# Tyre stud derived tungsten carbide particles in urban street dust

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In countries where studded winter tyres are used they contribute to the generation of street dust by grinding the road surface and traction sand into finer particles. At the same time the hard metal tips of the studs, made out of tungsten carbide (WC), wear to finer particles dispersed into the environment. Elevated tungsten concentrations in different sampling media, probably caused by the use of studded tyres, have also been reported. In this study three size fractions of street dust sampled in Turku, Finland, were investigated. Tungsten and various other element concentrations were determined with ICP-MS after total dissolution, pseudo total concentration (aqua regia) and a weaker extraction (1M $NH_4Ac$). A visual analysis was made with a SEM-EDX to study the presence and size fraction of WC particles, which has not been studied before. The total concentrations (median values) of tungsten in the fractions were 9.2 $\mu$g g$^{-1}$ (100 $\mu$m–2 mm), 21 $\mu$g g$^{-1}$ (45 $\mu$m–100 $\mu$m) and 39 $\mu$g g$^{-1}$ (< 45 $\mu$m). As expected, tungsten showed a tendency to accumulate into the finer size fractions. However, more surprising was the result that out of all elements determined, tungsten had the greatest (median values) relative enrichment in the fine fraction. In the SEM-EDX analysis particles consisting of tungsten were identified and ruled out to be WC abraded from tyre studs. The WC particles occurred either separately or in clusters with size range of 0.1–1.4 $\mu$m.

## Introduction

Suspended urban street dust is a recurrent springtime problem in densely populated areas in Finland. The airborne particle loads are usually at their highest in spring after snow melting (Laiterä *et al.* 2004). The dust is created when vehicle traffic wears the pavement and the applied traction sand. The dust concentrations are further increased by the common use of studded winter tyres that effectively wear both the road surface and applied sand, grinding the components into finer particles. This

has been a hot topic for recent research into the cause-effect relationship of the springtime urban dust problem in Finland (Kukkonen *et al.* 1999, Pakkanen *et al.* 2001a, 2001b, Kupiainen *et al.* 2003, 2005). Hence, the street dust consists mainly of minerogenic material from the pavement and traction sand together with particles emitted from tyres, brakes, engines (combustion and friction) and corrosion of vehicles. The tyre studs, containing a friction increasing hard metal tip made out of tungsten carbide (WC), also wear and inevitably produce WC particles. In Finland special winter tyres (studded or not) have been
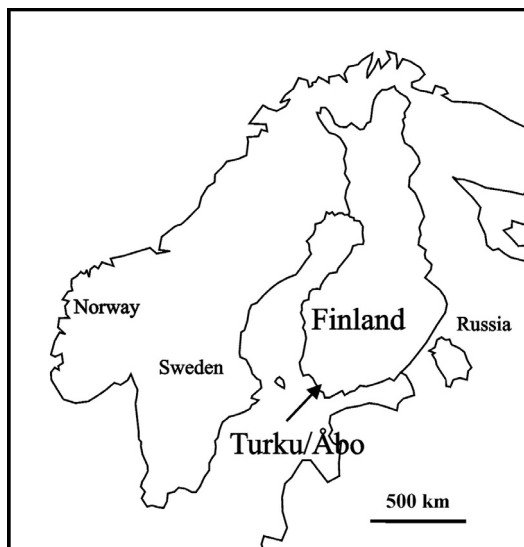
**Fig. 1**. The location of Turku.

compulsory since the beginning of the 1960s and they are today compulsory from 1 November to 31 March. In 1999 approximately 84% of the winter tyres sold in Finland were studded. In the Nordic countries approximately 70% of the travelled distance during winter is done with studded tyres (Folkeson 1992). The main material used in common studs is a light metal root (ca. 0.85 g) usually made of aluminium and a hard metal tip usually made of WC (ca. 0.25 g). Each tyre has about 100 studs.

In countries or regions where studs are used, elevated tungsten concentrations have been found in several types of sampling media. Bourcier *et al*. (1980) found elevated concentrations in wintertime road runoff in USA. In Sweden Bäckström *et al*. (2003, 2004) found that up to 90% of the tungsten mass transport in road runoff occurred during the winter and that roadside topsoil was clearly elevated in tungsten. Also a more general enrichment of tungsten has been noted in urban areas. Ljungqvist (2003) noted a clear elevation of tungsten in moss samples towards Stockholm city centre and Peltola and Åström (2003) found a 50% (median concentrations) increase of tungsten in urban humus compared with rural humus in a small Finnish town. In the above studies the elevated tungsten concentrations were believed to be mainly caused by the wearing of WC from tyre studs. The aim

of this study is to determine the tungsten concentrations in springtime urban street dust with ICP-MS determination and to analyse the size of the WC particles with a scanning electron microscope coupled with an energy dispersive X-ray analyser (SEM-EDX). Street dust itself has been studied and analysed for many elements (e.g. Pakkanen *et al*. 2001b), but less information can be found on the concentrations of tungsten and particles derived from studs in street dust.

Tungsten carbide is the most common tungsten product. It is a hardwearing material usually produced by about 0.5 to 50 $\mu$m WC aggregates bonded with cobalt (~3% to 20% by weight) or some other suitable metal such as titanium, Ta or Nb (Sudarshan *et al*. 1998; www.itia.org. uk/tungsten/tungsten_app_cem.html). Tungsten carbide has a density of ca 15 g cm$^{-3}$, a melting point of 2982 °C and hardness of over 9.5 on the Mohs scale (Brady *et al*. 1997). Tungsten carbide is mainly used in hard metal edges in tools such as bores and blades. Tungsten steel alloys are common in industrial use but contain less than 10% tungsten (www.itia.org.uk/tungsten/tungsten_app_steel.html). Metallic tungsten is commonly used as light filaments. In an urban street setting various tools could potentially disperse both tungsten alloy and WC particles into the environment. However, comparing the frequency of traffic with the occasional use of tools, especially during winter and spring, the tyre studs must be considered to be the main potential source for WC emissions into urban street dust. Other tungsten emissions, e.g. from filaments, are unlikely since they are unexposed and not subjected to physical wear.

## Material and methods

The sampling area was the centre of Turku (175 000 inhabitants) located on the west coast of Finland (Fig. 1). The sampling was done at ten different sites in the city centre in March 2003, at the time of snow melting but before the thorough cleaning of the streets had started. Street dust was swept up from the kerb with a plastic brush and put into airtight plastic bags. The sampling area was approximately 0.5–1 m$^{-2}$. Seven of the sampling sites were chosen because

they are roads with heavy traffic, and for three of these sites traffic amounts of 21 500 to 27 500 vehicles per day have been recorded. Two of the sampling sites supposedly have relatively low traffic amounts and one was characterised as intermediate. All roads had speed limits between 40 and 60 km h$^{-1}$.

The samples were dried at room temperature (23 °C) for two weeks and sieved into three fractions. The samples were first sieved with a 2 mm sieve to remove the coarsest material. The resulting material was then sieved with 100 $\mu$m and 45 $\mu$m sieves. The fractions used for further analyses were 100 $\mu$m–2 mm, 45 $\mu$m–100 $\mu$m and < 45 $\mu$m. Between the sample treatments, the sieves where cleaned with distilled water in an ultrasound bath.

From all samples a total digestion was done in which about 0.25 g of material was digested in a mixture of HF-HClO$_4$-HNO$_3$-HCl and diluted to 10 ml. For the < 45 $\mu$m fraction two separate leaches were made. Approximately 1 g of material was leached in 6 ml of hot (95 °C) aqua regia (HNO$_3$-HCl-H$_2$O in proportions 2-2-2) for one hour and diluted to 20 ml. In the weak leach circa 1 g of material was rolled for two hours in 30 ml of 1 M (pH 7) ammonium acetate (NH$_4$Ac). On all digestions/leaches the following elements were determined with ICP-OES/MS: Ag, Al, As, Au, B[1,3], Ba, Be, Bi, Ca, Ce, Cd, Co, Cr[1], Cs[2], Cu, Dy[2], Er[2], Eu[2], Fe, Ga[2], Ge[3], Gd[2], Hf, Hg[3], Ho[2], In[2,3], K, La, Li, Lu[2], Mg, Mn, Mo, Na[1], Nb, Nd[2], Ni, P, Pb, Pr[2], Re[3], Rb, S[1], Sb, Se[3], Sc, Sm[2], Sn, Sr, Ta, Tb[2], Te[3], Th, Ti, Tl[3], Tm[2], U, V, W, Y[2], Yb[2], Zn and Zr ([1]elements not determined from the NH$_4$Ac leach, [2]elements not determined from the aqua regia leach, [3]elements not determined from the total digestion). All leaches and element determinations were carried out in a commercial accredited (ISO 9001) laboratory. Certified reference material and seven blind replicate samples were used to secure the reliability of the analyses (five for the total digestion and one each for the aqua regia and NH$_4$Ac leach). The duplicate/replicate concentrations ($\mu$g g$^{-1}$) of tungsten in these samples were the following: 7.9/9.2, 8.1/8.5, 19.1/19.2, 28.3/30.6, 28.7/31.3, 15.9/16.2 and 0.6/0.4. Special attention was paid to the calibration of tungsten. When analysing tungsten Gustafsson (2003) observed that

as much as 30%–40% of the element can be adsorbed to the surface of some test tubes. To avoid such reactions the analyses were carried out within 24 hours after leaching.

The SEM-EDX analyses were made for three samples from the < 45 $\mu$m fraction, on two samples from the 45–100 $\mu$m fraction and for both used and new studs. A small fraction of each sample was adhered to a conductive carbon tape and the surface was air dusted to prevent particle emissions into the SEM vacuum chamber. An operation mode with 15 and 20 kV energy intensity and backscatter imaging was chosen so that dense particles, such as metals, were easily identified as light spots against the darker and less detailed background. These particles were then identified by collecting an X-ray spectrum. The analysis of the studs was done without any preparation and with both backscatter and secondary electron imaging. The SEM analysis was done at the Department of Inorganic Chemistry at Åbo Akademi University with a LEO 1530 coupled with an EDX (Thermo Noran Vantage). The SEM analysis was performed in such a way that only qualitative data, such as size measuring on single particles, could be extracted. Only the relative number of different particle types could be quantified, since particles could be hidden behind larger mineral grains.

## Results and discussion

The minimum, median and maximum concentrations of tungsten determined in the different chemical extractions and fractions are presented in Table 1. The minimum value of the coarsest fraction, 5.7 $\mu$g g$^{-1}$, is clearly above the concentrations found in bedrock materials (gabbro and granite) where it ranges from 0.4 to 1.6 $\mu$g g$^{-1}$ (Koljonen 1992). Bäckström *et al.* (2004) found tungsten concentrations of 64 and 94 $\mu$g g$^{-1}$ in a roadside topsoil and highway road dust, respectively (< 2 mm fraction, XRF determination). These values are comparable to the total concentrations (sum of sieve classes for each site) of the seven complete samples of this study, ranging from 60 to 138 $\mu$g g$^{-1}$. The limited number of samples prohibited an extensive comparison of tungsten concentrations with the traffic inten-
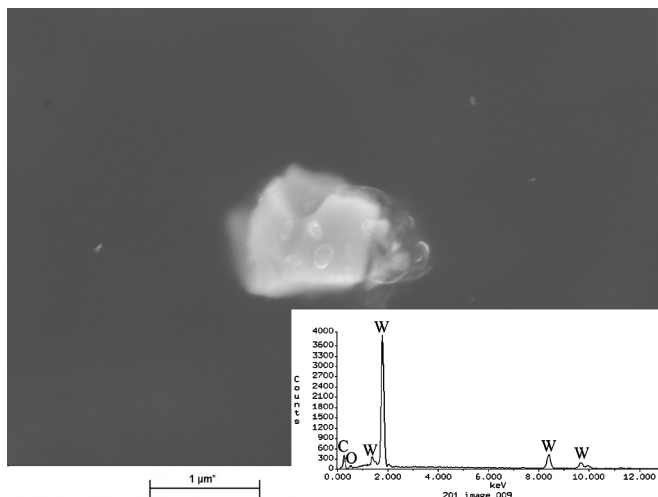
**Fig. 2**. One of the larger tungsten particles found. The insert graph shows the elemental signature of the particle. Note that the lower and higher energies are heavily suppressed, which means that the real count rate for especially carbon is in fact much higher (*see* Fig. 4).

sity. However, the site with low traffic always had concentrations at a median or lower range of the concentrations measured in the different size fractions or leaches. Of the weaker leaches, the aqua regia produced concentrations that were approximately 60% of the respective total concentrations. This was comparable to elements such as molybdenum, Cu, Pb and Zn (48%–86% of total concentrations), while elements deriving mainly from silicates such as sodium, K, Al, Sc and Zr had much lower values (8%–28%). The $NH_4Ac$ leach showed that only a small fraction was leachable with a weaker reagent, comparable with the 1 M NaAc leach (pH 5) used by Bäckström *et al.* (2004). The highest concentration (6.4 $\mu g$ $g^{-1}$) found with the $NH_4Ac$ leach is clearly an outlier both in this study and the one referred to above. As expected, the concentrations of many elements, especially metals, increased in the finer fractions. What was notable, however, was that tungsten was most enriched when comparing the differences in

median concentrations between the size fractions (Table 2). While there were only a small number of samples in this study, the enrichment was still distinctive. A probable reason for this could be the high density of the tungsten particles. This could result in a more efficient physical enrichment in the sieving process, or in enrichment when the snow-melt water and rainwater washes out less dense compounds from the finer dust fractions.

Particles consisting predominantly of tungsten were readily identifiable with the SEM-EDX (Fig. 2). The size range of the tungsten particles was found to be between 0.1 $\mu m$ (and probably smaller) and 1.4 $\mu m$ (Figs. 2 and 3). A more precise chemical analysis of the tungsten particles was hindered by their small size, which made the X-ray spectra accumulate information from the surrounding area as well. Thus it was not possible to determine whether the particles consisted specifically of WC rather than metallic tungsten, or of bonding metals used in WC. This kind of

**Table 1**. Total tungsten concentrations (µg g⁻¹) in the different fractions and the results for the two separate leaches on the < 45 µm fraction.

| Digestion/leach | Total | | | Aqua regia | $NH_4Ac$ |
|---|---|---|---|---|---|
| Fraction | 100 µm–2 mm | 45–100 µm | < 45 µm | < 45 µm | < 45 µm |
| No. of samples | 10 | 8 | 7 | 7 | 7 |
| Min. | 5.7 | 12 | 31 | 16 | 0.40 |
| Median | 9.2 | 21 | 39 | 26 | 0.73 |
| Max. | 31 | 48 | 60 | 35 | 6.4 |

**Table 2.** Median values of total concentrations (μg g⁻¹) of elements determined and a comparison of the median enrichment in different size fractions. [1] enrichment (%) between fraction < 45 μm and 45 μm–100 μm. [2] enrichment (%) between fraction < 45 μm and 100 μm–2 mm.

| | Ag | Al | As | Ba | Be | Bi | Ca | Cd | Ce | Co | Cr | Cs | Cu | Dy | Er | Eu | Fe | Ga |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 μm–2 mm (F1) | 0.06 | 56850 | 11.2 | 465 | 2.0 | 0.14 | 57350 | 0.17 | 43 | 11 | 847 | 4.2 | 46 | 3.1 | 1.9 | 0.80 | 45900 | 18 |
| 45 μm–100 μm (F2) | 0.09 | 58850 | 20 | 470 | 2.0 | 0.25 | 63050 | 0.32 | 70 | 17 | 1593 | 3.7 | 67 | 4.7 | 3.5 | 1.0 | 61550 | 18 |
| < 45 μm (F3) | 0.14 | 58800 | 25 | 489 | 2.0 | 0.36 | 74800 | 0.48 | 87 | 22 | 2169 | 4.2 | 101 | 5.6 | 3.5 | 1.1 | 63400 | 19 |
| F2–F3[1] (%) | 51 | –0.08 | 22 | 4.2 | 0 | 44 | 19 | 52 | 24 | 30 | 36 | 15 | 51 | 20 | 1.4 | 10 | 3.0 | 5.9 |
| F1–F3[2] (%) | 125 | 3.4 | 121 | 5.2 | 0 | 167 | 30 | 182 | 102 | 103 | 156 | 2 | 121 | 84 | 84 | 38 | 38 | 4.9 |

| | Gd | Hf | Ho | K | La | Li | Lu | Mg | Mn | Mo | Na | Nb | Nd | Ni | P | Pb | Pr | Rb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 μm–2 mm (F1) | 2.9 | 4.1 | 0.60 | 18600 | 20 | 29 | 0.20 | 10900 | 3795 | 2.0 | 14975 | 28 | 18 | 23 | 880 | 23 | 4.6 | 92 |
| 45 μm–100 μm (F2) | 5.3 | 7.7 | 0.90 | 16500 | 38 | 30 | 0.40 | 14350 | 5082 | 3.0 | 15860 | 32 | 32 | 40 | 1175 | 25 | 8.3 | 86 |
| < 45 μm (F3) | 6.4 | 11 | 1.0 | 17400 | 47 | 38 | 0.40 | 1.6 | 5032 | 4.0 | 14960 | 36 | 40 | 50 | 1310 | 38 | 10 | 96 |
| F2–F3[1] (%) | 21 | 41 | 11 | 5.5 | 24 | 26 | 0 | 14 | –1.0 | 33 | –5.7 | 11 | 24 | 24 | 11 | 55 | 25 | 12 |
| F1–F3[2] (%) | 121 | 164 | 67 | –6.5 | 135 | 29 | 100 | 50 | 33 | 99 | –0.10 | 28 | 127 | 111 | 49 | 63 | 126 | 4.8 |

| | S | Sb | Sc | Sm | Sn | Sr | Ta | Tb | Th | Ti | Tm | U | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 μm–2 mm (F1) | 1500 | 2.0 | 8.2 | 3.6 | 3.4 | 192 | 0.90 | 0.40 | 6.7 | 3800 | 0.25 | 1.9 | 1253 | 9.2 | 16 | 1.9 | 116 | 143 |
| 45 μm–100 μm (F2) | 1950 | 3.7 | 11 | 6.7 | 4.2 | 210 | 1.3 | 0.90 | 10 | 4820 | 0.40 | 3.3 | 1545 | 21 | 25 | 3.2 | 172 | 254 |
| < 45 μm (F3) | 2200 | 6.4 | 12 | 8.1 | 5.2 | 236 | 2.0 | 1.10 | 14 | 5630 | 0.40 | 4.6 | 1236 | 39 | 27 | 3.2 | 222 | 364 |
| F2–F3[1] (%) | 13 | 71 | 11 | 22 | 25 | 12 | 54 | 22 | 37 | 17 | 0 | 39 | –20 | 87 | 8.6 | 0 | 29 | 43 |
| F1–F3[2] (%) | 47 | 225 | 48 | 125 | 55 | 23 | 122 | 175 | 114 | 48 | 60 | 149 | –1.4 | 330 | 69 | 68 | 91 | 154 |

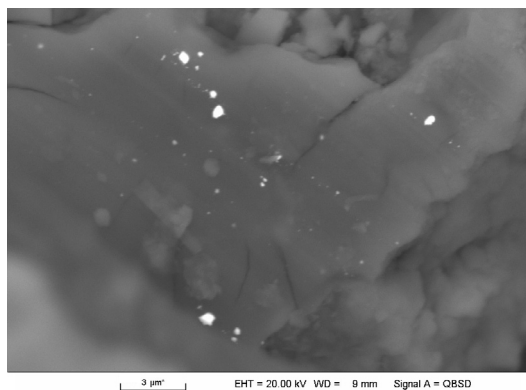**Fig. 3**. A cluster of < 1 μm WC particles, probably attached to the mineral grain below.

determination was, however, possible from the studs where tungsten and carbon were found in relatively equal amounts together with minor amounts of titanium, Co and C (possibly graphite) (Fig. 4). Note that both the low and high energies are suppressed in the analysis, which results in a lower apparent count rate. Both the worn and new studs showed surfaces made up of WC granules in the size range from smaller than 1 $\mu$m up to 5 $\mu$m (Fig. 4). The larger structures in the stud surface reflect the WC quality used for these specific studs.

The results presented above, together with the high traffic volumes at the sampling sites and the sparse use of metallic tungsten subjected to abrasion, strongly indicate that the tungsten particles were WC derived from tyre studs (referred to as WC particles below). Due to the fact that the WC particles could be hidden behind mineral grains, only the relative number of the particles could be estimated. About seven WC particles were found in each of the three samples, excluding a few distinctive clusters with tens of WC particles (Fig. 3). The WC particle shown in Fig. 2 seems to be loose, whereas the cluster in Fig. 3 is likely to be attached to the mineral grain. These features could affect the presence of WC particles in the different sieved size classes and could thus also affect their transport in the environment.

Although many particle types were found with the SEM, only iron containing particles (some with minor concentrations of chromium) occurred more frequently than the WC particles.

Also Platinum, Pb and Ce particles (one of each) were found. This result is surprising, considering that there are a number of publications discussing the circulation of metals originating from the traffic in the urban environment. However, the high energy used in the SEM analysis made it particularly easy to visually identify dense metallic particles with the backscatter detector. Another reason for not identifying other metallic particles could be that many metals oxidise more easily than WC and Pt. The SEM analysis was not calibrated to visually identify different types of oxides that are probably less visible than the particles identified here. The ICP-MS results (aqua regia and total digestion) include also the metals not visible in the SEM-EDX analysis.

Few studies exist on the health effects of tungsten and WC particles on the general population, whereas adverse health effects have been identified among people exposed to tungsten in the hard metal industry. Especially WC containing cobalt is more harmful than pure WC (Zanetti and Fubini 1997). Considering the relatively low concentrations of tungsten, and the multitude of various particles and toxic compounds in the urban dust and exhaust fumes, the potential additional effects are probably limited. The size of the WC particles found in the street dust puts them in the category of respirable particles (Hinds 1999). While the high-density WC particles certainly do not behave similarly to silicate or carbonate particles of the same size, their transportation into human lungs cannot be excluded. Consequently, it is interesting to note that the concentrations of tungsten in human blood serum have been found to be approximately 50% higher in a group of Swedish people compared with Italian people (Bárány *et al.* 2002). This indicates that there could be a measurable effect on humans of the WC spread out in the Nordic countries.

## Conclusions

Studded winter tyres are most likely the main diffuse source of WC particles in countries or regions where such tyres are commonly used. In contrast to industrial use, the abrasion of tyre studs makes WC unavailable for recycling but

**Fig. 4**. The surface of a new stud. The lighter blocks are WC, the grey blocks are cobalt and titanium and the dark material is mainly carbon (possibly graphite). The inserted spectra show the chemical signature of a ca. 20 × 20 µm area of the picture. Note that the lower and higher energies are heavily suppressed which means that the real count rate for especially carbon is in fact much higher.
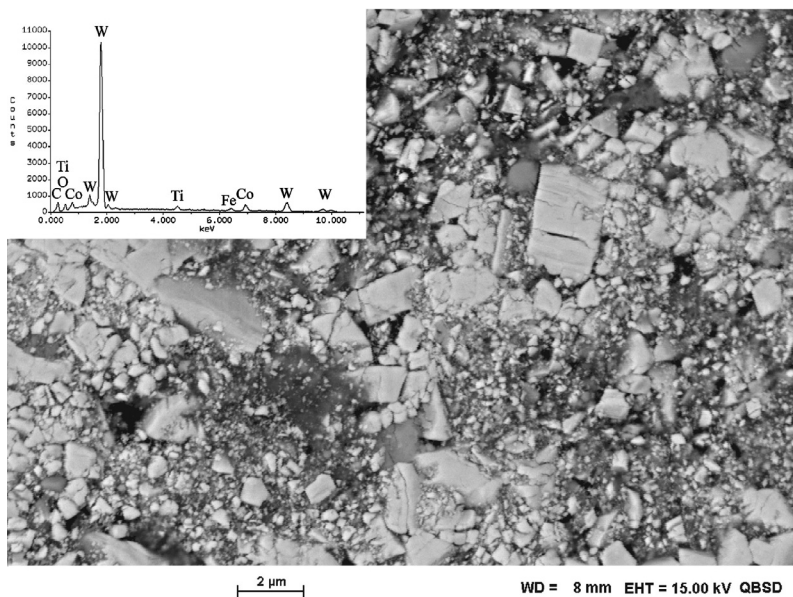
available for relocation in the environment. This has been shown in several studies as elevated tungsten concentrations in different sampling media such as dust, soil, humus and moss. In this pilot-scale study the aim was to determine the tungsten concentration in three size fractions of street dust and to determine the size of the WC particles abraded from the studs. The total concentrations of tungsten in all fractions were well above the local bedrock concentrations and comparable with highway dust studied in Sweden. Tungsten was more enriched in the finer fractions as compared with other elements determined. The WC particles found in the street dust were in the size range of 0.1–1.4 $\mu$m, thus belonging to the respirable size fraction. Further studies should be made on air filters from various urban and rural locations. The presence of traffic-derived WC particles in human lungs could also be studied.

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