



# Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies

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## Abstract

Metal emissions from road traffic were studied in two heavily trafficked tunnels in Gothenburg, Sweden. Five runs were made in each tunnel, generally extending over several hours, during which air concentrations of metals in tunnel inlet and outlet, traffic flow and composition, and air ventilation were determined. Emission factors for Cu, Zn, Cd, Sb, Ba and Pb in TSP were derived from these data, mainly representing vehicle emissions. For these metals, results from the two tunnels were fairly consistent and the variability of the emission factors was generally within the experimental uncertainty. In contrast, concentrations of TSP, PM<sub>10</sub> and a number of other metals differed widely between the two tunnels. This difference was caused by different magnitudes of resuspension, mainly reflecting that the two tunnels were investigated at different seasons and that one of the tunnels was newly cleaned. Aerosol concentrations of larger particles and of several metals are apparently dominated by resuspended matter, rather than by emissions from vehicles. The vehicle-derived metals (Cu, Zn, Cd, Sb, Ba and Pb) mainly derive from wear rather than from combustion; Cu, Ba and Sb are probably dominated by brake wear. There are also indications that heavy duty vehicles are stronger emitters of Ba and Sb, but not of Cu, than light duty vehicles.

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## 1. Introduction

Airborne particles are important carriers of metals, certain of which possess toxic properties and commonly are present in excess of natural levels. Consequently, it has been proposed that the toxic properties of particles in part may be due to the biochemical activity of metals (e.g., Smith and Aust, 1997; Lighty et al., 2000). Regarding health effects, much focus is on smaller particles (PM<sub>10</sub> and less) that may penetrate deeply into the lungs. However, even larger particles can be inhaled and may be an important source of biochemically active metals in the guts. Larger metal-containing particles are also of ecotoxicological concern due their more rapid deposition to soils and surface waters.

In urban areas, road traffic is recognised as an important source of both particles and certain metals (e.g., Kowalczyk et al., 1982; Gertler et al., 2000; Wróbel et al., 2000; Pakkanen et al., 2001). Understanding emissions from traffic includes identification of the sources, which is also crucial for designing control measures. Road traffic involves numerous potential sources of metals, e.g., combustion products from fuel and oil, wear products from tires, brake linings, bearings, coach and road construction materials, and resuspension of soil and road dust. Therefore, emission measurements in conventional dynamometric tests alone are not sufficient to fully address this problem. In order to do so, studies need to be performed under realistic driving conditions in environments where the contribution from other emission sources is eliminated. Measurements in traffic tunnels have been used successfully for quantifying emissions of a large number of both

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gaseous and particulate pollutants (El-Fadel and Hashisho, 2001, for a review). Most such studies, in particular where metals are studied, have been performed in the US. Because composition of both fuel and construction materials in vehicles evolve over time and may show regional differences, there is a need for measurements also outside the US.

In this paper, emission factors for metals from road traffic are derived from measurements of metals in the TSP fraction in two tunnels. These emission factors represent those metals that may contribute to local and regional environmental impact through inhalation or deposition to ecosystems. The goals were to (1) identify metals typical for road traffic emissions; (2) determine emission factors for these metals; (3) investigate the factors controlling emission factors. This was achieved by performing mass balance studies in two heavily trafficked tunnels for different fleet compositions. Emissions of a number of gaseous pollutants and PAH were determined jointly with the metals and are reported elsewhere (Sjödin et al., 2001; Wingfors et al., 2001).

## 2. Sampling strategy and site descriptions

Measurements were performed under a wide range of driving conditions and fleet compositions. Mass balance was made possible by simultaneous measurements at the inlet and outlet of the tunnels, together with measurements of the air ventilation and detailed registrations of the fleet characteristics (intensity, speed, acceleration and fleet composition by traffic analysers, with additional information on fleet composition obtained from video recordings). Most runs lasted for 2 h but some runs were longer or shorter. Details of the runs are presented in Table 1.

Two tunnels were investigated, the 450 m long and straight Tingstad tunnel and the 2060 m long slightly bent Lundby tunnel, both located in central Gothen-

burg, Sweden. The road surface is asphalt in both tunnels. Both tunnels are shaped as shallow V's and have separated bores for each driving direction; the Tingstad tunnel has three lanes in each direction and the Lundby tunnel two. The Tingstad tunnel was sampled in November 1999 and the Lundby tunnel in early April 2000. At the latter occasion, studded tires were common, contrary to the situation in November 1999. On an average, the heavy duty vehicle (HDV) composition was 10% in Tingstad and 14% in Lundby. HDVs were 100% diesel whereas light duty vehicles (LDVs) were 11% diesel and 89% gasoline.

## 3. Methods

Samples were taken inside the tunnels, ca. 50 m (Tingstad tunnel) and 150 m (Lundby tunnel) from the out- and inlet. Total suspended particles (TSP) were collected on Teflon membrane filters ( $\phi$  47 mm; 0.4  $\mu$ m) that were mounted on Teflon filter holders. The pumping rate was ca. 20 l min<sup>-1</sup>. A few PM<sub>1</sub>/PM<sub>10</sub> samples were collected using a KleinfILTERgerät impactor, also using Teflon filters, at a pumping rate of ca. 38 l min<sup>-1</sup>. The particles were digested in aqua regia and metals were analysed with ICP-MS for Li, Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, Ba, La, Ce, Pr, W, Pb and Bi. For certain runs and certain metals, either blank values were not negligible or concentrations were below detection limit. This mainly concerns Ni and Co in both tunnels and Cr, La and Pr in Tingstad, for which no data are presented. In the PM<sub>1/10</sub> fraction, this also concerns Bi, Ca, Al, Cd and Mn. Analytical precision is within 10%.

All metal data presented are from the TSP fraction, unless anything else is stated explicitly. Particle mass was determined gravimetrically. For Tingstad, particle mass was only determined on three out of five runs. To calculate air ventilation fluxes through the tunnels,

Table 1  
Driving conditions during the runs

Run <sup>a</sup>	Time	Vehicles (1/h)	Average speed (km/h)	HD-vehicles (%)	Weather
T-1	07:30–08:30	3404	40.9	10.7	Dry
T-2	11:17–12:15	3002	64.9	13	Dry
T-3	13:15–15:45	3599		12.3	Dry
T-4	16:30–18:30	3069	66.3	5.9	Dry
T-5	04:00–09:00	2180			Rainy
L-1	9:00–11:00	947	76.8	23.7	Dry
L-2	16:00–18:00	1835	75.0	8.5	Rainy
L-3	7:00–9:00	1595	77.3	11.6	Dry
L-4	11:50–16:10	1394	79.1	16.9	Dry
L-5	17:10–19:10	1266	79.8	7.6	Dry

<sup>a</sup>T—Tingstad tunnel, L—Lundby tunnel.

known fluxes of SF<sub>6</sub> were emitted at the inlet and concentrations were measured at the outlet, generally every 15 min. No forced ventilation occurred during the runs.

#### 4. Results and discussion

##### 4.1. Concentrations and major sources

Metals, TSP and PM<sub>10</sub> generally displayed higher concentrations at the outlets compared to the inlets (Table 2). Concentrations of TSP, PM<sub>10</sub> and metals such as Al, Ca, Ce, Fe, Mg, Mn, and Ti were present in much higher concentrations in the Lundby tunnel as compared to the Tingstad tunnel, both at the inlet and the outlet (Table 2; Fig. 1). The difference was generally a factor 5–10. These metals correlated strongly with each other as well as with TSP ( $r^2 > 0.63$ ;  $P < 0.005$ ; correlations with Mn less significant) and showed pronounced dips during the rainy runs (Fig. 1). In contrast, neither in the inlets nor in the outlets did the concentrations of Cu, Zn, Cd, Sb, Ba and Pb differ significantly ( $P > 0.05$ ,  $t$ -test) between the two tunnels. These metals did not correlate with the former group of metals or TSP, and were not typically lower during the rainy runs (Fig. 1, Table 2).

Aluminium, Ca, Ce, Fe, Mg, Mn, and Ti are all typical geological marker elements suggesting that resuspension controls their aerosol abundance. This interpretation is also consistent with the fact that these metals as well as TSP were much more abundant in the Lundby tunnel than in the Tingstad tunnel; the Lundby tunnel was sampled during late winter with a sparse vegetation cover facilitating resuspension of soil, and Tingstad was newly cleaned at the sampling moments. Road sanding was not applied in this region and did thus not contribute to the high levels in Lundby. The predominance of resuspended particles of geological origin was also verified by SEM-EDS studies that we performed on filters from the inlet and outlet of one of the tunnels. The absolute majority of particles we could observe mainly consisted of Al, Si, Ca and Fe.

The mutual relationships of several of the geological marker elements in the aerosols are fairly close to those in average upper crust (e.g., Wedepohl, 1995), which is commonly used as a representative of the composition of resuspended natural material. In this case, however, average upper crust may not be a suitable analogue because (1) we used aqua regia digestion and did probably not recover the most resistant minerals, and (2) the resuspended material derives from urban soils that are commonly polluted with respect to several

Table 2  
Average concentrations of metals (ng/m<sup>3</sup>) and TSP and PM<sub>10</sub> (µg/m<sup>3</sup>) in the tunnel inlets and outlets

	Tingstad inlet average ± s.d.	Tingstad outlet average ± s.d.	Lundby inlet average ± s.d.	Lundby outlet average ± s.d.
TSP	90 ± 36	254 ± 120	826 ± 543	1530 ± 660
PM <sub>10</sub>	122 ± 18	215 ± 106	247 ± 111	645 ± 287
Al	632 ± 217	3270 ± 1280	7530 ± 5530	11950 ± 2940
Ba	111 ± 28	312 ± 130	221 ± 133	569 ± 237
Bi	n/a	n/a	0.17 ± 0.18	0.22 ± 0.11
Ca	511 ± 141	2830 ± 1520	6050 ± 3280	8710 ± 4310
Cd	0.50 ± 0.10	0.99 ± 0.39	0.43 ± 0.19	0.83 ± 0.23
Ce	2.37 ± 0.51	15 ± 6.0	24 ± 18	31 ± 17
Cr	b/d	b/d	21 ± 5	55 ± 24
Cu	152 ± 56	417 ± 184	182 ± 35	404 ± 65
Fe	4050 ± 1370	12,170 ± 5310	14,620 ± 7670	20,690 ± 6560
La	b/d	b/d	10.6 ± 8.0	13.1 ± 7.9
Li	0.43 ± 0.15	2.00 ± 0.78	n/a	n/a
Mg	212 ± 42	1050 ± 461	3510 ± 2030	3700 ± 1500
Mn	55 ± 15	171 ± 67	223 ± 109	261 ± 134
Na	n/a	n/a	3900 ± 4940	8640 ± 12,200
Pb	46 ± 13	104 ± 37	59 ± 29	113 ± 16
Pr	b/d	b/d	2.64 ± 2.05	3.22 ± 2.01
Sb	28 ± 10	75 ± 35	34 ± 12	107 ± 14
Ti	43 ± 10	194 ± 92	408 ± 205	589 ± 334
V	15 ± 15	22 ± 18	40	60 ± 58
W	1.63 ± 0.87	7.73 ± 5.45	30 ± 31	80 ± 57
Zn	191 ± 95	542 ± 316	395 ± 327	759 ± 234

n/a not analysed; b/d below detection limit.

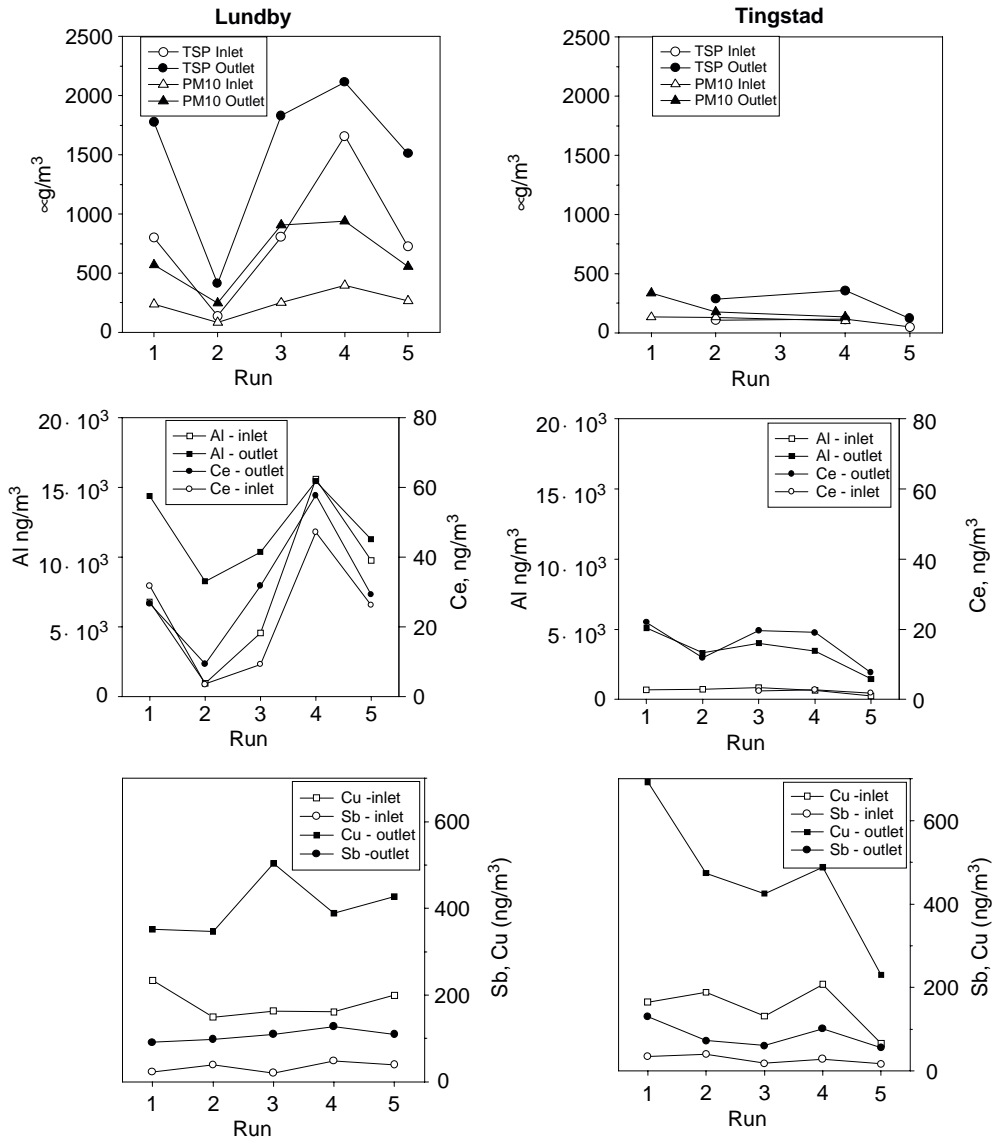


Fig. 1. Concentrations of TSP,  $\text{PM}_{10}$  and a few selected metals (Al, Ce, Cu och Sb) at the inlet and outlet during the different runs in the Lundby tunnel (left) and the Tingstad tunnel (right). Run no. 2 in Lundby and no. 5 in Tingstad were performed under rainy conditions.

elements. In effort to select a more suitable reference, we sampled soils at several places in the immediate vicinity of the road outside one of the tunnels. Five samples were analysed in the  $<0.5\text{mm}$  fraction and the average composition was used as a measure of the resuspended matter.

In Fig. 2, average concentrations in the inlet and outlet aerosols are plotted versus concentrations in the soil. A linear relationship is apparent for the geological marker elements. This fit is much better than when average upper crust data are used. The relationship for

the Tingstad tunnel is 1:1, indicating that the mass concentration of TSP in the aerosol is dominated by resuspended matter. For the Lundby tunnel this pattern is clear for Fe, Al, Mg and Ca, whereas the aerosol is depleted in REE (rare earth elements: La, Ce, Pr) and Ti. Our interpretation is that these metals reside in particles that are less easily resuspended. The emission factors of Ce, La and Pr are strongly correlated for the Lundby tunnel ( $r^2 > 0.99$ ,  $P < 0.05$ ) supporting the interpretation that REE are mainly hosted in a mineral phase separate from bulk Al or Mg.

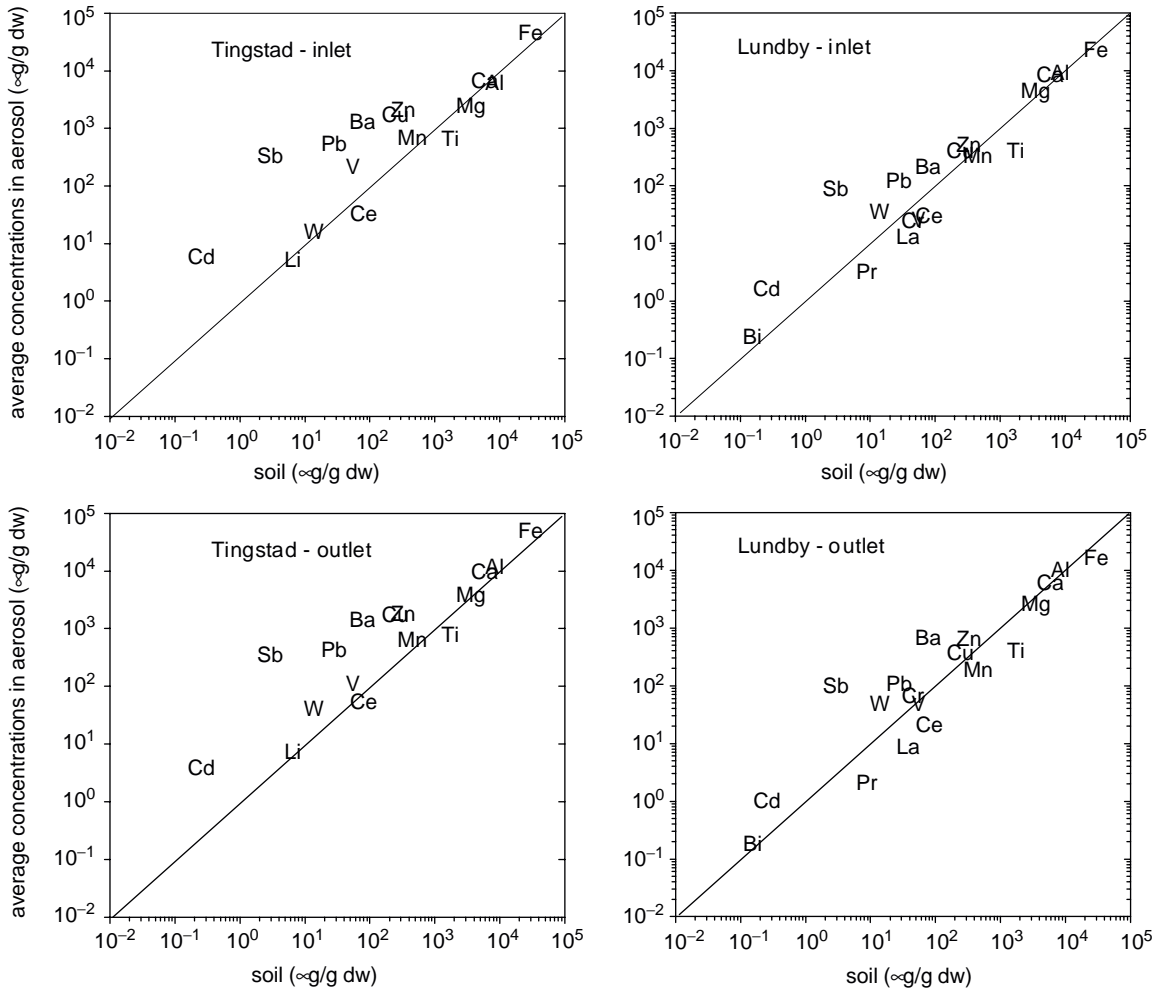


Fig. 2. Metal concentrations in aerosol versus local soil. The straight line shows where concentrations are equal in soil and in aerosol.

Ba, Cd, Cu, Pb, Sb and Zn were consistently enriched in the tunnel aerosols (Fig. 2). For the Lundby tunnel this is also true for W and there are several elements whose position in the graphs indicate a weak enrichment. However, Cu, Zn, Cd, Sb, Ba and Pb were the most strongly enriched metals for which vehicle emissions are much more important than resuspension for their presence in the aerosols. Several other metals (e.g., Fe) are most likely also emitted from vehicles, but the magnitudes of these emissions are insignificant relative to the effect of resuspension in the tunnels.

4.2. Emission factors

The data allow us to calculate emission factors ( $e$ ,  $\mu\text{g vkm}^{-1}$ ) for large vehicle fleets under real and varying driving conditions. Emission factors for any metal,  $i$ , are

calculated as

$$e_i = (\Delta c_i \times V) / (T \times L), \tag{1}$$

where  $\Delta c_i$  ( $\text{ng m}^{-3}$ ) is the concentration gradient (outlet–inlet),  $V$  ( $\text{m}^3 \text{s}^{-1}$ ) is the ventilation flow through the tunnel,  $L$  (m) is the distance between the sampling stations and  $T$  (vehicles  $\text{s}^{-1}$ ) is the traffic flow.  $V$  is calculated from the emitted amount of  $\text{SF}_6$  and the outlet concentration of  $\text{SF}_6$ .

When considering the impact of traffic on air quality the effect of resuspension may be considered separately from direct vehicle emissions, because control measures for these two processes are completely different. As discussed above, our data clearly illustrate that resuspension is more dependent on ambient conditions such as wet or dry weather, the presence of a protective vegetation cover and tunnel cleaning, than on fleet characteristics. Vehicle emissions could be estimated by

subtracting the resuspended component from the measured concentrations. The aerosol concentrations of metals such as Al or Mg were shown above to almost exclusively derive from resuspension. The resuspended component of any metal could then, in theory, be estimated using the measured concentration of, e.g., Al and the ratio of any metal to Al in the resuspended matter.

However, this correction for resuspended matter is based on two assumptions that are probably not met: the composition of the resuspended matter is known with high precision, and it is constant over time. Unknown and possibly large errors may thus be introduced by subtracting the resuspended component. A broad classification of metals that are predominated by resuspension or by vehicles may nevertheless be performed with Al or Mg as a tracer for resuspension. It shows that >70%, generally much more, of Cu, Cd, Ba, Sb, Pb and Zn are vehicle derived. Therefore, we chose not to correct concentrations of Cu, Cd, Ba, Sb, Pb and Zn for resuspension. Resulting vehicle emission factors may be slightly overestimated, in a few single cases by up to 30%. Emission factors are not presented for the other metals because resuspension is the underlying mechanism for the observed emissions.

Average metal emission factors for metals in the TSP fraction for the two tunnels are shown in Table 3. Data from the two tunnels are generally consistent, although the standard deviation for Ba is high; only Sb display a statistically significant ( $P < 0.05$ ,  $t$ -test) difference. These emission factors are considered fairly representative for urban driving but possibly too high for highway driving, as will be discussed later. The emission factors of TSP and PM<sub>10</sub> (Table 3) vary much more between the tunnels than do emission factors for these metals, re-emphasizing the importance of resuspension on TSP and PM<sub>10</sub> levels.

Table 3

Average emission factors for metals in the TSP fraction and for TSP, PM<sub>10</sub> and PM<sub>1</sub> ( $\mu\text{g vkm}^{-1}$ ). The metal emission factors essentially represent vehicle emissions whereas the particle emission factors mainly are due to resuspension. The error estimates are the standard deviations for all runs in each tunnel

	Tingstad	Lundby
Ba	136 ± 54.6	293 ± 153
Cd	0.289 ± 0.147	0.244 ± 0.045
Cu	172 ± 37	147 ± 32
Pb	36.9 ± 7.7	35.1 ± 13.6
Sb	31.8 ± 11.6	50.8 ± 14.2
W	—	44.2 ± 9.3
Zn	205 ± 87.5	239 ± 25
TSP	108 ± 58 × 10 <sup>3</sup>	518 ± 324 × 10 <sup>3</sup>
PM <sub>10</sub>	44 ± 33 × 10 <sup>3</sup>	285 ± 115 × 10 <sup>3</sup>
PM <sub>1</sub>	—	88.5 ± 34.4 × 10 <sup>3</sup>

#### 4.3. Experimental uncertainties

Before we discuss the variation in emission factors, their experimental uncertainty should be estimated. This was calculated from the relative standard deviations ( $\sigma_x/x$ ) for each parameter ( $x$ ) in Eq. (1) according to

$$\frac{\sigma_e}{e} = \sqrt{\sum \left(\frac{\sigma_x}{x}\right)^2}, \quad (2)$$

where  $\sigma_e$  is the standard deviation of the emission factor  $e$ . The values of  $\sigma_x/x$  were as follows: ±2% for particle sampling, tunnel length and number of vehicles; ±1% for the duration of each run; and ±5% for the emitted amount and the concentration of SF<sub>6</sub>. The relative standard deviation of the concentration gradient was calculated according to the propagation of error for a difference, with the analytical uncertainty of ±10%. This value will differ for each metal and for the different runs; values are presented in Table 4. The resulting experimental uncertainties of the emission factors are also shown in Table 4. For the Lundby tunnel, certain runs had high inlet concentrations of Pb and Zn, resulting in high experimental uncertainties.

The experimental uncertainties can be compared to the observed variation in emission factors between different runs (Table 3). The observed variation is generally within the experimental uncertainty, although real differences in the emissions cannot be excluded. Experimental uncertainty cannot explain the variation of Ba and Sb in either tunnel nor of Cd in the Tingstad tunnel. Real differences in emission factors between the runs could arise due to, e.g., differences in fleet composition or in driving pattern.

Table 4

Average relative standard deviation ( $\sigma_x/x$ ) for the concentration gradient of each metal, and total experimental uncertainty for the emission factors

Metal	Tingstad tunnel		Lundby tunnel	
	$\sigma_x/x$ conc. gradient (%)	$\sigma_e/e$ emission factor (%)	$\sigma_x/x$ conc. gradient (%)	$\sigma_e/e$ emission factor (%)
Ba	15	17	16	18
Cd	20	22	24	26
Cu	15	17	22	23
Pb	17	19	37	38
Sb	16	18	16	18
Zn	16	18	29	30
W	—	—	19	21

4.4. Dependence of emission factors on fleet composition

HDV are stronger emitters of fine particles and soot than LDV, in particular when emissions are expressed on a km-basis. The same ranking may apply for wear of brakes and tires and perhaps other pathways of large particle formation. Whether the emission factors were correlated with the HDV fraction in the tunnel was therefore investigated. Only data from the Lundby tunnel were used because the variation of HDV in the Tingstad tunnel was considered not large enough (Table 1). In addition, run number 2 was excluded because of possible underestimation of emissions due to particle aggregation under wet conditions (Table 1). It can be seen from Table 5 that Ba is significantly ( $P < 0.05$ ) and positively correlated to HDV, and Sb shows a fairly strong but not statistically significant correlation to HDV. In support for these correlations, both the average emission factors of Ba and Sb (Table 3) and the average HDV fraction (Table 1) are higher in the Lundby tunnel than in the Tingstad tunnel.

4.5. Origin of the metals

The emission factors obtained are the integrated result of several possible emission pathways from vehicles. Some clues to which pathways are important for different metals can be gained if the emission factors are compared to source specific values. A few such data sets exist, not obtained from on-road studies though. We have used data on exhaust emissions and on the wear of brakes. Speciated exhaust emission data have been obtained from dynamometer tests. Summer and winter driving was simulated for 5 cars produced during 1991–1996 (Cadle et al., 1999) and there are also data for high emitting vehicles (Cadle et al., 1997). Emissions from brake linings were estimated for the most common cars in Stockholm by investigating their brake lining composition and the mass lost at replacement (Westerlund, 2001). Many brake linings contain high metal

concentrations but there is also a large variation between different brands. The study cited here analysed a large share of the brakes in high-volume use in Stockholm.

The comparison indicates that combustion is an insignificant source of Ba, Cu, Pb and Sb, but that it may contribute to the emissions of Cd and Zn (Fig. 3). In agreement, the  $PM_{10}/TSP$  ratios of Ba, Cu, Pb and Sb were fairly low (7–17%; six samples), but slightly higher for Cd and Zn (23–35%).

When assessing the role of brake wear, it must be determined whether the driving conditions in the tunnels were representative for urban driving, which the brake wear estimates were based upon (Westerlund, 2001). Our observations of the brake lights in the tunnels

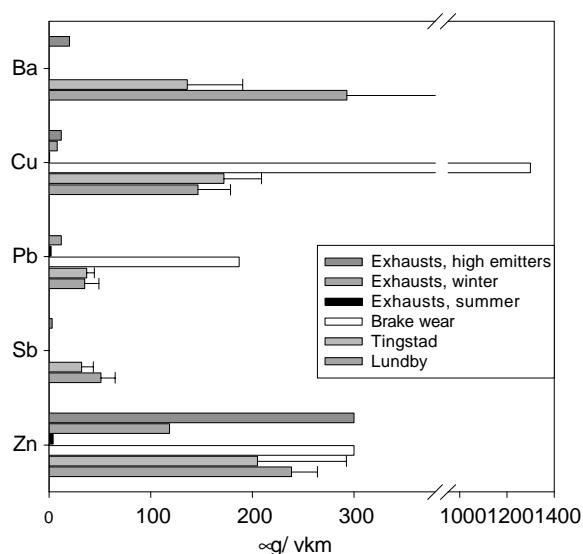


Fig. 3. Comparison of emission factors from the tunnels, from brake linings (Westerlund, 2001) and from exhaust measurements (Cadle et al., 1997, 1999). The bars appear in the same order as in the legend. Please note the broken scale.

Table 5

Correlation coefficients ( $R$ ) for emission factors and HDV in the Lundby tunnel. Run 2 was excluded because of possible artifacts during rain

	%HDV	TSP	$PM_{10}$	Ba	Cd	Cu	Pb	Sb	Zn
TSP	0.553								
$PM_{10}$	0.659	-0.067							
Ba	<b>0.983</b>	0.614	0.513						
Cd	0.700	-0.939	0.325	0.888					
Cu	-0.804	-0.834	-0.087	-0.891	-0.689				
Pb	-0.542	-0.999	0.062	-0.599	0.956	0.817			
Sb	0.927	0.650	0.341	<b>0.980</b>	<b>0.999</b>	-0.946	-0.630		
Zn	-0.210	-0.888	0.512	-0.336	0.589	0.716	0.883	-0.452	

Values in bold are statistically significant ( $P < 0.05$ ).

indicate that most vehicles did brake in the tunnels. In addition, several runs were performed in the rush hours, when start-stop driving was frequent. Brake frequency can be considered roughly related to traffic density if expressed as the number of vehicles per lane and time. The traffic density during our measurements amounted to 430–1100 vehicles (lane × h)<sup>-1</sup>. These are typical values for major roads in, e.g., central Stockholm. However, there are no traffic lights in the tunnels. Overall, we consider the frequency of braking in the tunnels to be somewhat lower than that of urban driving, but higher than in highway driving.

It is therefore surprising that the estimated brake wear emissions are 10 and 5 times higher than the measured emissions for Cu and Pb, respectively (Fig. 3). Experimental studies on brake wear show that all wear particles are not airborne (Garg et al., 2000a). The discrepancy between measured and calculated emissions may thus be due to accumulation of wear particles on the wheelrims or to formation of large, nonsuspendable particles. In roadside soils, Cu concentrations have been found to level off very sharply with distance from the road (Sutherland and Tolosa, 2001), also suggesting the presence of a coarse-grained Cu component. However, it should also be noted that the brake wear estimates lack uncertainty assessments.

Assuming that brake linings are the major source of Cu, one could expect emissions to increase during dense traffic when decelerations are more frequent. Except for one outlier in each tunnel fairly good correlations are obtained (Fig. 4). The two outliers actually represent the runs during wet conditions, and abraded brake particles are likely to stick more strongly to the wheelrims under wet conditions. We consider this correlation as a support for the hypothesis that brake linings are the source of Cu. The relationship is not statistically significant, but a dip in emissions at low vehicle densities would be expected rather than a perfectly linear relationship.

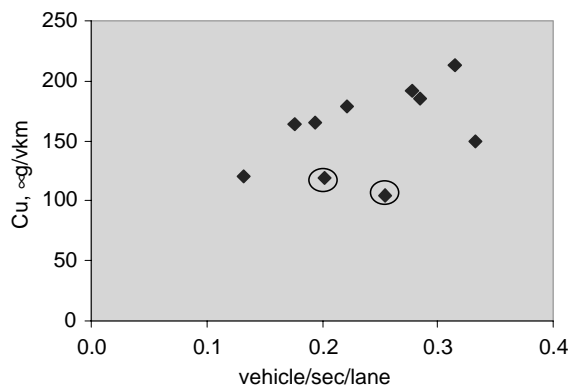


Fig. 4. Copper emission factors as a function of traffic density per lane. The circled values were obtained during rainy runs.

Several studies show that Sb concentrations are elevated close to major roads, both in soils and in air (e.g., Stechmann and Dannecker, 1990; Dietl et al., 1997; Cal-Prieto et al., 2001). A strong correlation between Cu and Sb has been observed both in tunnel aerosols and in urban aerosols (Stechmann and Dannecker, 1990; Pakkanen et al., 2001). Although Cu and Sb were not strongly correlated in our dataset, the average Cu:Sb emission factor ratio is 4.6:1, close to the value found in German tunnels (5.6:1; Stechmann and Dannecker, 1990). These facts indicate that brake linings also are the source of Sb. Actually, Sb<sub>2</sub>S<sub>3</sub> is used in many brake linings up to at least 5–7% by weight (e.g., Garg et al., 2000a, b). The fact that emission factors of Sb did not correlate with those of Cu (Table 5) would then seem unexpected, but may be due to the fact that Sb and Cu do not always go together in brake linings.

We propose that a Cu:Sb ratio of  $4.6 \pm 2.3$  is a diagnostic criteria for brake wear particles. Unpublished tunnel data show that this ratio is very similar also in PM<sub>10</sub> and PM<sub>2.5</sub>. This ratio is at least one order of magnitude lower than that in, e.g., average upper crust and most soils. Furthermore, we have data on metals in 20 flyash samples from waste incineration, showing a significantly lower Cu:Sb ratio ( $1.3 \pm 0.4$ ).

Road traffic emissions of Sb have also been explained by the use of certain organic Sb compounds in greases and motor oils (Huang et al., 1994; Cal-Prieto et al., 2001), but according to the Swedish National Chemicals Inspectorate those substances are not used in Sweden. Conclusively, we are confident that the emitted Sb mainly derives from brake linings. This emission may be of environmental significance because bioaccumulation of Sb close to roads has been observed (Dietl et al., 1997) and Sb(III) is a suspected carcinogenic (Gebel, 1997).

A correlation between Ba emissions and HDV was found in this study (Table 5). This agrees with previous studies where the correlation was explained by the use of BaSO<sub>4</sub> as a smoke depressant in diesel (Pierson and Brachaczek, 1983; Stechmann and Dannecker, 1990), but Ba is not used as a fuel additive in Sweden. BaSO<sub>4</sub> is a common filler in brake linings, occurring in concentrations up to 40% (e.g., Garg et al., 2000a, b), and we also found Ba to correlate significantly with Sb (Table 5), an element that we also attribute to brake wear. Our indications of HDV being stronger emitters of Ba than LDV (Table 5) may be due to larger wear at each braking for a HDV compared to a LDV. We found no correlation to HDV for Cu, which can be explained by data showing that Cu is much less abundant in brake linings from HDVs than from LDVs (Westerlund, 2001).

The emission factors of Zn agree fairly well with brake wear estimates (Westerlund, 2001; Fig. 3). In analogy with Cu and Pb, however, a lower contribution from brakes would be expected. Tires but also motor oils are

commonly considered as major sources of Zn from road traffic (Pierson and Brachaczek, 1983; Huang et al., 1994; Sörme et al., 2001). Calculations showing that tires are the major Zn source from road traffic (Sörme et al., 2001) have been based on a concentration of 1.6% Zn in tires and tire wear corresponding to ca. 150 mg vkm<sup>-1</sup>. This gives an emission factor of 2400 µg vkm<sup>-1</sup>, more than one order of magnitude higher than our total emission factor. This value lacks confidence limits and much lower values for tire wear can also be found in the literature. For instance, the USEPA PART5 model uses a value for PM<sub>10</sub> corresponding to 5 mg vkm<sup>-1</sup> for a four-wheel car. A slightly higher value would be expected for TSP, but still much lower than the value cited above. Tire wear would be expected to be higher when changing lanes and at curves as compared to straight driving. Lane changing is not permitted in Tingstad, which also is a straight tunnel compared to the slightly bent Lundby tunnel. Tire wear should thus be higher in the Lundby tunnel as compared to the Tingstad tunnel, but the observed Zn emissions are not significantly higher. In conclusion, this indicates that both brake linings and tires are likely to contribute significantly to the observed Zn emissions.

Certain studs that are used during the winter season in Sweden contain tungsten. Tungsten concentrations in excess of a resuspended fraction could be identified in Lundby but not in Tingstad, suggesting that the use of studded tires gives rise to W emissions. Our results do not support certain earlier studies stating that road traffic is an important source of Cr and the light REEs La, Cr and Pr (e.g., Sörme et al., 2001; Kitto et al., 1992).

## 5. Conclusions

Cu, Zn, Cd, Sb, Ba and Pb are emitted from road traffic in considerable quantities. Emission factors obtained from two different tunnels agree well for these metals. Brake wear is a major emission pathway for, at least, Cu, Sb and Ba. A Cu:Sb mass ratio of  $4.6 \pm 2.3$  is proposed as a diagnostic criteria for brake wear particles in ambient air. The ratio is at least one order of magnitude lower than that in natural particles. Except for Ba and possibly also Sb, a clear influence from HDV on the emission factors could not be elucidated.

The influence of resuspension has a major effect on the presence of many metals and larger particles in air close to roads. Disregarding this process in tunnel studies leads to considerably overestimated vehicle emissions of many metals and coarse particles. Resuspension is also important to consider when designing control measures for reducing levels of many metals and coarse particles in air.

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