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Metal Emissions from Brake Linings and Tires: Case Studies of Stockholm, Sweden 1995/1998 and 2005

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Road traffic has been highlighted as a major source of metal emissions in urban areas. Brake linings and tires are known emission sources of particulate matter to air; the aim of the current study was to follow the development of metal emissions from these sources over the period 1995/1998–2005, and to compare the emitted metal quantities to other metal emission sources. Stockholm, Sweden was chosen as a study site. The calculations were based on material metal concentrations, traffic volume, particle emission factors, and vehicle sales figures. The results for metal emissions from brake linings/tire tread rubber in 2005 were as follows: Cd 0.061/0.47 kg/year, Cu 3800/5.3 kg/year, Pb 35/3.7 kg/year, Sb 710/0.54 kg/year, and Zn 1000/4200 kg/year. The calculated Cu and Zn emissions from brake linings were unchanged in 2005 compared to 1998, indicating that brake linings still remain one of the main emission sources for these metals. Further, brake linings are a source of antimony. In contrast, Pb and Cd emissions have decreased to one tenth compared to 1998. The results also showed that tires still are one of the main sources of Zn and Cd emissions in the city.

Introduction

Globally, metals are accumulated in the technosphere, especially in urban areas where the in-use stock is increasing, e.g., for copper (*1*) and zinc (*2*). From the stock, metal emissions to the biosphere may be significant, e.g., refs *3* and *4*. Several studies have stressed road traffic as a source of metal emissions, particularly in urban areas (e.g., refs *5* and *6*), and brake linings as well as tires are known emission sources of particulate matter to the surrounding environment (*7–10*).

Asbestos was used in brake linings until the 1980s when it was banned in Sweden to improve both working environments and the outdoor air quality of cities. The replacement material was a complex mixture of various substances: reinforcement fibers of glass, steel, and plastic; "friction modifiers"; fillers in the form of antimony compounds and brass chips; and iron filings and steel wool as heat-conducting materials (*11*). The materials used in brake linings are of environmental relevance as a greater part of the material is dispersed directly into the environment when used. Westerlund (*12*) measured metal concentrations in brake linings and calculated the metal emissions in Stockholm for 1998 for a number of metals including cadmium, copper, lead, and zinc. It has clearly been shown that brake linings are a major source of metal emissions in urban areas (e.g., refs *13* and *14*). As there are only a few similar studies, EMEP (the Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) has based its calculation model for brake lining emissions mainly on data from the Westerlund study(*14*). With an increasing willingness to phase out a number of metals in the past decade, as well as the introduction of "lead-free" brake linings (*11*), there is a need to update Westerlund's study to enable the changes in material and emissions to be monitored. Further, studies have shown that large amounts of antimony might be emitted from brake linings, as antimony (Sb_2S_3) is used by some manufacturers as a filler and lubricant in brake linings (e.g., *refs 5*, *15–17*). Further, Uxeküll et al. (*17*) emphasize that Sb in friction material might pose a human cancer risk and its use should, therefore, be discouraged.

The total Zn emissions from tires in Sweden have been calculated at 150 tonnes/year, which is a significant figure when compared to other sources (*18*). The metal emissions in Stockholm have been briefly quantified earlier (1995) (*19*). Furthermore, Sörme and Lagerkvist (*20*) calculated metal emissions from tires via stormwater to the drainage area for one of Stockholm's wastewater treatment plants. The calculated emissions in their study are based on the metal concentrations in tires given by Legrett and Pagotto (*21*). This is one of the few studies to analyze metal concentrations in the part of the tire that wears while driving. Most other studies have analyzed the total concentration in tire chips, as they focused on emissions from tires as a combustion fuel. This method might result in overestimation as the tire body often contains metal reinforcements. An updated calculation of Cd emissions from tires in Stockholm can be found in Hjortenkrans (*22*), who concludes that there is a lack of relevant metal analysis studies of tire tread rubber.

According to the directive of the European Parliament and Council (*23*), materials and components in vehicles produced after July 2003 should not contain lead, mercury, cadmium, or hexavalent chromium. Brake linings were one of the components added in June 2002 to Appendix II of the directive as an exception to these restrictions (*24*). This appendix states that the use of copper containing more than 0.5 weight percentage lead in brake linings is allowed for vehicle models approved before July 2003, including maintenance of these vehicles until July 2004. After that time, a concentration of up to 0.4 weight percentage lead in copper in brake linings is permissible until July 2007, provided that it is not intentionally added. In Sweden, the directive has only been implemented for pick-up trucks and private cars that are not approved EU models (*25*). In practice this means that Swedish EU-approved models of private cars are allowed to use replacement brake linings containing lead.

The aim of the current study was to follow the development of metal emissions from brake linings and tire tread rubber over the period 1995/1998–2005, and to put the emitted metal quantities in relation to other metal emission sources in an urban area. The focus was on Cd, Cu, Pb, Sb, and Zn, and for tires, chromium and nickel. Stockholm, the capital of Sweden, was chosen as a study site. The city is relatively densely populated with approximately 700 000 inhabitants in an area of 190 km^2.

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Materials and Methods

Sampling. Westerlund's (*12*) study of metal emissions from brake lining wear was based on a manual vehicle count, with brake linings of the most common 63% of vehicles analyzed for metals. As vehicle counts are rare, the current study uses vehicle sales figures for 2004 (Supporting Information Table S1), reflecting the vehicle pool that will contribute to metal emissions from brake linings for several years to come. In accordance with Westerlund, brake linings from the two most common lorry and bus models were also examined. Some of the brake linings were of the same kind for different models. A total of 42 vehicle replacement brake linings were sampled.

As not all owners of private cars use branded replacement brake linings, brake lining samples from independent suppliers were needed. The independent sector has seen a large increase in market share since new EU regulations were introduced in 2003 (*26*). The new regulations allow independent garages to service and repair new cars, as long as the vehicle manufacturer's requirements are met. Accordingly, the proportion of repairs carried out by independent garages is expected to continue to increase. Today, the independent sector represents approximately half of the aftersales market for spare parts. To analyze the metal concentrations in replacement brake linings for private cars from independent suppliers, the two largest suppliers in Sweden were selected, namely Mekonomen and Meca (*26*). Based on brake linings sales figures (*27*−*29*), five car models were chosen and brake linings for front and rear wheels sampled. A total of 20 brake linings from independent suppliers were analyzed. Titanium-covered drills where used to obtain samples from the brake linings, as titanium was not included in the analysis.

The composition of tire rubber varies by year of manufacture, make and model, factory and rubber mass batch. For economic, practical, and environmental reasons, discarded tires were sampled. The aim was to take tire tread rubber samples from manufacturers corresponding to 75% of the total annual turnover of tires in 2005 (Supporting Information Table S2). Make, model, and year were noted, and a total of 52 tires were sampled. Rubber samples from the outer 5 mm of the tread were removed with a knife. The rubber chips were fragmented with scissors and then washed repeatedly in 18.2 MΩ/cm^2 Milli-Q water.

Analytical Methods. Samples were dried to constant weight at 60 °C. About 0.4000 g of sample was digested in 3 mL concentrated HNO_3 and 3 mL concentrated HCl in closed vessels in a microwave oven (Perkin-Elmer). The program used was 400 W for 6 min, 900 W for 10 min, and cooling for 15 min. The vessels were not opened until the temperature of the solution had decreased to below 30 °C to avoid evaporation of volatile metal compounds (such as antimony chlorides). The samples were finally diluted to 100 mL with 18.2 MΩ/cm^2 Milli-Q water. The metal concentrations were analyzed using an atomic absorption spectrophotometer (AAS) and a graphite furnace atomic absorption spectrophotometer (GFAAS) (Perkin-Elmer Aanalyst 800). Details of the instrumental parameters are given in Tables S3 S4 in the Supporting Information.

Variation and Quality Control. To analyze the variation of metal concentrations within one unit, six replicates of two brake linings and two to six replicates from 10 different tires were made. To control the precision of the analysis method, six brake lining and six tire tread samples were sent to an external accredited laboratory for control (Analytica, Luleå Sweden). Analytica is not accredited for metal analyses of brake lining and tire rubber composition; instead they used two different accredited digestion methods for plastic. Those methods differed slightly from those used in our study, as aqua regia (1:3) was used for brake linings and concentrated HNO_3 and H_2O_2 for tires. Both digestion methods used closed vessels in a microwave oven. Analytica's results were compared with our analyses using a one-sample *t* test for all metals. The precision, accuracy, and reproducibility were checked with control blanks and quality control solutions (SPS-SW1, SPS-WW1, Spectrapure Standards AS, Oslo, Norway and Certified Reference Material TM-15, Environment Canada, National Water Research Institute, Burlington, Ontario, Canada).

Calulation of Metal Emissions. The amount of particulate matter from brake linings was calculated differently depending on the type of vehicle. Calculations were based on the wear of brake linings before replacement, the weight of the brake linings, the distance driven before replacement, and the total distance driven per year for each vehicle type (for details see Westerlund, ref *12*). The amount of particulate matter from each axle was corrected for updated traffic volumes. The assumption that brake linings from branded and independed suppliers have the same lifetime has been made. Westerlund assigned 40% of traffic volume to new vehicles (less than 4 years old) and 60% to older vehicles, making the assumption that all new vehicles were using branded brake linings and all old vehicles were using unbranded brake linings. For the sake of comparability, the same assumptions were made in this study.

The calculations of metal emissions from brake linings were made according to eq 1.

$$\mathrm{ME} = \sum_{\mathrm{v}} \left[\frac{(P_{\mathrm{front}} \times C_{\mathrm{front}}) + (P_{\mathrm{rear}} \times C_{\mathrm{rear}})}{1000} \right] \qquad (1)$$

where ME is the amount of metal emitted per year (kg/year), v is the type and make of vehicle (type: private car, pick-up, bus, or lorry), *P* is the the total amount particulate matter emitted from brake linings from each axle per year (tonnes/year) and includes particulate matter emitted per kilometer and distance driven by a specific type and make of vehicle, and *C* is the mean metal concentration in brake linings for each axle (mg/kg).

The tire emission calculations were based on traffic volume for Stockholm and Sweden, respectively (Supporting Information Table S5), sale figures for tires (where the annual percentages sales of each brand are assumed to reflect the distance driven with that brand), particle emission factors for tire wear, and analyzed metal concentrations in tires. The calculations of metal emissions from tires were made according to eq 2.

$$\mathrm{ME} = \sum_{\mathrm{v}} \left[\frac{P \times C \times \mathrm{TV} \times F}{1000} \right] \qquad (2)$$

where TV is traffic volume (Mvkm/year) and *F* is the proportion driven with each type of vehicle and brand, expressed as annual sales figures.

A more straightforward calculation excluding sales figures was also performed.

Particle emission factors for tires have been compiled by the EEA (*14*) and Gustavsson (*30*). The factors vary by 1 order of magnitude depending on which references are used. The emission factors for private cars range from 24 to 360 mg/vkm (vehicle kilometers) (mean ± standard deviation 122 ± 96 mg/vkm), for pick-ups 53−112 mg/vkm (102 ± 16 mg/vkm), and for heavy vehicles 136−1403 mg/vkm (628 ± 450 mg/vkm). A mean metal concentration of a brand regardless of model has been used in the calculations.

Calculations for pick-ups follow the market shares for private cars. As no newer statistics for heavy vehicles were known to us, we followed the Swedish market share data of Ahlbom and Duus (*9*) (Supporting Information Table S6).

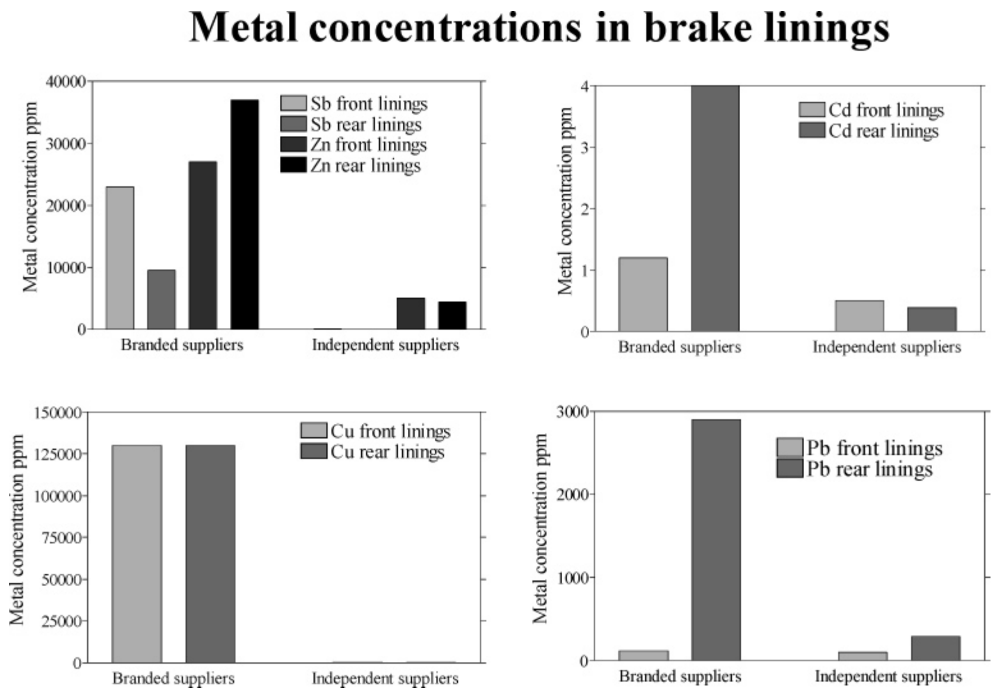

FIGURE 1. 1. Mean metal concentrations (Cd, Cu, Pb, Sb, and Zn) in private car brake linings from branded and independent suppliers in 2005 in Sweden (mg/kg) (as antimony and copper concentrations were low in brake linings from independent suppliers, the columns are not shown).

Estimates of traffic volumes nationally are made every 4 years. The most recent calculations are from 2002. However, traffic volume has increased at a rate of 3.5% from 2002 to 2005, and thus the values used here are figures for 2002 adjusted by 3.5% (*31*). For Stockholm the increase for the period 2002−2005 is estimated to be 2.5% (*32*). Traffic volumes were divided according to type of vehicle, as shown in Table S5 in the Supporting Information.

The calculated emissions for Stockholm are presented as means ± relative standard deviation (rsd) as a percentage, together with an interval with minimum and maximum values based on the relative standard deviation.

Calulations of Uncertainties. As the calculations are multiplicative expressions, the uncertainties have been calculated according to eq 3.

$$\text{r.s.d.} = \frac{\sigma_{\text{ME}}}{\text{ME}} = \sqrt{\left(\frac{\sigma_P}{P}\right)^2 + \left(\frac{\sigma_C}{C}\right)^2 + \left(\frac{\sigma_{\text{TV}}}{\text{TV}}\right)^2 + \left(\frac{\sigma_F}{F}\right)^2} \quad (3)$$

where r. s. d. is the relative standard deviation (%), σ_{ME} is the standard deviation for amount of metal emitted per year, ME is the amount of metal emitted per year, σ_P is the standard deviation for emitted amount of brake lining or tire compound, P is the mean for emitted amount of brake lining or tire compound, σ_C is the standard deviation for metal concentration in brake lining or tire compound, C is the mean for metal concentration in brake lining or tire compound, σ_{TV} is the standard deviation for traffic volume, TV is the mean for traffic volume, σ_F is the standard deviation share of traffic volume, expressed as annual sales figures, for tires only, and F is the mean for share of traffic volume, expressed as annual sales figures, for tires only

Results and Discussion

Metal Concentrations. The mean metal concentrations in analyzed *branded brake linings* for private cars from 2005 were for front/rear brake linings 1.2/4.0 ppm Cd, 130 000/130 000 ppm Cu, 120/2900 ppm Pb, 23 000/9500 ppm Sb, and 27 000/37 000 ppm Zn (Figure 1, for details see Supporting Information Table S7). Here, Cu and Zn concentrations are high in both front and rear brake linings and of the same magnitude as in 1998. Antimony also shows a high concentration, especially in front brake linings (antimony was not analyzed in 1998). The mean Pb concentration in branded brake linings from 2005 is much lower than the corresponding values from 1998. In 1998 the Cd concentrations were between <0.974 and 19.9 ppm, most around 10 ppm. No Cd mean was calculated, however, as data were often near or below the detection limit. For 2005 the Cd mean was 1−4 ppm, i.e., most likely a decrease from 1998.

The metal concentrations in private car replacement *brake linings from independent suppliers* are considerably lower for 2005 than for 1998. The mean metal concentrations for front/rear brake linings were 0.5/0.39 ppm Cd, 200/110 ppm Cu, 100/290 ppm Pb, 29/10 ppm Sb, and 5000/4400 ppm Zn. (Figure 1, for details see Supporting Information Table S8). The fact that brake linings from different independent suppliers have been analyzed hinders comparison between the years. However, the Cu and Pb concentrations in 2005 are only a fraction of the concentrations in 1998.

The differences in metal concentrations in brake linings for private cars from branded and independent suppliers for 2005 are shown in Figure 1.

There is a clear difference between metal concentrations in branded and independent brake linings, with the latter having the lower concentrations. If consumers wish to limit their contribution of Cu and Sb emissions to the traffic environment, brake linings from independent suppliers are to be preferred. There are also large differences within branded brake linings; for example, one supplier has brake linings with Pb concentrations between 14 and 21 000 ppm. The concentrations of Pb and Cu were below the stipulated 0.4% in 41 of 48 brake linings from branded suppliers; however, all of the brake linings from independent suppliers exceeded this level (Supporting Information Table S9). The choice of a Pb/Cu quota in the regulatory document makes it difficult to assess the environmental relevance of the directive. Despite the fact that brake linings from independent suppliers have lower metal concentrations than branded brake linings, the latter ones are those that will pass the EU

TABLE 1. Calculated Total Metal Emissions from Road Traffic from Brake Linings in Stockholm (kg/year) for 1998 and 2005

	2005					1998[a]				
	Cd	Cu	Pb	Sb	Zn	Cd	Cu	Pb	Sb	Zn
private cars	0.052	2400	24	360	710	*b*	3731	549	–	771
lorries	0.005	1200	4.8	350	180	*b*	68	3.9	–	68
buses	0.007	210	6.5	0.33	110	*b*	76	3.2	–	56
total	0.064	3800	35	710	1000	*b*	3900	560	–	900

[a] From ref *12*. [b] Could not be calculated due to metal concentrations near or below the detection limit.

TABLE 2. Calculated Metal Emissions (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) from Tire Tread Rubber in Stockholm (kg/year) for 2005[a]

	Cd	Cr	Cu	Ni	Pb	Sb	Zn
private cars	0.33	0.54	3.7	0.97	2.6	0.37	2900
pick-ups	0.033	0.054	0.37	0.097	0.26	0.037	290
lorries	0.11	0.17	1.2	0.30	0.85	0.14	1000
total	0.47	0.76	5.3	1.4	3.7	0.54	4200

[a] Calculations are based on traffic volume for Stockholm, tire sales figures, particle emission factors for tire wear, and metal concentrations in tire tread rubber.

TABLE 3. Calculated Metal Emissions (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) From Tire Tread Rubber in Stockholm (kg/year) Using a Simplified Calculation, Where the Mean of All Metal Concentrations Was Used Instead of Sales Figures

	Cd	Cr	Cu	Ni	Pb	Sb	Zn
private cars	0.31	0.62	2.8	1.2	3.1	0.42	3400
pick-ups	0.031	0.062	0.28	0.12	0.31	0.042	340
lorries	0.11	0.17	1.2	0.31	0.88	0.13	970
total	0.45	0.85	4.3	1.6	4.3	0.60	4700

regulations. This indicates the problem with having a quota rather then an absolute value as a regulatory limit.

Cu concentrations increased for both lorries and buses between 1998 and 2005, while the other metals remained approximately the same (Supporting Information Tables S10 and S11). Cu, Pb, and Sb have higher concentrations in disk brake than drum brake linings. This agrees with the findings of Uexküll et al., (*17*) as do the metal concentration levels.

The mean metal concentrations in analyzed *retread tire tread rubber* were 0.86 ppm Cd, 1.3 ppm Cr, 7.4 ppm Cu, 2.9 ppm Ni, 9.5 ppm Pb, 1.1 ppm Sb och, and 12 000 ppm Zn. In analyzed *nonretread tire tread rubber* the mean metal concentrations were 1.1 ppm Cd, 1.7 ppm Cr, 8.6 ppm Cu, 3.2 ppm Ni, 9.4 ppm Pb, 1.0 ppm Sb och, and 9400 ppm Zn (for details see Supporting Information Tables S12 and S13). The values are in the same order of magnitude as those of Legret and Pagottos (*17*) (i.e., 2.6 ppm Cd, 1.8 ppm Cu, 6.3 ppm Pb, and 10 000 ppm Zn). The date of production for the analyzed tires varied between 1985 and 2004. Thirty-one of the tires were from 1999–2001 (Tables S12 and S13). Metal concentrations in retread and nonretread tires showed significant differences for Zn only (Mann–Whitney U test, $p < 0.05$). The Zn concentration was highest for retread tires.

Metal Emissions in Stockholm. The calculated *total metal emissions from brake linings in Stockholm* from road traffic (eq 1) are presented in Table 1. There are no notable changes in Cu and Zn emissions between 1998 and 2005, whereas Pb emissions decreased significantly.

The low metal concentrations in brake linings from independent suppliers (calculation based on 60% usage) influence the results significantly. An alternative calculation was made with an assumption that half of the worn brake linings were replaced by branded brake linings (30% usage of brake linings from independent suppliers). The results of these calculations gave 35–50% higher emissions: 0.088 kg Cd/year, 5700 kg Cu/year, 48 kg Pb/year, 970 kg Sb/year, and 1400 kg Zn/year.

TABLE 4. Total Calculated Metal Emissions from Road Traffic from Brake Linings in Sweden 2005, (kg/year)

	2005				
	Cd	Cu	Pb	Sb	Zn
private cars	0.79	37 000	370	5400	11 000
lorries	0.15	35 000	140	10 000	5400
buses	0 20	6400	200	10	3330
total	1.1	78 000	710	15 000	20 000

The calculated *total metal emissions from tire tread in Stockholm*, based on market share (eq 2), are presented in Table 2. The emissions were calculated for each vehicle type and then added together. The calculated total metal emissions from tire tread in Stockholm in 2005 were as follows: 0.47 kg Cd/year, 0.76 kg Cr/year, 5.3 kg Cu/year, 1.4 kg Ni/year, 3.7 kg Pb/year, 0.54 kg Sb/year, and 4200 kg Zn/year.

A simplified calculation, where only a mean of all metal concentrations was used instead of sales figures, gave similar results (Table 3).

These simplified calculations gave −4.2% for Cd, +12% for Cr, −19% for Cu, +14% for Ni, +16% for Pb, +11% for Sb, and +12% for Zn.

Metal Emissions in Sweden. Corresponding calculated *total metal emissions from brake linings for Sweden* (based on 60% usage of brake linings from independent suppliers) are shown in Table 4. The traffic volume in Stockholm is 6.3% of the total national traffic volume, whereas the metal emissions represent about 5%. The differences result from different proportions of heavy traffic in Stockholm and Sweden.

The corresponding calculated *total metal emissions from tire tread for Sweden*, based on market share, resulted in 8.8

TABLE 5. Calculated Metal Emissions (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) from Tire Tread Rubber in Sweden (kg/year) in 2005[a]

	Cd	Cr	Cu	Ni	Pb	Sb	Zn
private cars	5.5	9.1	62	16	44	6.3	49 000
lorries	3.3	5.2	37	9.0	26	3.7	29 000
total	8.8	15	99	25	70	10	78 000

[a] Calculations are based on national traffic volume, sales figures for tires, particle emission factors for tire wear and metal concentrations in tire tread rubber.

TABLE 6. Calculated Metal Emissions (Cd, Cu, Pb, Sb, and Zn) in Stockholm from Brake Linings, 1998 and 2005

		metal emissions 2005 (kg/year)	
metal	metal emissions 1998 (kg/year)[a]	mean ± r.s.d. (%)	interval
Cd	not calculated	0.061 ± 57%	0.026−0.096
Cu	3731	3 800 ± 57%	1600−6000
Pb	549	35 ± 62%	13−57
Sb	not calculated	710 ± 69%	220−1200
Zn	771	1000 ± 54%	460−1500

[a] Westerlund, K.-G. *Metal emissions from Stockholm traffic − Wear of brake linings.* Reports from SLB-analys, 2:2001, Environment and Health Protection Administration Stockholm, 2001.

kg Cd/year, 15 kg Cr/year, 99 kg Cu/year, 25 kg Ni/year, 70 kg Pb/year, 10 kg Sb/year, and 78 000 kg Zn/year (Table 5).

Uncertanties. The *mean coefficient of variation of metal concentrations within one brake lining* was 5.3% for Cd, 2.7% for Cu, 19% for Pb, 27% for Sb, and 1.5% for Zn. This indicates that the friction material in brake linings is relatively homogeneous. The external control of the precision of the metal analyses showed that there were differences between our and Analytica's analyses. These were 21% for Cd, 20% for Cu, 26% for Pb, 35% for Sb, and 7.5% for Zn. None of the laboratories was accredited for metal analysis on friction materials, and different strengths of acids were used. The differences between the methods have been used as possible uncertainty in the analytical method.

The *total uncertainties of metal concentrations in the friction material* are based on both the variation within one brake lining as a result of inhomogeneous material and the uncertainty of the analytical method. In this case, it has been calculated according to $\sqrt{(\text{meanerror}(\%)\text{brakelining})^2 + (\text{meanerror}(\%)\text{analyticalmethod})^2}$, giving ±21% for Cd, ±20% for Cu, ±32% for Pb, ±44% for Sb, and ±7.7% for Zn.

The *uncertainty of the wear of the friction material* is estimated by Hedbrant and Sörme (*33*) to be ±33%. The EEA's (*14*) compilation of friction material wear gives an emission of 18.8 ± 42% mg friction materials per private car kilometer. Westerlund (*12*) and the current study (for the sake of comparability) use 17 mg/vkm. The uncertainty used was ±42% even if the recommendations are lower.

The *variation coefficients of metal concentrations within a single* tire were in the following range: 2.2−38% for Cd, 0.38−38% for Cr, 2.1−32% for Cu, 4.7−83% for Ni, 0.32−9.2% for Pb, 1.9−73% for Sb, and 1.3−6.4% for Zn. In the external control of the analytical precision, it was unclear whether there was a significant difference between our and Analytica's analyses (Supporting Information Table S14). However, the control showed that significant results also included higher exchange in our method. As our method used stronger acids, this was to be expected. The differences in outcome between the two methods are used as potential analytical uncertainty.

The *total uncertainties of metal concentrations in tire tread rubber* are based on both the variation within a single tire due to inhomogeneities of the material and the uncertainty of the analytical method. In this case it has been calculated according to $\sqrt{(\text{meanerror}(\%)\text{tiretreadrubber})^2 + (\text{meanerror}(\%)\text{analyticalmethod})^2}$, giving ±35% for Cd, ±19% for Cr, ±18% for Cu, ±39% for Ni, ±15% for Pb, ±25% for Sb, and ±3.7% for Zn.

The *uncertainty of the particulate wear of the tire tread rubber* was calculated at ±79% for private cars, ±16% for pick-ups, and ±72% for lorries. As pick-ups have only a limited contribution to emissions, we used ±75% in the calculations.

The *uncertainty of the traffic volume* figures are difficult to estimate. The Swedish Road Administration cannot state the uncertainty of its figures, as these are partly modeled. Here Hedbrant and Sörme's (*33*) recommendation of ±33% for official statistics at regional/national level has been used.

The *uncertainty of the distance driven (km) with each tire brand*, expressed as a percentage of the annual sales figures, could be a matter of debate. The differences (4−19%) between emissions calculated with or without sales figures were used as the potential uncertainty even though this will overestimate the error term.

The *relative standard deviation R.S.D. for metal emissions from brake linings* (total uncertainty for calculated amount of metal emission) is, according to eq 3, ±57% for Cd and Cu, ±62% for Pb, ±69% for Sb, and ±54% for Zn. For tires, *the relative standard deviation R.S.D.* is ±89% for Cd, ±85% for Cr, ±86% for Cu, ±92% for Ni, ±85% for Pb, ±86% for Sb, and ±83% for Zn. The greatest part of the uncertainty derives from the particulate emissions of tire tread rubber. The large variation in emission factors is probably correct, as different tires (e.g., soft/hard rubber) with different compositions result in different amounts of wear per kilometer. However, the mean values of the wear probably reflect the situation on the road.

Comparison of Metal Emissions Between Years. This study allows us to follow the development of *calculated metal emissions from brake linings* in Stockholm for the period 1998−2005. Depending on the proportion of branded and nonbranded brake linings used as replacements, the calculated metal emissions for 2005 differ. Considering this, the most plausible "true" value for 2005 will be found in the upper part of the intervals presented here (Table 6).

The calculated Cu and Zn emissions for 2005 are on the same order of magnitude as for 1998. Lead and probably Cd emissions have decreased to a tenth of 1998 levels.

TABLE 7. Metal Emissions (Cd, Cr, Cu, Ni, Pb, Sb, and Zn) in Stockholm from Tire Tread Rubber Wear for 1995, 2002, and 2005[a]

metal	metal emissions 1995 (kg/year)[b]	metal emissions 2002 (kg/year)[c]	metal emissions 2005 (kg/year) mean (kg/year) ± r.s.d. (%)	metal emissions 2005 (kg/year) interval
Cd	0.2–3	1.5	0.47 ± 89%	0.050–0.89
Cr	200	NC	0.76 ± 85%	0.11–1.4
Cu	200	1.1	5.3 ± 86%	0.74–9.9
Ni	200	NC	1.4 ± 92%	0.11–2.7
Pb	300	2.7	3.7 ± 85%	0.56–6.8
Sb	N.C.	NC	0.54 ± 86%	0.074–1.0
Zn	10 000	6200	4200 ± 83%	720–7700

[a] NC, not nalculated. [b] From ref *19*. [c] From ref *20*. Corrected to include all emissions from tire tread wear in Stockholm rather than only emissions ending up in stormwater (×2.7).

Brake linings are also a source of Sb emissions. Two studies have found the average Cu:Sb ratio in road tunnel aerosols to be 5.6:1 (*34*) and 4.4:1 (*15*). As our average Cu:Sb ratio is 5.3:1, brake linings must also be considered a major road traffic source of Sb.

Manufacturers seem to have taken seriously their responsibility for phasing out Cd and in particular Pb. The concentrations in the friction material have been reduced, resulting in lower emissions. The independent manufacturers have shown that it is possible to produce brake linings with lower amounts of both Cu and Sb while maintaining quality.

The *calculated metal emissions (2005) from tire tread rubber* are lower for all metals than corresponding figures for 1995 (Table 7). This is probably not a result of decreasing metal concentrations in the tire treads, rather a lack of data in the 1990s when the only reliable data were for Cd (*35*). The Zn concentrations were estimated from the amount ZnO added in production and were, therefore, only approximate. The other metals were estimated from a few available references. The calculated metal emissions of Sörme and Lagerkvist (*20*) from 2002 are approximately the same as in the current study.

For Zn, an optimized consumption of ZnO in the production stage could reduce the emissions from tires. Cd is also probably derived from ZnO as a contaminant. If all manufacturers could deliver tires with the lowest measured Cd concentration, emissions should decrease to a tenth of their current levels.

Metal Emissions from Brake Linings and Tires Compared to Other Sources of Concern. For 1995, the total metal emissions (Cd, Cr, Cu, Ni, Pb, and Zn) from the Stockholm technosphere were calculated, e.g., from vehicles, buildings, infrastructure, and households. Some major identified emission sources were artists paint (Cd), tap water system/ roofs (Cu), ammunition/sinkers (Pb), and roofs/tap water system/ galvanized goods (Zn). However, emissions related to the road traffic sector were dominant (approximately 50% or more of total emissions depending on metal) for Cd (car washes), Cr (road pavements, tires), Cu (brakes, road pavement, tires), Ni (road pavements, tires), Pb (brakes, tires, ammunition/sinkers excluded), and Zn (tires, brakes, road pavements) (*13*). From 1998 to 2005 no major changes in emissions from tap water system, roofs, and galvanized goods are to be expected, but the results for 2005 show that tires can be excluded as a significant source of Cr, Cu, Ni, Pb, and (probably) Sb compared to other sources of concern in Stockholm. However, tires remain one of the largest sources of Zn and a significant source of Cd. Further, brake linings must still be considered as a major source of emissions of Cu and Zn (and probably Sb) in Stockholm. As Stockholm represents a rather average city in most respects, the results from this study may be relevant for many other urban areas.

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Supporting Information Available

Details of the analytical instrumental parameters and detailed tables on special brands and models of brake linings and tires. This material is available free of charge via the Internet at http://pubs.acs.org.

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