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Journal of Cleaner Production 13 (2005) 19–31

Journal of Cleaner Production

www.elsevier.com/locate/jclepro

Antimony in brake pads-a carcinogenic component?

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Received 1 November 2002; accepted 24 October 2003

Abstract

Antimony trisulfide (Sb_2S_3) is used as a lubricant in friction material. X-ray diffraction analysis revealed Sb in 3/3 disc brake pads (range 41,000–46,000 mg/kg) and in 2/2 disc brake dust samples (21,000 and 17,000 mg/kg) from trucks. Considerably lower concentrations were found in drum brake pads (3/5, 59–6400 mg/kg) and in drum brake dust (4/18, 78–2800 mg/kg). Other toxic metals were also detected in pads and dust.

The health risk of Sb in particulate brake emissions should be dependent on particle size and chemical entity, in particular solubility. A significant amount of the emitted dust was shown by size-fractionated optical particle counting to be inhalable in environmental (>90% mass) and occupational (>50% mass) exposure situations. Differentiation via selective solubility showed a considerable amount of Sb_2S_3 to oxidize during the braking process, likely leading to the formation of Sb_2O_3, a suspected human carcinogen. Sb in brake dust was soluble in calf serum ($8.5 \pm 1.2\%$, 8.9 ± 1.7 mg/l at 37 °C for 3 d).

Hence, the use of Sb in friction material should be suspected to pose a human cancer risk and be deterred. To design healthy and environmentally sound alternatives, we propose to apply the Intelligent Product System that distinguishes products of consumption and products of service. Brake pads are true products of consumption, because they are released to biological cycles, and should thus consist of materials with positively defined health and environmental properties.

Keywords: Antimony; Brake pads; Inhalation; Carcinogenic potential; Intelligent Product System

1. Introduction

1.1. Antimony in brake pads

The Intelligent Product System (IPS) [1] has proved to be a successful concept for the development of healthy and environmentally sound products [2]. The IPS suggests to distinguish between products of consumption (e.g. shampoos), which have positively defined health and environmental properties and can thus enter safely into biological cycles, and products of service (e.g. TV sets), which are continuously reused in technical cycles and can thus be prevented from entering the environment. Products of service should be perceived as services by the customer rather than as objects for sale, and the manufacturer should maintain the ownership giving him an incentive to reuse the valuable material. The products of service concept can be expected to be increasingly used for cars. However, cars also contain some consumption parts that cannot be recycled, e.g. brake pads. These deserve special attention, because they are released to the environment as particulate matter, so that hazardous substances contained in them contaminate biological cycles.

A component in brake pads that seems especially problematic from a toxicological point of view is the heavy metal antimony (Sb), that is contained in a range of products, e.g. in drinking bottles made from polyethylene terephthalate (PET) [3]. Brake pads (synonym "brake linings") are polymer matrix composites consisting of fibers, fillers and modifiers (solid lubricants, elastomers), held together by a binder [4,5].

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doi:10.1016/j.jclepro.2003.10.008

Approximately 150 compounds are currently used in the production, and one pad usually consists of more than 10 compounds. Sb is used in the form of Sb_2S_3 that serves as a lubricant to reduce vibrations and to improve friction stability.

Sb has been found in passenger car brake linings [6] and increased concentrations of Sb in biota are associated with road traffic [7,8]. No studies of truck brakes are known to us, in spite of the fact that their higher particle emission factors compensate, in terms of environment relevance, for their lower frequency in road traffic. Brake pad manufactures are currently developing Sb-free brake linings that were first introduced to the market about 3 years ago, but the impact of this is yet unknown.

1.2. *Antimony toxicology*

Despite its widespread use, Sb has received little attention from toxicological and occupational health points of view [9–11]. Thus, the International Agency for Research on Cancer (IARC) considers Sb_2S_3 to be "not classifiable as to its carcinogenicity to humans (Group 3)" [12]. However, Sb_2O_3, Sb's most important oxide, is classified as "possibly carcinogenic to humans (Group 2B)". The toxicity of Sb compounds depends on their solubility and valence, with Sb(III) being more toxic than Sb(V) [10].

1.3. *Potential effects of exposure to antimony-containing brake dust*

Sb proves to be a chromosomal mutagen (but not a gene mutagen) [10,11]. Thus, a linear dose–response relation can be suspected. This makes carcinogenicity a more relevant end-point than other human health effects, because even very low doses might cause some cases of cancer in large populations. We therefore focus on inhalation exposure, which is the only path reported to cause cancer [12]. The possible effects of ingestion of Sb contained in biota are discussed elsewhere [7].

If inhalation exposure to Sb from brake dust is a health concern, then (1) Sb must still be present in brake pads and dust, (2) brake dust has to be inhalable and (3) Sb contained in brake dust has to be in a toxic form. The inhalability of particles, and deposition in different parts of the respiratory tract, is a function of their size. We count particles with a diameter <10 μm to be inhalable *per definitionem*. It has been shown that more than 90% (mass) of brake dust generated in dynamometer braking simulations is emitted as inhalable particles according to this definition [6], but the mass distribution of brake dust that mechanics in garages are exposed to is so far unknown.

To determine whether Sb contained in brake dust is in a toxic form, one must know the chemical entity, which can change due to chemical reactions of Sb_2S_3 in the braking process. Under experimental conditions, Sb_2S_3 oxidizes to Sb_2O_3 at 380 °C in air [13], a temperature that is easily reached in brakes. In the same type of experiment, Jang and Kim [5] show a series of thermal decomposition of Sb_2S_3 above 300 °C. In braking simulations, they note a change in the friction coefficient of Sb_2S_3-containing pads, which they attribute to the formation of Sb oxides at elevated temperature. However, to our knowledge, no one has proven the presence of Sb oxides in brake dust by means of chemical analysis.

When the chemical entity is unknown, it can still be stated that the toxicity of the Sb compounds in brake dust depends largely on their solubility in physiological fluid. There are no studies on the solubility in physiological fluid of Sb from brake dust or pure Sb compounds known to us. The best estimate for pure Sb_2O_3, and Sb contained in copper smelter dust, comes from a study by Leffler et al. [14] who find 4% (Sb) (4.5 g/l), and 4% (Sb) (0.14 g/l), respectively, to be soluble in 0.9% saline at 20 °C. Literature statements about the solubility of Sb_2S_3 and Sb_2O_3 in water are inconsistent, and range for both compounds from insoluble [15,16] to slightly soluble [16,17].

1.4. *Aims*

The aim of this study is to investigate the three prerequisites that have to be fulfilled if the use of Sb_2S_3 in brake pads poses a human cancer risk, i.e.

1. To investigate if Sb is still contained in brake pads and dust.
2. To determine if brake dust generated in environmental and occupational exposure situations is inhalable.
3. To find out if Sb contained in brake dust is in toxic form by determining (a) its chemical entity (Sb_2S_3 or Sb_2O_3) and (b) its solubility in physiological fluid.

If these prerequisites are fulfilled, Sb contained in brake dust is not necessarily proven to be a carcinogen, as only a large inhalative carcinogenicity study with animals could provide such evidence. But a positive result of the relatively easy and cheap experiments that we propose can at least provide an indication whether Sb in brake pads should be suspected to pose a cancer risk. From an IPS perspective, this suspicion would be sufficient to deter Sb as an ingredient in brake pads and to replace it with materials that are positively defined with respect to their health and environmental impact.

2. Materials and methods

2.1. Composition of brake pads and dust

Trucks are equipped with either drum or disc brakes, so both were included in our study. Drum brake dust from 15 different trucks and three trailers was sampled with a clean plastic spoon from newly opened drums at Swedish garages repairing brakes or replacing pads. In five cases, the pads had been changed and could be taken for analysis. Because disc brakes do not accumulate dust, we took disc brake dust from the exhaust air filters of brake dynamometers used for the testing of pads and discs at the R&D departments of two German truck brake manufacturers.

At brake manufacturer A, we could sample pure dust from the pocket filter (Wieninger W55-610 EU5, 4 × 592 × 592 × 625, Augsburg, Germany) of a Schenck dynamometer. This filter had been in place for 20 months (ca. 4900 h in operation). During this period, ca. 45 different brake pads and discs had been tested on the dynamometer, including the pad brands Jurid (Honeywell Bremsbelag, Glinde, Germany), Textar and Don (both TMD Friction, Leverkusen, Germany).

At brake manufacturer B, we sampled dust from the filter (Atex Feinfilter, filter class F6, Sprockhövel, Germany) of another Schenck dynamometer (Darmstadt, Germany) modernized by ABB (Mannheim, Germany). The dust was so firmly attached to the filter, that we took pieces of an exchanged filter instead of pure dust. The filter had been in place for 18 months. During this period, over 15 different disc/pad combinations had been tested on the dynamometer, including pads of the brands Jurid, Textar, Ferodo/Beral (Federal Mogul Friction Products, Southfield, MI, USA) and Pagid (Rütgers, Essen, Germany), paired with 19.5″ and 22.5″ discs and a 500 mm × 180 mm drum. (Because primarily disc brakes were tested on the dynamometer and the drum was very sparsely used, we counted this sample as disc brake dust.)

We took two of the disc brake pads used on the A dynamometer, Jurid 539-20 and Textar 4700, for analysis. Also, we obtained a Bendix disc brake pad (Honeywell Bremsbelag, Glinde, Germany) at a garage, where it had just been changed on an Iveco EuroCargo truck.

Samples of the eight pads were removed and ground with a 100 g hammer, coating the pad with 20 layers of paper to avoid direct contact. Then they were homogenized with an agate mill (Retsch RMO, 130 Watt, Haan, Germany). The B filter pieces were washed with water, which was sieved through a 63 μm sieve and then evaporated. After this treatment, a few small filter fibers could still be seen in the dust.

The composition of all samples was determined with energy-dispersive X-ray fluorescence analysis (XRF; Spectro XEPOS, Kleve, Germany) of tablets pressed from ca. 4 g dust/ground pad and ca. 1 g micro-wax (Wachs C, Spectro Art. No. 80-004005, Höchst, Frankfurt, Germany) with a manual 15 t oil pressure press (Graseby Specac, Kent, UK). The detection limits are displayed in Tables 1 and 2. Duplicate analysis of two tablets of each of the four sample types (disc brake dust and pads, drum brake dust and pads) revealed a generally good precision (<10% difference), but with some outliers probably due to heterogeneity in the samples, and a lower precision near the detection limits. Analysis of 0.2 g of seven brake dust samples with inductively coupled plasma atomic emission spectrometry with axial dual view (ICP-AES; Perkin Elmer 3300 DV, Überlingen, Germany) according to the water and sludge analysis standard EN ISO 11885:1997, after micro-wave dissolution in 4 ml HNO_3, 1 ml HCl and 0.5 ml H_2O_2, revealed a varying accuracy for different elements (Tables 1 and 2).

The concentrations of O and C, which remain undetected by XRF und ICP-AES, were estimated by semi-quantitative energy-dispersive X-ray microanalysis (EDX; Röntec M series, Berlin, Germany) of two different areas (100–500× magnification) of 10 drum brake dust samples under a scanning electron microscope (SEM; Zeiss Digital Scanning Microscope LEO982, Oberkochen, Germany).

2.2. Particle inhalability and morphology

The particle size distributions of the emissions from a truck brake operated with a 19.5″ disc (Fritz Winter Gießerei, Stadtallendorf, Germany) and Jurid 539-20 pads were counted during braking simulations on the B dynamometer. Each count lasted for 120 s (sample volume = 5.66 l of air). Throughout the count, the brake disc was rotating at a constant speed, corresponding to 85 km/h velocity of a truck. In the beginning, it was continuously braked with a momentum of 2400 Nm, and after 40 s the brake was released. This is a common brake test, that simulates a truck on a downhill slope, where the driver brakes to maintain a constant speed. The temperature, measured by a thermoelement soldered into the brake disc, was cooled to 50 °C at the beginning of every count, and rose to an approximate $T_{\max} = 450\ ^\circ C$. During the experiments, the whole set-up was covered with a sliding roof and the ventilation was turned off. Particle counts in the fractions 0.3–0.5, 0.5–1, 1–5, 5–10 and 10–25 μm were made with an optical particle counter (OPC; Climet Innovation CI-500A-12, Redlands, CA, USA) placed 25 cm diagonally under, or 65 cm above, the brake disc. At both positions, background counts were made under the same conditions, but with the brake disc at rest and the pads released.

The particle size distributions of the emissions from a truck brake operated with a 22.5″ disc and Jurid 539-20, Textar T3020 and Don 7400 brake pads were counted during braking simulations on the A dynamometer. Again, a count lasted for 120 s. At the beginning of each count, the brake disc was accelerated from 0 to a speed corresponding to 60 km/h in 16 s, then braked to 0 in 8 s with a brake cylinder pressure of 2 bar and a 20% deceleration (0.2 g, earth's acceleration of gravity), and then again accelerated after a 2 s pause. This procedure was repeated three times. The program simulates typical city traffic. The start temperature rose from count to count. Counts were made with start temperatures from 35 °C ($T_{\max} = 180$ °C) to 420 °C ($T_{\max} = 500$ °C). Temperature measurement, covering and ventilation were treated as described above. Particle counts (including background) were made with the OPC placed 25 cm diagonally under the brake disc.

Interviews with truck mechanics revealed that they are exposed to the highest brake dust concentrations when cleaning brake saddles with a steel brush after removing the pads. Three saddles (Volvo original) from the drum brakes of a Volvo FL6 truck were brushed for 120 s with a steel brush and, during this time, particles were counted, with the OPC 40 cm beside the saddle, a typical occupational exposure distance. As particles in the 0.3–0.5 and 0.5–1 μm fractions could not be counted, due to the high particle load at this distance, counts were also made at 200 cm. These counts were started 60 s after the end of the brushing, because we noticed that particle counts were higher at this time, when compared to counts during brushing. Background counts were made without brushing.

From the particle number distributions obtained in the particle counts, mass distributions were calculated according to the formula $m = \rho\pi \times 6d^3$, assuming spherical particles. The density ρ was obtained by weighing and measuring the size of a tablet pressed from the A dust sample combined with micro-wax of known density. The log-means of the interval of upper and lower limits were used as particle diameters d for each size fraction, because the particle number concentrations were assumed to be log-normally distributed.

The calculated mass in all intervals, except 10–25 μm, was summed up to a calculated PM10 concentration. The PM10 concentration is normally defined as the mass concentration of airborne particulate matter with an aerodynamic diameter <10 μm, but we neglected particles <0.3 μm and used the geometric instead of the aerodynamic diameter.

Magnified pictures of brake dust were made with the SEM. Special attention was given to fibers (defined as particles with a length/width ratio >5) in the micrometer range to check that no prohibited asbestos was contained in the dust.

2.3. Chemical entity and solubility of antimony contained in brake dust

(a) Chemical entity. The most elegant method to determine the chemical entity of Sb contained in brake dust would be X-ray diffraction (XRD). However, XRD analysis (Seifert XRD 3003 TT, Ahrensburg, Germany) of the A dust sample (containing 2.1% Sb according to the XRF measurements) showed no Sb compounds. (Because it is well known that XRD fails to detect a compound if it is not crystalline or if it is "hidden" in the noise of other compounds of higher concentration, we see no reason to distrust our XRF and ICP-AES measurements, which found Sb in the sample.)

As a less exact method, we differentiated Sb_2S_3 and Sb_2O_3 with tartaric acid, which is cited in the literature to be a poor solvent for Sb_2S_3, but a good one for Sb_2O_3 [18]. To verify this, and to check what other Sb compounds dissolve in tartaric acid, ca. 2 mg (measured as Sb) of Sb_2S_3, Sb_2O_3, $Sb_2(SO_4)_3$, $SbCl_3$ and SbF_3 were boiled for 15 min in 20 ml 10% tartaric acid solution, and left at 16 °C for 2 weeks. Thereafter, the solutions were filtered through a 0.45 μm membrane filter (Eijkelkamp, Art. No. 12.30.01, Giesbeek, The Netherlands) and the Sb concentrations were determined by ICP-AES, according to EN ISO 11885:1997.

Approximately 2 mg (Sb) of three dust samples (2.1%, 0.28% and 0.17% Sb) were treated in the same way. To see if oxidation occurs, ca. 2 mg (Sb) of Sb_2S_3 were kept in an oven at 400 °C for 30 min, and were then also treated in the same way.

(b) Solubility. To find out whether Sb from brake dust is soluble in physiological fluid, ca. 0.5 mg (Sb) of the A dust sample was mixed with 5 ml calf serum (fetal bovine serum, Cat. No. 10106-151, Lot. No. 40F8104F, Life Technologies/Gibco BRL, Carlsbad, CA, USA) and left at 37 °C for 3 days. It was then filtered and analyzed like the solutions above. The same was done with water as control.

3. Results

3.1. Composition of brake pads and dust

We found more than 4% Sb in all three disc brake pads (Table 1). In the A and B dynamometer dust samples, we found 2.1% and 1.7% Sb. Three out of five drum brake pads contained Sb (max 0.64%) and four out of 18 drum brake dust samples (max 0.28%). Apart from Sb, the toxic metals Pb, Cd (only in disc brake samples), Hg, As, Ni, Cr, Mn, Al, Sr, Sn and the ecotoxic Cu were found in both pads and dust.

Of the other analyzed elements, Fe, Si, Ca, Ba, Mg, S, Zn, Cl, K and Ti were found in almost all samples,

Table 1
Concentration of toxic metals in brake pads and dust, determined with energy-dispersive X-ray fluorescence analysis (XRF)

Type of brake	Type of sample	Brake pads	Element concentration (mg/kg)											
			Sb	Pb	Cd	Hg	As	Ni	Cr	Mn	Al	Sr	Sn	Cu
		Detection limit	50[a]	2	2[a]	2	5	1	5	10	1000	1	30[a]	1
		Accuracy[b]	[c]	–	?	n.a.	0	++	––	++	+	+	?	++
Disc	Dust	[A air filter]	21,000	260	8	40	24	400	12,000	2500	17,000	150	2600	61,000
		[B air filter][d]	17,000	250	11	20	53	310	6900	2300	20,000	46	230	27,000
	Pads	(Jurid 539-20)	46,000	350	71	3	83	230	26,000	1100	71,000	67	–	18,000
		(Textar 4700)	41,000	670	55	–	51	180	–	2900	6500	790	850	14,000
		Iveco EuroCargo (Bendix)	41,000	500	45	16	140	150	–	2500	2800	1100	220	27,000
Drum	Dust	BPW trailer	–	91	–	13	29	220	–	2000	16,000	410	–	1500
		BPW trailer	–	14	–	31	27	230	670	1800	12,000	210	–	390
		SAF trailer	–	170	–	20	54	200	1300	1700	16,000	130	35	5500
		Volvo FH12	–	32	–	8	45	210	420	2600	8500	240	–	820
		Volvo FH12	–	110	–	9	42	160	150	2400	10,000	430	–	6700
		Volvo FH12	–	38	–	37	26	190	820	2000	9100	110	–	580
		(1) *Volvo FH12*	*78*	*81*	–	*25*	*36*	*190*	*1000*	*1700*	*24,000*	*140*	–	*520*
		Volvo FL6	–	170	–	15	87	460	1400	2500	28,000	88	150	5400
		Volvo FL7	–	190	–	16	40	220	400	2700	12,000	210	–	8100
		(2). *Volvo FL10*	–	*87*	–	*32*	*15*	*950*	*890*	*1900*	*11,000*	*130*	–	*530*
		Scania 143	–	150	–	24	–	200	1100	3300	8200	120	–	920
		(3) *Scania R143*	–	*220*	–	*15*	*69*	*290*	*1000*	*2200*	*9000*	*130*	*34*	*1900*
		Scania 143 (Sv. Bromsbf.[e])	–	85	–	28	59	410	970	3800	4300	130	–	700
		Scania 143 (ROR original)	–	110	–	13	41	270	460	2100	21,000	550	–	980
		(4) *Mercedes 18.24 (Beral)*	–	*9*	–	*22*	*43*	*240*	*350*	*2000*	*6100*	*430*	*47*	*680*
		(5) *Mercedes 18.24 (Jurid 505)*	*2800*	*82*	–	*14*	*150*	*530*	*8300*	*3100*	*15,000*	*58*	*72*	*2100*
		Mercedes 11.17 (Textar)	190	61	–	30	56	280	460	1900	9300	490	–	1200
		MAN 930 (Jurid 505)	1700	52	–	19	12	450	5200	2700	13,000	40	–	700
		Mean	270	97	–	21	46	320	1400	2400	13,000	230	19	2200
	Pads	(1) Volvo FH12	59	36	–	4	–	64	290	410	34,000	340	–	49
		(2) Volvo FL10	93	37	–	11	–	110	370	740	13,000	160	–	120
		(3) Scania R143	–	180	–	9	9	120	180	1900	14,000	390	–	210
		(4) Mercedes 18.24 (Beral)	–	5	–	11	32	110	–	2900	3700	1400	–	300
		(5) Mercedes 18.24 (Jurid 505)	6400	48	–	7	18	130	36,000	990	67,000	77	–	76
		Mean	1300	61	–	8	12	110	7400	1400	26,000	470	–	150

Italicized drum brake dust samples (1–5) stem from brakes operated with pad of corresponding number. Higher concentrations in the dust than in the pad indicate a contribution from the disc/drum. All brake pads are original truck manufacturer equipment, but they are not produced by the truck manufacturers. Means include samples with concentrations under detection limit, counted as 0.

[a] Detection limit adjusted, because comparison with ICP-AES revealed that XRF failed to detect concentrations above its nominal detection limit.

[b] Signs in this row indicate analytical accuracy based on the ratios of the concentrations measured with ICP-AES/concentrations measured with XRF, in seven brake dust samples: ++, all seven ratios within the range 3/4–4/3; +, all ratios within the range 3/4 × mean to 4/3 × mean and mean < 0.8, probably because of incomplete dissolution prior to ICP-AES; 0, some concentrations found by XRF are undetected by ICP-AES, probably because of very incomplete dissolution prior to ICP-AES; –, all ratios within the range 0.5 × mean to 2 × mean; ––, ratios outside the range 0.5 × mean to 2 × mean; ?, too few data; n.a., not analyzed by ICP-AES.

[c] The analytical accuracy for Sb cannot be determined with certainty, because only one of the seven samples also analyzed with ICP-AES contained >50 mg (Sb)/kg. After decomposition with 4 ml HNO_3, 1 ml HCl and 0.5 ml H_2O_2 ($4 + 1 + 0.5$), ICP-AES found only 290 mg/kg in the A sample. However, after decomposition with $3 + 3 + 0.5$, $1 + 5 + 0.5$ or $0 + 6 + 0.5$, ICP-AES found 16,000 mg/kg, ca. 3/4 of the XRF value, suggesting a good accuracy and likely an incomplete decomposition prior to ICP-AES.

[d] Sample contaminated with filter fibers.

[e] Svenska Bromsbandsfabriken.

Table 2
Mean concentration of elements in brake pads and dust, determined with energy-dispersive X-ray fluorescence analysis (XRF) or inductively coupled plasma atomic emission spectrometry (ICP-AES; only Ir)

Type of brake	Type of sample	Brake pads	Element concentration (mg/kg)													Explained (%)
		Detection	Fe	Si	Ca	Ba	Mg	S	Zn	Cl	K	Ti	Zr	Mo	Ir	
		limit	15	100	100	20	500	30	1	1	100	2	50	50[a]	80	
		Accuracy[b]	+	0	+	–	––	––	++	n.a.	–	0	––	–		
Disc	Dust	[A air filter]	400,000	22,000	26,000	9400	8200	12,000	22,000	1000	1300	880	3700	4500	21,000	63
		[B air filter][c]	450,000	72,000	4400	4700	4600	5200	8100	400	2800	380	660	730	n.a.	63
	Pads	Mean ($n = 3$)	200,000	14,000	6600	28,000	15,000	21,000	20,000	3800	2100	2400	4000	680	n.a.	42
		1.96 standard deviations	130,000	18,000	13,000	47,000	52,000	36,000	50,000	9400	4400	2300	6400	2100		8
Drum	Dust	Mean ($n = 18$)	390,000	55,000	27,000	9600	5300	4200	3400	5900	4100	900	1100	150	600	53
		1.96 standard deviations	150,000	38,000	44,000	21,000	9600	5300	8600	10,000	3300	790	4000	390	1300	8
	Pads	Mean ($n = 5$)	160,000	61,000	41,000	13,000	24,000	9400	8100	2100	7400	1700	310	–	n.a.	37
		1.96 standard deviations	180,000	50,000	66,000	25,000	27,000	17,000	15,000	4100	6300	2000	690			11

Means include samples with concentrations under detection limit, counted as 0. The last column shows the percentage of sample mass accounted for by all elements we analyzed with XRF.

[a] Detection limit adjusted, because comparison with inductively coupled plasma atomic emission spectrometry (ICP-AES) revealed that XRF failed to detect concentrations above its nominal detection limit.

[b] Signs in this row indicate analytical accuracy based on the ratios of the concentrations measured with ICP-AES/concentrations measured that XRF, in seven brake dust samples: ++, all seven ratios within the range 3/4–4/3; +, all ratios within the range 3/4 × mean to 4/3 × mean and mean < 0.8, probably because of incomplete dissolution prior to ICP-AES; 0, some concentrations found by XRF are undetected by ICP-AES, probably because of very incomplete dissolution prior to ICP-AES; –, all ratios within the range 0.5 × mean to 2 × mean; ––, ratios outside the range 0.5 × mean to 2 × mean; ?, too few data; n.a., not analyzed by ICP-AES.

[c] sample contaminated with filter fibers.

and Zr and Mo were found frequently (Table 2). Ir was detected in all seven samples, in which it was analyzed. The composition of the samples varied considerably. The elements we analyzed with XRF accounted for 63% of the mass of the dynamometer dust, 42 ± 8% (mean± 95% confidence interval, $n=3$) of the mass of the disc brake pads, 53 ± 8% ($n=18$) of the mass of the drum brake dust and 37 ± 11% ($n=5$) of the mass of the drum brake pads.

3.2. Particle inhalability and morphology

In the braking simulations with constant velocity, the particle number concentrations exhibited a skew distribution, with a maximum in the 0.5–1 μm fraction (data not shown). The calculated mass concentrations were log-normally distributed, with a maximum in the 1–5 μm fraction for both the counts under and above the brake disc. Based on the shape of the mass distribution curves, we estimated that >90% (mass) of the dust was inhalable (PM10).

In the stopping simulations, again the particle number concentrations exhibited a skew distribution, with a maximum in the 0.5–1 μm fraction, and the calculated mass concentrations were log-normally distributed, with a maximum in the 1–5 μm fraction for counts with $T_{max} < 450\ ^{\circ}C$, while both distributions exhibited a sharp increase in the 0.3–0.5 μm fraction for counts with $T_{max} > 450\ ^{\circ}C$ (Fig. 1). This pattern was confirmed in eight more $T_{max} < 450\ ^{\circ}C$, and three more $T_{max} > 450\ ^{\circ}C$ counts with the Jurid, Textar and Don pads (data not shown). The brakes began to smoke lightly during braking with $T_{max} = 420\ ^{\circ}C$ and the smoke became increasingly more dense at braking with higher T_{max}. Again, we estimated >90% (mass) to be inhalable.

For the particle number concentrations counted during the brushing of brake saddles, no maximum could be determined (Fig. 2). The mass concentrations at both distances had a maximum in the 5–10 μm fraction. Possibly due to very high particle load, all counts in the 0.3–0.5 μm fraction, and the 40 cm counts in the 0.5–1 μm fraction, were below background, so they were excluded. Based on the shape of the mass distribution curves, we estimated that >50% (mass) of the dust was inhalable.

The calculated PM10 concentrations are highly uncertain as total values, because of the assumptions needed for the calculation of the particle mass from the size, but it is valid to relate them to each other. A comparison shows that the stopping simulations produced the lowest PM10 concentrations at 25 cm distance, while the constant velocity braking simulations produced a higher, and the saddle brushing experiment (at 40 cm) an even higher PM10 concentration (Table 3). The variation was high in the stopping simulations, because those counts were conducted over a range of temperatures. In the constant velocity braking simulations, the PM10 concentrations were higher 65 cm above the brake disc than 25 cm diagonally under the brake disc.

The SEM pictures showed particles in the nanometer and micrometer range. Most frequent were semi-spherical agglomerates (Fig. 3a–c). Non-agglomerated particles of flat (d) and semi-spherical (e) shapes were also found. Few particles showed a noticeable layer structure (f). No fibers could be detected.

3.3. Chemical entity and solubility of antimony contained in brake dust

(a) Chemical entity. Tartaric acid was a poor solvent for Sb_2S_3 and a good one for Sb_2O_3 (Table 4).

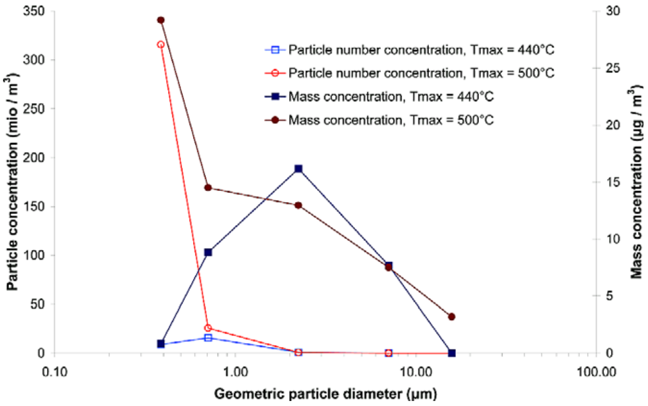

Fig. 1. Particle number and mass distributions of brake dust emitted from stopping three times from 60 km/h with Jurid 539-20 pads on a 22.5″ disc with a deceleration of 20%, counted 25 cm diagonally under the disc at different temperatures, $n=1$.

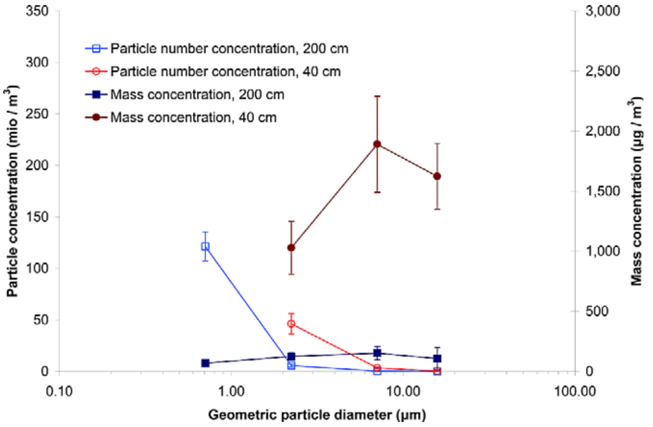

Fig. 2. Particle number and mass distributions of brake dust emitted during the brushing of three Volvo brake saddles, counted at 40 and 200 cm distance. Note that no data are shown for the 0.3–0.5 μm fraction. Bars represent 95% confidence intervals, $n=3$.

Table 3
Calculated PM10 concentrations from two different braking simulations and brushing of brake saddles (mean ± 95% confidence interval, *n*= 3)

Simulation	Brake pad/saddle	Position of OPC[a]	Calculated PM10 ($\mu g/m^3$)
Stopping from 60 km/h	Jurid 539-20	25 cm under brake disc	150 ± 150
	Textar T3020	25 cm under brake disc	150 ± 150
	Don 7400	25 cm under brake disc	200 ± 300
Braking at constant 85 km/h	Jurid 539-20	25 cm under brake disc	3300 ± 400
		65 cm above brake disc	4600 ± 1200
Brushing of brake saddle	Volvo FL6 original saddle	40 cm beside saddle	14, 000 ± 2700
		200 cm beside saddle	1300 ± 350

[a] OPC, optical particle counter.

However, it was a good solvent for the other tested Sb compounds as well. For heated Sb_2S_3 and all three brake dust samples, the solubility of Sb in tartaric acid was higher than for Sb_2S_3 and lower than for Sb_2O_3.

(b) Solubility. From the Sb contained in the A dust sample, 8.5± 1.2% (8.9 ± 1.7 mg/l) dissolved in calf serum and 1.1± 0.3% (1.1 ± 0.3 mg/l) in water (mean ± 95% confidence interval, *n*= 3).

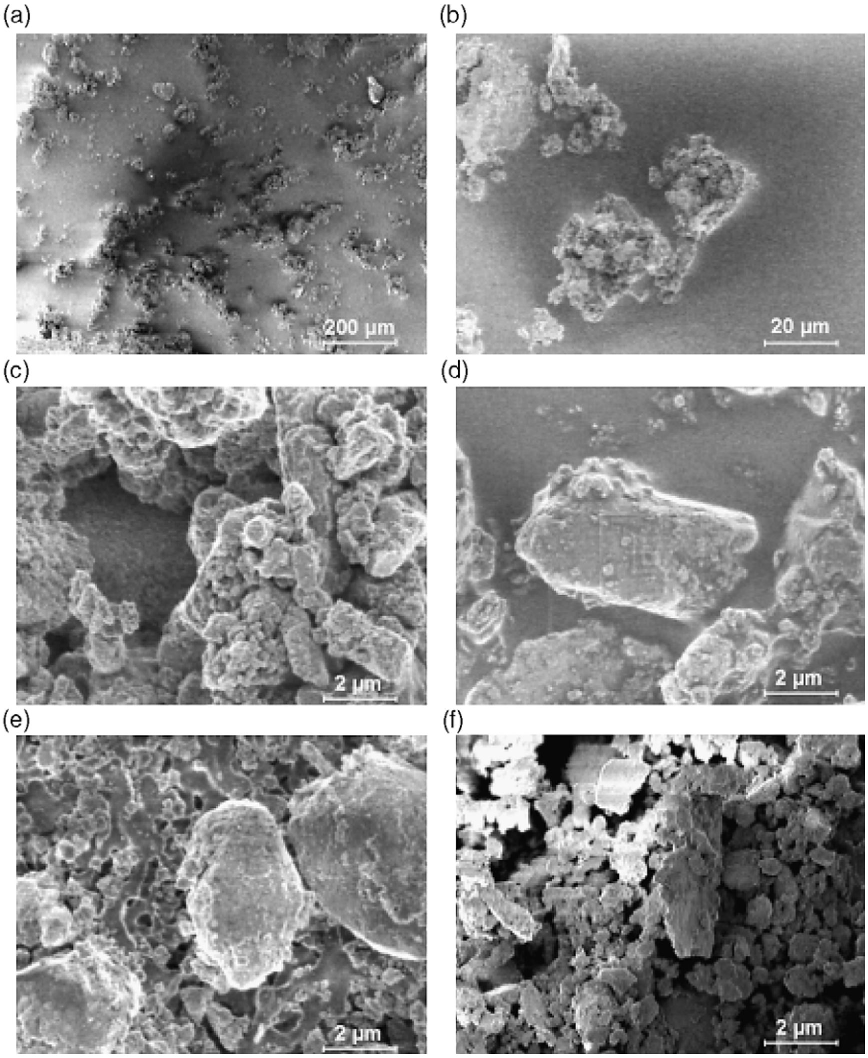

Fig. 3. Scanning electron microscopy pictures of brake dust. (a) 100× microscope magnification of typical semi-spherical agglomerates; (b) 1000× magnification of the same sample; (c) 10,000× magnification of the same sample; (d) 10,000× magnification of non-agglomerated flat particles from other sample (rectangles on particle originate from microscope electron beam); (e) 10,000× magnification of non-agglomerated semi-spherical particles attached on a cellulose acetate filter (seen in the background); (f) 10,000× magnification on layer structures in still another sample.

Table 4
Antimony dissolved in 10% tartaric acid solution after boiling for 15 min

Sample	Dissolved (%)
Antimony trisulfide [Sb_2S_3]	10
Antimony trioxide [Sb_2O_3]	100[a]
Antimony trisulfate [$Sb_2(SO_4)_3$]	88
Antimony trichloride [$SbCl_3$]	82
Antimony trifluoride [SbF_3]	90
Heated antimony trisulfide (30 min at 400 °C)	34
Brake dust	
A dynamometer (2.1% Sb)	70 ± 13
Beral pad on MB 18-24 (0.28% Sb)	31
Jurid 505 on MAN 930 (0.17% Sb)	43

Chemicals and dust were added to 20 ml solutions in quantities corresponding to ca. 2 mg Sb. $n = 1$, except A dynamometer dust: $n = 3$, mean ± 95% confidence interval.

[a] Measured: 110.aMeasured: 110.aMeasured: 110.aMeasured: 110.

4. Discussion

4.1. Main results

1. Sb was present in brake pads and dust (with higher concentrations being found in disc than in drum brake pads and dust).
2. A significant amount of brake dust was inhalable in environmental and occupational exposure situations.
3. (a) Sb in brake dust exhibited a better solubility in tartaric acid than Sb_2S_3, suggesting an oxidation to Sb_2O_3 in the braking process. However, it could not be determined with certainty, what Sb compounds were present in the dust. (b) Sb from brake dust was soluble in physiological fluid in significant amounts.

In addition to these findings, other toxic metals were detected in pads and dust, but no asbestos fibers were found in dust.

4.2. Methodological concerns

1. The duplicate XRF analysis of tablets showed, with some exceptions, a good precision, suggesting a mostly homogeneous composition of the brake dust. The ratios of the ICP-AES and XRF values showed a varying accuracy for different elements (Tables 1 and 2). For some elements (including Sb and other heavy metals), the lower concentrations found by ICP-AES were probably due to incomplete dissolution, i.e. the XRF values can be assumed to be closer to the true concentration. The reason for the high variations in the ratios of other elements (especially alkali and alkaline earth metals and non-metals) could partly be, that they occur as different chemical entities, with very different solubility. Also, the XRF method we used was programmed for the detection of heavy metals in sediments, sludge and soil, so it may have exhibited a poorer accuracy for lighter metals. Differences between ICP-AES and XRD values are normal for matrices with difficult dissolution. The accuracies for Sb and other toxic metals are sufficient to support our main results.

The B sample was contaminated with filter fibers of unknown composition, but at least heavy metal concentrations were probably not affected considerably.

EDX found 25–50% of O plus C and XRF found 37% of other elements in drum brake dust samples (no other samples analyzed by EDX), so that most of the mass was accounted for. We assume this to be true for the other samples as well.

2. The OPC was calibrated for spherical particles (oil droplets), so there was a risk that it assigned the non-spherical brake dust particles to wrong fractions. This introduced an uncertainty in the particle number and mass distributions and the calculated PM10 concentrations. However, even if the OPC generally underestimated the particle size by as much as 50%, the inhalable amount would still be considerable. The calculated PM10 concentrations had other uncertainties as well, and should be seen with great skepticism (see above).

The particle counts at the two brake dynamometers were made at a distance (25 cm), which was not representative, as environmental exposure can be assumed to take place at distances from ca. 2 m to several kilometers. However, a comparison of the counts 25 cm under and 65 cm above the brake disc showed that (i) the mass and particle number distributions had the same maxima and similar shapes, indicating that this would be similar even at 2 m distance, and (ii) the PM10 concentration was higher above than under the brake disc, indicating that the particles were elevated by the rising warm air and would become airborne rather than directly deposited. The smallest particles, which are most relevant from a toxicological point of view, can be airborne for the longest time and may accordingly be transported a long way.

The distances used in the occupational exposure experiments (40 and 200 cm) were representative of the exposure. The failure of particle counts in the 0.3–0.5 and 0.5–1 μm fractions decreased the validity of the size distributions displayed in Fig. 2. However, by extrapolation of the mass distribution curve, we estimated the error introduced in the calculated PM10 concentration to be less than 15%.

We slightly overestimated the inhalability of the particles, because we used the geometric instead of the aerodynamic particle diameter and their density ρ was about 3 g/cm^3. However, the findings that >90% or >50% (mass) were inhalable, are still true.

3. a) The tartaric acid solubility experiment was not an exact method to investigate the possible oxidation of Sb_2S_3 to Sb_2O_3, as the solubility change could be due to the formation of other compounds. $SbCl_3$ and SbF_3 cannot account for much of the solubility change, because the A dust amounts added to the solutions contained 17 μmol Sb and only 3 μmol Cl, and the literature gives no reason to assume that other halogens are contained in brake dust in significant amounts. However, the formation of intermediate Sb–S–O compounds, like $Sb_2(SO_4)_3$ or kermesite (Sb_2OS_2), could also be the reason for the solubility change. This is the most serious uncertainty in our results.

3. b) We can be sure that the Sb we measured in calf serum really was dissolved and not suspended as particles that had passed through the filter, because if that had been the case, we would have found a similar percentage of other metals from the brake dust in the serum. However, only <0.5% of several metals were found.

Calf serum has a different protein composition than extra cellular fluid in the lung. Hence, if the concentration of albumin controls the solubility of Sb, we may have overestimated the in vivo solubility, because the albumin concentration is lower in extra cellular fluid than in serum. However, the purpose of this experiment was to show semi-quantitatively that the solubility in physiological fluid of Sb from brake dust is significant, which would be true even if the solubility was somewhat lower.

4.3. Comparison with other studies

1. The Sb concentrations we found in truck disc brake pads were in approximate accordance with previous studies on passenger car disc brake pads (Table 5). Sb concentrations in truck drum brake pads were two orders of magnitude lower than in truck and passenger car disc brake pads. The reason may be that drum brake pads have a larger area than disc brake pads, so the friction per area is smaller and they do not need as much lubrication.

Garg et al. find 6.1% Sb in dust generated from one out of six passenger car and pickup disc brake pads, but no Sb in dust from the remaining five linings (detection limit not indicated) [4]. Thus, the mean Sb concentration is of the same order of magnitude as what we found in disc brake dust.

However, for some other metals, we measured concentrations considerably different from previous studies (Table 5). The lower Pb and Cu and the higher Cr concentrations as compared to Westerlund and Rauterberg-Wulff are likely explained by different formulas for passenger car and truck brake pads. Also, there is obviously a differences between formulas for disc and drum brakes regarding Pb, Cd, Cu and Zn.

Table 5
Comparison with concentrations of toxic metals in brake pads in other studies [6,19,20]

	Element concentration (mg/kg)				
	Ökotest[a] (2001)	Rauterberg-Wulff (1996)	Westerlund (1998)	Present study (2001)	
	29 disc brake pads mean (max)	18 disc brake pads mean (max)	48 unspecified brake pads mean (max)	3 disc brake pads mean (max)	5 drum brake pads mean (max)
Sb	44,000 (120,000)	23,000 (52,000)		43,000 (46,000)	1300 (6400)
Pb	8300 (42,000)		14,000 (57,000)	510 (670)	61 (180)
Cd			10 (24)	57 (71)	– (–)
Ni			110 (380)	190 (230)	110 (130)
Cr			110 (310)	8700 (26,000)	7400 (36,000)
Cu	>100,000 (?)	130,000 (250,000)	110,000 (230,000)	20,000 (27,000)	150 (300)
Zn		16,000 (69,000)	20,000 (110,000)	20,000 (49,000)	8100 (18,000)

Indicated is the year of the analysis, which in all cases is earlier than the year of publication. Pads in the present study stem from trucks, and pads in all other studies from passenger cars. Means include samples with concentrations under detection limit, counted as 0. Blank field indicates not analyzed.

2. The shapes we found for particle number and mass distributions from braking simulations with $T_{max} < 450\ ^{\circ}C$ were congruent with those found by Rauterberg-Wulff [6]. No previous studies of occupational exposure to brake dust could be found. Our finding of a dramatic increase of particles $<1\ \mu m$ at $T_{max} > 450\ ^{\circ}C$ confirmed the data of Garg et al. [4], who determine brake wear to increase with temperature, but do not distinguish particle fractions. Because it correlated with the formation of smoke from the pads, we attributed the rise of emissions in fractions $<1\ \mu m$ to thermal wear of the carbonaceous components of the pad.

3. a) Our finding that Sb_2O_3 was probably formed in the braking process was in accordance with the studies cited in Section 1 [5,13].

3. b) The literature considers Sb_2S_3 and Sb_2O_3 to be insoluble [15,16] or slightly soluble [16,17] in water, which may explain why only 1.1% Sb from the A dust sample dissolved in water. The fact that we found 8.5% Sb to be soluble in calf serum is probably due to the fact that proteins, like albumin, can bind Sb and shift the equilibrium.

4.4. Conclusion

The use of Sb_2S_3 in brake pads should be suspected to pose a human cancer risk, because (1) considerable Sb concentrations are found in brake pads and dust, (2) a significant amount of brake dust is inhalable and (3) Sb in brake dust is probably partly present as Sb_2O_3 and is soluble in physiological fluid.

The uncertainty about what exact Sb compounds are present in the brake dust does not hamper this conclusion, because:

- The toxicity of the toxicologically not classified Sb–O–S intermediates should be suspected to resemble the toxicity of Sb_2O_3, the more oxygen they contain and the more similar their chemical structure is. Also, they may finally be oxidized to Sb_2O_3 in the environment.
- Calabrese and Kenyon [21], in contradiction to the IARC [12], propose to treat both Sb_2O_3 and Sb_2S_3 as potential human carcinogens, based on an inhalation study in rats [22].
- Whatever different Sb compounds may be present in brake dust, we showed the solubility in physiological fluid, which should control their mutagenic potential and possibly differentiates the toxicity of Sb_2S_3 and Sb_2O_3, to be significant for Sb in brake dust.

4.5. Practical implications

Calabrese and Kenyon [21] estimate the unit cancer risk for life-long inhalation exposure to 0.3 ng (Sb)/m^3 (time-weighted average) to be 1:100,000, assuming a 70 kg human, breathing 20 m^3 of air per day. Applying the PM10 concentration we calculated to be present at 40 cm distance, this means that a life-long occupational exposure (1 h/d, 200 d/a) to brake dust containing 2% Sb might pose a 20% additional risk to develop cancer. Persons who live near a congested road and are exposed for their entire lives to 1% of the PM10 concentration calculated to be present 65 cm above the brake would run a 3% additional risk. However, Calabrese's model has been criticized [11] to be highly uncertain, because the study it is based on uses only one, very high, exposure concentration. Note also that the calculated PM10 concentrations are highly uncertain, as described above.

According to Lohse et al. [23], 26,000 t of friction material are worn off in Europe each year. If half of this wear had the same mean composition as the disc brake dust we analyzed, and the other half had the same composition as the drum brake dust, the following amounts of toxic metals would be emitted in Europe each year: 250 t Sb, 5 t Pb, 100 kg Cd, 650 kg Hg, 1 t As, 9 t Ni, 150 t Cr, 60 t Mn, 400 t Al, 4 t Sr, 20 t Sn and 600 t Cu. The carcinogens Sb, As, Ni and Cr are especially problematic because of their probably linear dose–response relation (see Section 1). Pb, Cd and Hg are also toxic environmental contaminants.

4.6. Possible solutions from the perspective of the Intelligent Product System

These emissions demonstrate that cars do not only contain potentially reusable materials but also components that are released to the biosphere. From an environmental point of view, it is crucial to distinguish these two material flows and to turn them into closed cycles. The IPS [1] proposes that products of service consist of substances that can be continuously reused in technical cycles (technical nutrients) and products of consumption consist of substances that can be safely introduced into biological cycles (biological nutrients). Most components of a car can potentially be reused as technical nutrients, but brake pads are true products of consumption. The materials used in them must therefore be positively defined with respect to their health and environmental impact. However, our analysis has provided indications for possible carcinogenic effects of Sb used in brake pads. From an IPS perspective, these indications are sufficient to deter the use of Sb in brake pads. To use substances with an uncertain toxicology as long as harmful effects have not been proven beyond all doubt, can lead to massive contamination of the biological metabolism.

Industry is slowly beginning to recognize the environmental and toxicological uncertainties associated with Sb use in brake pads. Automotive safety systems producer, TRW Automotive, has already developed Sb-free brake pads which, according to the Center for Advanced Friction Studies "match and in many instances exceed original equipment (OE) friction materials with reduced stopping distances, high durability and improved driver comfort characteristics" [24]. Bulgarian producer Kanex Ltd. has also developed Sb-free braking systems which make use of natural fibers such as flax, cellulose and sisal [25].

From the perspective of the IPS, however, Sb or heavy metal-free does not necessarily qualify a product as appropriate for use as a biological nutrient, or a product of consumption. Rather, the development of brake pad friction material suitable for return to natural systems must begin with positive definition of all friction materials within the pad. This necessitates conscious identification and use of materials that have the most positive impact upon human and ecological health with regard to such parameters as carcinogenicity, endocrine disruption, irritation of skin and mucous membranes, sensitization, mutagenicity, teratogenicity, genetic engineering, persistence and biodegradation, bioaccumulation potential, global warming potential, and ozone depletion potential.

An example of such a positively defined product from another industry is the Climatex® Lifecycle fabric designed by Design Tex in cooperation with Rohner Textil, EPEA Umweltforschung, and MBDC LLC [26]. The fabric is made of blended wool and ramie and is dyed with non-toxic chemicals. After its useful life, the fabric can be returned to natural systems as garden mulch or composted safely into the soil. The same process of positive materials definition has been applied to replace Sb with Ti as a catalyst in PET and polyester products to create a potential technical nutrient or a product of service.

Potential replacements for Sb in brake pads include other metals that are less toxic to humans and the environment, such as Zn, Mg and Mn. Ultimately, however, replacements made from natural fibers, plant resins and other materials that could serve as true nutrients to natural systems would be most desirable from an IPS perspective.

Acknowledgements

We gratefully acknowledge the assistance of Irmtraud and Jürgen-Herrmann Voss at the Nordostniedersachsen University of Applied Sciences at Suderburg, as well as the help of Olav Becker, Armin Reller and Silke Waigel at the University of Augsburg, including the possibility to use their labs. We are especially grateful for the friendly support we received from the two brake manufacturers, especially for the possibility to use their equipment and take samples. Achim Schmottlach at the Indikator Laboratory in Wuppertal supported this work with decisive ideas and sent us urgently needed chemicals, for which we are very thankful. We would like to express our gratitude to Peter Hermes and Jürgen Stellpflug at the Ökotest Magazin in Frankfurt for fruitful discussions. Thomas Lundh at the Department of Environmental and Occupational Medicine, Lund University Hospital, was of immense help for the calf serum experiment and Anders Gudmundsson at the Division of Ergonomics and Aerosol Technology, Lund Institute of Technology, greatly supported our particle measurements. Andrew Bollinger at EPEA Umweltforschung, Hamburg, provided most valuable assistance in the review process. Last but not least, our warmest thanks go to the Lund Graduate School of Biomedical Research, in particular Anders Malmström, for financial support and inexhaustible inspiration.

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