on the fact that both the number of passenger cars in traffic, the weight of collected tires and the share of cars that have studded tires during winter have remained fairly constant over time in Sweden (Edeskär, 2006, 2015; Swedish Transport Administration, 2015; Transport Analysis, 2016). For example, the weight of collected tires in Sweden has been about 70 000 ton/year between 2006 and 2014 (Edeskär, 2006, 2015) and the share of cars with studded tires during winter has been about 70% between 2005 and 2015 (Swedish Transport Administration, 2015). All flows are given as mass flows of tungsten, which is the main constituent of the pins, while the use-phase release is presented both as flows of tungsten and as WC-Co. Resource implications were assessed by estimating the share of tungsten in tire studs that dissipates (Zimmermann and Gößling-Reisemann, 2013) and is functionally recycled (Guinée et al., 1999). The magnitude of the WC-Co release in the form of nanoparticles was estimated and the result was put in perspective by comparison with estimated release of some engineered nanomaterials (ENMs) in Sweden.

2.1. Dissipation and functional recycling

The flows of tungsten were assessed in terms of dissipation and functional recycling. Dissipation means that the concentration of the material, in this case tungsten in WC-Co, becomes so low in the receiving medium that it is unfeasible to recover from an economic or technical point of view (Zimmermann and Gößling-Reisemann, 2013). This concept of dissipation includes losses to the environment as release (e.g. diffuse emissions), losses to long or short-term anthropogenic stocks such as landfill and losses to other material flows. The dissipation rate is thus calculated as the share of the tungsten flows that undergo any of these three fates. Functional recycling in terms of material recovery means that a metal is returned to products or materials in which the metal has a specific function to fulfil (Guinée et al., 1999). The functional recycling rate is the share of the metal’s flows that are functionally recycled.

2.2. Base case and sensitivity analysis

A base case, representative for the year of 2015, was constructed for the current flows of tungsten due to the use of tire studs in Sweden. A sensitivity analysis was conducted in order to illustrate how changes in parameter values affect the results. Input parameters were varied one at a time and changes in the results were compared relative to the base case for the two output parameters; tungsten release from the use phase and the total tungsten input.
In addition to the base case and the adherent sensitivity analysis, low and high estimates were constructed for the WC-Co nanoparticle release. The rationale for this was to enable a comparison with other estimations of ENM release, which have largely been conducted in terms of low and high estimates (Keller and Lazareva, 2014).

3. Calculations

3.1. Estimation of tungsten flows

The tungsten flow calculations depart from two estimates of tungsten flows in the use phase: One estimate of the annual inflow of tungsten in tire studs to the use phase and one estimate of the flow of tungsten going out from the use phase. These two estimates are described in Sections 3.1.1 and 3.1.2, respectively. Together with the utilization of mass balances, these estimates enabled the quantification of use phase losses as well as flows upstream and downstream of the use phase. The use phase losses of tungsten were estimated as the difference between the flow of tungsten to the use phase, and out from the use phase to the waste management phase. A more detailed description of the tungsten flow calculations is given in Section S2 in the SM. All the data used in the calculations can be found in Section S1 in the SM and is representative for the year of 2015.

3.1.1. Estimation of the inflow to the use phase

The annual inflow of tungsten in tire studs to the use phase in year $i$, $F_{to u, i} [\text{kg/year}]$, was estimated for passenger cars according to:

$$F_{to u, i} = m_{pin} \times S_{pin, W} \times N_{ts} \times N_{tires} \times N_{new\ cars, i} \times S_t$$

(1)

where $m_{pin} [\text{kg}]$ is the mass of one WC-Co pin, $S_{pin, W} [-]$ is the share of a WC-Co pin that is tungsten, $N_{ts} [-]$ is the number of studs per tire, $N_{tires} [-]$ is the number of tires on a passenger car, $N_{new\ cars, i} [-]$ is the number of passenger cars that are new on the Swedish market in year $i$ and $S_t [-]$ is the share of passenger cars that had studded tires in year $i$ in Sweden. Buses and light trucks might also have studded tires but were excluded due to limited data on what share of these vehicles have that worn under during winter. The average share of one pin is approximately 0.2–0.4 g (Peltola and Wikstrom, 2006; Vogler, 2016) and the share of tungsten in pins is 75–86% (Vogler, 2016). Average values for these parameters were applied in the base case while the ranges were tested in the sensitivity analysis. The original number of studs in a studded tire was set to 130, while the range from 61% to 99% was tested in the sensitivity analysis.

3.1.2. Estimation of the outflow from the use phase

The estimation of the flow of tungsten out from the use phase was based on the inflow of tungsten to the use phase, the assumption of steady state, knowledge of what share of a pin that is worn during the tires' lifetime and the number of whole tire studs lost during use (Hjort et al., 2017; Vogler, 2016). In this way, the flow of tungsten from the use phase going to the waste management phase in year $i$, $F_{to\ wm, i} [\text{kg/year}]$, could be estimated according to:

$$F_{to\ wm, i} = F_{to\ u, i} \times S_{wts} \times (1 - S_{pin\ worn})$$

(2)

where $S_{wts} [-]$ is the share of the total number of studs per tire that remains in the tire after use and $S_{pin\ worn} [-]$ is the share of a pin that is worn during the lifetime of studded tires. The average share of the total number of tire studs per tire that remains in the tire after use was based on data from Hjort et al. (2017), who investigated used studded tires stored at Swedish storage facilities for tires. The used studded tires were in average six years old while the lifetime of these tires in general is six to seven years (Swedish Transport Administration, 2015). Therefore, this data was considered to be representative for studded tires in their end-of-life. The average share of tire studs left in the studded tires was 80%, with a standard deviation of 19% (Hjort et al., 2017). The average share of 80% was used in the base case for $S_{wts}$, while the range from 61% to 99% was employed in the sensitivity analysis. During the entire lifetime of a studded tire, approximately 75% of the weight of the pin is lost due to wear (Vogler, 2016) and the range of 50%–100% was tested in the sensitivity analysis.

3.1.3. Estimation of the use phase losses of tungsten

The use phase losses of tungsten in year $i$, $F_{lossu, u, i} [\text{kg/year}]$, were estimated as the difference between the inflow of tungsten to the use phase and the outflow of tungsten from the use phase to the waste management phase:

$$F_{lossu, u, i} = F_{to\ u, i} - F_{to\ wm, i}$$

(3)

The use phase losses of tungsten consist of two interconnected parts occurring due to the friction between the tire studs and the road: Losses of whole tire studs and release of WC-Co (nano)particles. The tungsten in whole tire studs lost during use in year $i$, $F_{wts\ lost, i} [\text{kg/year}]$, was estimated according to:

$$F_{wts\ lost, i} = F_{to\ u, i} \times (1 - S_{wts}) \times (1 - S_{wts\ lost\ worn}) \times S_{pin\ worn}$$

(4)

where $S_{wts\ lost\ worn}$ is the share of the total wear of a pin that was worn away before the whole tire stud was lost. $S_{wts\ lost\ worn}$ was assumed to be 0.5 in the base case, while 0 and 1 were tested as a low and high value in the sensitivity analysis, respectively. The low value corresponds to the whole tire studs lost not being worn at all, and the high value corresponds to the whole tire studs lost being worn as much as the tire studs remaining on scrambled studded tires. The value of 0.5 used in the base case represents an average situation between the two extremes.

The particle release originating both from tire studs that remain on the tires during the tires' whole lifetime and from tire studs that are lost at some point during the tires' lifetime. The release of...
particles worn from pins during use in year \(i\), \(F_{re_i}\) [kg/year], was estimated according to:

\[
F_{re_i} = F_{to u_i} \times (S_{wts} \times S_{pin worn} + (1 - S_{wts}) \times S_{wts \; lost \; worn} \times S_{pin worn})
\]  

(5)

\(F_{re_i}\) was also recalculated into WC-Co by dividing \(F_{re_i}\) by the tungsten share of a WC-Co pin, \(S_{pin_w}\).

3.1.4. Mining and production

The product chain for tungsten used in tire studs begins with the mining phase, where tungsten is extracted from either scheelite or wolframite mineral ore (Leal-Ayala et al., 2015). The tungsten-containing mineral is crushed, milled and then an ore beneficiation process is conducted in order to increase the tungsten content. During the beneficiation process, 10–43% of the original content of tungsten from ore is lost (Leal-Ayala et al., 2015). A loss of 25% was applied in the base case following Leal-Ayala et al. (2015), while the range from 10% to 43% was tested in the sensitivity analysis. Tungsten is also recycled from scrap and the main recycling routes are the so-called chemical process and the zinc process (Leal-Ayala et al., 2015). In the chemical process, tungsten scrap is used to produce intermediate tungsten compounds via the hydrometallurgy process, while in the zinc process, tungsten scrap is directly recycled into its powder.

In the production phase for tire studs, tungsten concentrates from the mining phase and tungsten scrap are used in the hydrometallurgy process to produce intermediate tungsten compounds, mainly ammonium paratungstate (APT) (Leal-Ayala et al., 2015). Then intermediates and additional recycled scrap are used in the pyrometallurgy process to produce tungsten metal powder, which is later turned into tungsten carbide powder in the powder metallurgy process, while in the zinc process, tungsten scrap is directly recycled into its powder.

3.1.5. Waste management

There is a national producer liability on tires in Sweden and at least 95% of scrap tires are collected and treated (Svahn, 2016). The mean value of 97.5% was used in the base case and a 95–100% range was applied in the sensitivity analysis. The majority of these tires are from passenger cars (Transport Analysis, 2016). No distinction is made between different tires (e.g. studded and non-studded) in Swedish waste management (Svahn, 2016). In 2015, treated tires were used in granulation (34%), for combustion in heat and power plants (27%), as an alternative fuel in the production of cement (17%), in construction materials (12%) and reused in other applications (10%) (SDAB, 2017). In the granulation process, the tire components are separated into different fractions (Svahn, 2016). These include a granulate fraction consisting of rubber in varying sizes, a steel fraction obtained by magnetic separation and a textile fraction. There is also a fourth fraction consisting mainly of stones and tire studs, which is landfilled (Svahn, 2016). The second largest waste treatment of tires in Sweden is as fuel in heat and power plants, where the pins will end up in the ashes after combustion due to their high melting point and since they are neither magnetic nor large enough to be easily separated by sieving. The ashes from these energy recovery processes are landfilled, used for backfilling and to cover landfills (Swedish Environmental Protection Agency, 2016). In cement production, scrapped tires are used as a supplementary fuel. The production of cement requires calcium, silicon, aluminum and iron, and the steel in scrap tires is used as an alternative source of iron (Nakomcic-Smaragdakis et al., 2016; Schneider et al., 2011). The pins become grinded together with other materials and end up in the cement (Larsson, 2017). In construction materials, shredded tires are used in different applications, such as lightweight filling material, frost insulation material and drainage material (Edeskär, 2006). The main use is as drainage material for the final cover of landfills, as draining layer for landfill gases and as component in riding tracks (Edeskär, 2015). Lastly, the scrap tires reused in other applications are used for different purposes, such as blasting mats and fenders.

3.2. Estimation of WC-Co nanoparticle release

The WC-Co nanoparticle release \(F_{re_{NP.i}}\) [kg WC-Co nanoparticles/year] was calculated by multiplying the use phase particle release from the tungsten flow calculations, \(F_{re_i}\) [kg WC-Co/year], with the share of this release that is nanoparticles, \(S_{re_{NP}}\). An estimate of \(S_{re_{NP}}\) was based on a personal communication with Tuoriniemi (2018) and the study by Tuoriniemi (2013) measuring WC-Co particles in road runoff from a Swedish freeway by the application of single particle inductively coupled plasma mass spectrometry for detection and transmission electron microscopy for particle characterization. In that study, road runoff samples collected at two rain events were first allowed to settle for 1–3 days and then filtered. During the settling, larger particles, e.g. sand particles, become sedimented while the WC-Co particles can be assumed to remain in the sample (as they primarily are in the form of smaller particles in the size of some micrometers) (Tuoriniemi, 2018). Thus, the WC-Co particles in the settled samples adequately represent the sizes of WC-Co particles worn from tire studs. Less than 10% of the WC-Co particles in the settled and filtrated samples was stated to pass a 450-nm filter (Tuoriniemi, 2013). These particles were in turn dominated by particles in the size range of 15–120 nm. Thus, it was assumed in this study that 5–10% of the particles released from worn tire studs are nanoparticles. This range was applied in the sensitivity analysis while 7.5% was used in the base case.

3.3. Estimation of engineered nanomaterial release in Sweden

The release of some ENMs in Sweden was estimated in order to compare to the release of WC-Co nanoparticles worn from tire studs. Comparing emissions of WC-Co nanoparticles in one single application with the release of ENMs in several applications was based on the fact that analytical studies consider the use of tire studs to be the predominant source of these particles in the environment (Backstrom et al., 2003, 2004; Bourcier et al., 1980; Bucko et al., 2011, 2013; Peltola and Wikstrom, 2006; Tuoriniemi, 2013). Since the use of materials has been shown to correlate well with the gross domestic product (GDP) (Anghelache, 2011; Simas et al., 2011; Steger and Bleischwitz, 2011), available data on EU (Sun et al., 2014) and European (Keller and Lazareva, 2014) ENM release were scaled using GDP as the scaling factor in order to estimate Swedish release of some ENMs under the assumption that these are used equally in all European countries. The release \(R_{j, Swe.i}\) [metric ton/year] of different nanomaterials \(j\) in Sweden in year \(i\) was estimated according to:

\[
R_{j, Swe.i} = R_{j, k, i} \times GDP_{Swe,i}/GDP_{k,i}
\]  

(6)

where \(R_{j, k, i}\) [metric ton/year] is the release of nanomaterial \(j\) in region \(k\) in year \(i\), GDP\(_{Swe.i}\) [current billion US$] is the gross domestic product of Sweden in 2013, and GDP\(_{k,i}\) [current billion US$] is the gross domestic product in region \(k\) in year \(i\) in 2013.
domestic product for Sweden in year \( i \) and \( GDP_k^i \) [current billion US$] is the gross domestic product for region \( k \) in year \( i \). See Section S3 in the SM for a description of the input data. This method used for scaling is similar to the one used by Sun et al. (2014), who applied GDP in order to extrapolate from global and regional use of ENMs to Europe and Switzerland. The values for the estimated \( R_j^{\text{Swe},i} \) are summarized in Table S8 in the SM and these were then compared with base case, low and high estimates of the release of WC-Co nanoparticles from the use phase of tire studs. The low estimate of WC-Co nano-release in this study was obtained by choosing parameter values in order to minimize the use-phase release, \( F_{re}^i \). Contrary, parameter values were chosen to maximize \( F_{re}^i \) in the high WC-Co nanoparticle release estimate. This correspond to the selection of all low and high parameter values used for the sensitivity analysis, respectively. All parameter values applied in the sensitivity analysis are presented in Table S2 in the SM.

4. Results and discussion

4.1. Tungsten flows and dissipation

The tungsten flow in the base case (Fig. 2a) indicate that the by far largest loss is the use phase particle release. This release is in the form of particles worn from pins during use. Losses of tungsten related to mining and whole tire studs lost in the use phase also constitute substantial losses.

Analyzing the tungsten flow results in Fig. 2a using the concepts of dissipation and functional recycling shows that the dissipation rate of tungsten in tire studs is 100% from the manufacturing process (i.e. powder metallurgy, shaping and sintering) to the waste management phase. The dissipation is dominated by the use phase particle release, accounting for 67% of the tungsten outflows in the base case (Fig. 2b). The loss of whole tire studs in the use phase account for 13%. The product-specific dissipation rate for tungsten in tire studs can be compared with the global dissipation rate of tungsten, which has been estimated to be >60% between manufacturing and waste management (Zimmermann and Gößling-Reisemann, 2013). The global dissipation was mainly in the form of losses to other material flows according to Zimmermann and Gößling-Reisemann (2013). This study thus shows that for the use of tungsten in tire studs, the dissipation rate is higher than the global dissipation rate and that the main type of dissipation differs. Despite the fact that almost all scrapped studded tires are collected in the waste management phase, there is effectively no recycling of tungsten contents of the pins and 0% of the tungsten is functionally recycled. This can be compared to the US functional recycling rate for different tungsten applications, which is 15–90% (Harper and Graedel, 2008), and to the global average functional recycling rate of tungsten after use, which is 10–25% (Graedel et al., 2011).

Landfill is the dominating waste management type for tire studs
(Fig. 2a and b). The flows of tungsten in the waste management phase going to the processes of granulation, heat and power plants as well as construction works are all landfilled. The pins that are combusted in heat and power plants are expected to end up in landfills together with the ashes from this process. Scrap tires used in construction works can be in the form of tire shreds that are put in the ground to provide drainage (Edeskär, 2006). Although this constitutes a recycling of the tires, the tungsten material is landfilled. Tungsten in tire studs present in scrapped studded tires not collected and in scrapped studded tires reused for other purposes generally deteriorate during their reuse. A likely future fate is therefore combustion in heat and power plants and the tungsten within is therefore considered to be landfilled. The pins in tires combusted in cement production become grinded and incorporated into the cement and therefore the tungsten is categorized as lost in another material flow. It is not categorized as being functionally recycled in this case, since tungsten is not one of the required input materials for the production of cement. Whole tire studs lost during use and losses during metallurgy, shaping and sintering could not be categorized as release, landfill or losses into other material flows due to lack of information.

Clearly, the use of tungsten in tire studs is problematic from a resource perspective, as indicated by the high dissipation rate and the non-existing functional recycling. The results from this study can provide a foundation for product-specific interventions. The results for tungsten flows in tire studs show that the largest contribution to dissipation is from the use phase and this release of tungsten is effectively unavoidable. Any reductions in use phase release can hardly be achieved by technical means. In the waste management phase, on the other hand, there are possibilities to recover tungsten. This can either be done by developing methods to remove the tire studs from the scrapped studded tires before they enter different waste management processes or by introducing methods to separate the tire studs in specific fractions in the outputs from waste management processes. An example is the fraction containing mainly stones and tire studs from the granulation process. Notably, one metric ton of the stone and tire stud fraction landfilled from the granulation process contains about 150 kg tire studs (Svahn, 2016), which corresponds to a tungsten fraction of 2–5%. This value is notably higher than the 0.08–0.8% tungsten in workable ores (Brown and Pitfield, 2014). Such efforts will, however, not solve the issue with the use phase tungsten release. An alternative is to use non-studded tires during winter. However, studded tires reduce fatal crashes on roads covered with ice or snow by 36–48% compared to non-studded winter tires (Strandroth et al., 2012). A more long-term possibility could be to substitute WC-Co in tire studs for other materials. When investigating different alternatives to WC-Co tire studs, the function of the tire studs, which is to save lives by reducing the number of accidents on slippery winter roads, must be considered. An alternative solution must provide a similar function. Furthermore, studded tires are also known to cause negative human health impacts from particles worn off from the road (Gustafsson et al., 2008; Hoek et al., 2002). These impacts, both negative and positive, need to be taken into consideration when studded tires and alternative solutions are further evaluated.

4.2. WC-Co nanoparticle release

The release of nanoparticles in the use phase was estimated to 1800 kg WC-Co nanoparticles/year for the base case. The low and high estimate of the WC-Co nanoparticle release, used in the comparison with the life cycle release of some ENMs in Sweden, are 210 and 6100 kg WC-Co nanoparticles/year, respectively. The use phase release dominates the life cycle outflows (see Fig. 2) why the use phase WC-Co nanoparticle emissions can be seen to approximately represent the total life cycle WC-Co nanoparticle release for tire studs. In Fig. 3, the low and high estimate as well as the base case for the use phase release of WC-Co nanoparticles worn from tire studs are compared to the life cycle release of some ENMs used in various applications.

The ENMs applied for the comparison in this study include

![Graph showing the comparison of the release of some engineered nanomaterials (ENMs) in Sweden from various applications based on Sun et al. (2014) (black crosses) and Keller and Lazareva (2014) (black ranges) to the estimated low and high Swedish release of cemented tungsten carbide with cobalt (WC-Co) nanoparticles from the wear of tire studs (in orange), as estimated in this study. The base case from this study is indicated with an orange cross. The ENMs are fullerenes, copper (Cu), silver nanoparticles (Ag), carbon nanotubes (CNT), cerium dioxide (CeO2), nanoclays, aluminum oxide (Al2O3), silicon dioxide (SiO2), zinc oxide (ZnO), iron (Fe) and titanium dioxide (TiO2). Note the logarithmic scale and that the low estimate for Cu is zero.](image-url)
oxides of titanium and zinc used in e.g. cosmetics; aluminum oxides, iron and copper in e.g. coatings, paints and pigments; oxides of silica and cerium in e.g. electronics and optics; carbon nanotubes and fullerences in e.g. polymer composites; nanoclays in e.g. automotive applications and silver used in e.g. consumer electronics and textiles (Keller and Lazareva, 2014; Sun et al., 2014). The comparison indicates that the release of WC-Co nanoparticles is of similar magnitude as the release of some ENMs in Sweden. The WC-Co nanoparticles show higher release than fullerences, copper nanomaterials and silver nanomaterials. The release of carbon nanotubes and cerium dioxide nanomaterials are in the same order of magnitude as the WC-Co nanoparticle release while the release of nanoclays is about the same order of magnitude as the WC-Co nanoparticle release. Nanomaterial release of the oxides of titanium, zinc, silicon and aluminum as well as iron nanomaterial release are higher than the WC-Co nanoparticle release. Thus, WC-Co could be seen as an incidental nanomaterial, which is released into the environment in higher or similar amounts as some ENMs, e.g. silver nanomaterials, carbon nanotubes and cerium dioxide. We hypothesize that similar relative release of incidental WC-Co nanoparticles from tire studs and ENMs could be present in other countries where tire studs are used as well. The method of this study, although here applied to Sweden, could be used to examine flows of tungsten, and the release of WC-Co nanoparticles, related to the use of tire studs in other countries. In order to facilitate such comparisons, transfer coefficients are provided in Section S2.4 in the SM. It can also be noticed that the uncertainty in the release of WC-Co nanoparticles from tire studs — spanning roughly one order of magnitude — is similar to that of the ENMs (Fig. 3). Less uncertain assessments results for all included nanomaterials would enable an improved ranking of the relative significance of their releases in Sweden. For example, the highest value for Cu nanomaterial release is even higher than the lowest value of the WC-Co nanoparticle release, but the lowest value for Cu nanomaterial release is zero and thus obviously lower than the entire WC-Co nanoparticle release range.

A slight underestimate of the flows and release of tungsten related to the use of tire studs in Sweden is probably present. Only passenger cars are included in the calculations while buses, light trucks and bicycles can also be equipped with studded tires. Furthermore, additional WC-Co nanoparticles may be released from other sources than tire studs. Potential sources in automotive applications include wear resistant parts such as gears and on the blades of road scrapers (Tuoriniemi, 2013). There are also dissipative losses from, for example, mining tools and metal cutting inserts being worn during use (Zimmermann and Gößling-Reisemann, 2013). A fraction of these dissipative losses may be in the form of nanoparticles. However, their magnitude is currently unknown but could constitute a substantial contribution. This means that the total WC-Co nanoparticle release may be substantially higher than the contribution from tire studs alone, resulting in an even higher significance of WC-Co release compared to the ENMs in Fig. 3.

This study thus shows that the release of WC-Co nanoparticles is at least of similar magnitude as the release of some ENMs in Sweden. Until now, however, WC-Co has not been included in environmental risk assessment studies of nanoparticles (Arvidsson, 2015; Gottschalk et al., 2009, 2013; Mueller and Nowack, 2008). The release estimates from this study provide a basis for risk assessments of WC-Co nanoparticles. Such risk assessments need to include also the form of WC-Co particles released, their fate in the environment and subsequent toxicity to relevant organisms. According to the framework by Nowack et al. (2012), the WC-Co nanoparticles from tire studs are not released in pristine form, but are rather modified (e.g. during sintering) and weathered (during use). The fate of WC-Co nanoparticles in surface water was investigated by Hedberg et al. (2017). They found that WC-Co nanoparticles undergo both agglomeration and sedimentation. Notably, in their study, all cobalt content was released from the WC-Co nanoparticles within a few hours, although it remained bound to the nanomaterials’ surface. The surface adsorption of cobalt furthermore enhanced the adsorption of humic acid-like substances, but this did not have a notable influence on sedimentation (Hedberg et al., 2017). The development of environmental fate models for WC-Co nanoparticles is recommended as well as additional studies on WC-Co nanoparticle ecotoxicity in aquatic environments.

Other potential comparisons that further could be made to put the results into context are to compare WC-Co nanoparticle release with emissions of nanomaterials from geogenic sources, or total WC-Co particle release to other traffic-related emissions such as tire wear particles. Nanominerals and nanoparticles, e.g. including mineral dust and volcanic emissions, are widely distributed throughout environmental compartments (Gustafsson and Gschwend, 1997; Hochella et al., 2008). Annual tire wear particle emissions have been reported for several countries, including Sweden at 10 million kg/year (Wik and Dave, 2009). This is considerably higher than the total particle use phase release of WC-Co at 25 000 kg/year (including nanoparticles) in the base case in this study, which is expected considering the higher hardness of tire studs compared to asphalt and tires.

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Base case</th>
<th>Low value</th>
<th>Release change</th>
<th>Total input change</th>
<th>High value</th>
<th>Release change</th>
<th>Total input change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of WC-Co pin (m_{pin})</td>
<td>0.3 g</td>
<td>0.2 g</td>
<td>−33%</td>
<td>−33%</td>
<td>0.4 g</td>
<td>+33%</td>
<td>+33%</td>
</tr>
<tr>
<td>Tungsten content in a WC-Co pin (S_{pin W})</td>
<td>0.805 g</td>
<td>0.75 g</td>
<td>−6.8%</td>
<td>−6.8%</td>
<td>0.86 g</td>
<td>+6.8%</td>
<td>+6.8%</td>
</tr>
<tr>
<td>Number of studs per tire (N_{studs})</td>
<td>127</td>
<td>119</td>
<td>−6.3%</td>
<td>−6.3%</td>
<td>135</td>
<td>+6.3%</td>
<td>+6.3%</td>
</tr>
<tr>
<td>Number of passenger cars that were new on the Swedish market in year i (N_{new cars, i})</td>
<td>362 000</td>
<td>229 000</td>
<td>−37%</td>
<td>−37%</td>
<td>388 000</td>
<td>+7.2%</td>
<td>+7.2%</td>
</tr>
<tr>
<td>Share of passenger cars with studded tires in Sweden in year i (S_{i})</td>
<td>0.663</td>
<td>0.636</td>
<td>−4.1%</td>
<td>−4.1%</td>
<td>0.723</td>
<td>+9.1%</td>
<td>+9.1%</td>
</tr>
<tr>
<td>Share of the total number of tire studs per tire that remains in the tire after use (S_{after use})</td>
<td>0.796</td>
<td>0.605</td>
<td>−11%</td>
<td>0%</td>
<td>0.987</td>
<td>+11%</td>
<td>0%</td>
</tr>
<tr>
<td>Share of the total wear of a pin that was worn away before the whole tire stud was lost (S_{wear lost worn})</td>
<td>0.5</td>
<td>0</td>
<td>−11%</td>
<td>0%</td>
<td>1</td>
<td>+11%</td>
<td>0%</td>
</tr>
<tr>
<td>Share of a pin that is worn during the studded tire’s lifetime (S_{wear wore})</td>
<td>0.75</td>
<td>0.5</td>
<td>−33%</td>
<td>0%</td>
<td>1</td>
<td>+33%</td>
<td>0%</td>
</tr>
<tr>
<td>Share of tungsten lost in the mining process (S_{mining loss})</td>
<td>0.25</td>
<td>0.10</td>
<td>0%</td>
<td>−12%</td>
<td>0.43</td>
<td>0%</td>
<td>+20%</td>
</tr>
<tr>
<td>Share of scrap tires that are collected and treated in various ways (S_{scrap tires, i})</td>
<td>0.975</td>
<td>0.95</td>
<td>0%</td>
<td>0%</td>
<td>1</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Table 1 Percentage change in results relative the base case for the tungsten release and total input from the sensitivity analysis. The base case tungsten release and total input of tungsten are 20 000 kg/year and 38 000 kg/year, respectively.
4.3. Sensitivity analysis results

The results from the sensitivity analysis indicate that several parameters contribute to uncertainties in the calculations (Table 1). Since all parameters have a linear influence on the total tungsten input and use phase release, those parameters with the highest sensitivity contribute most uncertainty in the results. The weight of a WC-Co pin, \( n_{\text{pin}} \), and the number of passenger cars that are new on the Swedish market, \( N_{\text{new cars}} \), both cause changes to the tungsten release and total input that are larger than 30% relative to the base case. The share of a pin that is worn during the lifetime of studded tires, \( \delta_{\text{pin worn}} \), change the tungsten release with more than 30% relative the base case. The parameter for the share of tungsten lost in the mining process, \( \delta_{\text{mining loss}} \), change the total input by -20% when the high value is applied. The dissipation rate does not change when parameter values are varied in the sensitivity analysis.

5. Conclusions

The use of tungsten in tire studs is disadvantageous from a resource use perspective. The dissipation rate between the high value is applied. The dissipation rate does not change when parameter values are varied in the sensitivity analysis.

Acknowledgements

The financial support from Mistra Environmental Nanosafety, funded by the Swedish Foundation for Strategic Environmental Research (Mistra), is gratefully acknowledged. In addition, we would like to thank Falko Vogler at Sitek Spikes, Peter Svanh at RagnSells AB, Johan Larsson at Cemena HeidelbergCement Group and Jani Tuoriniemi at the Swedish University of Agricultural Sciences who provided valuable information to this study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2018.10.004.

References


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