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A revised estimate of copper emissions from road transport in UNECE-Europe and its impact on predicted copper concentrations

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Abstract

Comparisons of measured and model-predicted atmospheric copper concentrations show a severe underestimation of the observed concentrations by the models. This underestimation may be (partly) due to underestimated emissions of copper to air. Since the phase out of asbestos brake lining material, the composition of brake lining material has changed and may contain up to ~15% copper. This makes brake wear from vehicles potentially an important source of atmospheric (particulate) copper concentrations. In this paper, we reassess the copper emissions due to exhaust emissions and brake wear from road transport. Overall, our reassessments result in an estimate of total copper emission to air in UNECE-Europe of 4.0–5.5 ktonnes yr^{-1}, which is substantially higher than the previous estimate of 2.8 ktonnes yr^{-1}. Copper concentrations over Europe are calculated with the LOTOS-EUROS model using the revised emission data as model input. The results show that the revised emission estimates are a major step towards gap closure of predicted versus observed copper concentrations in ambient air. Brake wear emissions may be responsible for 50–75% of the total copper emissions to air for most of Western Europe. The hypothesis that road transport is an important source of copper emissions is tested and confirmed by (1) reviewing available literature data of chemically speciated PM data from road tunnel studies and (2) the gradient observed in copper concentrations from ambient PM monitoring going from rural sites to street stations. The literature review and observational data suggest that the majority of the emitted PM10 brake wear particles is in the PM2.5–10 size range. The results of this study indicate that modification of brake lining composition is an important mitigation option to reduce copper exposure of the population in Western Europe.

Keywords: Particulate emissions; Brake wear; Copper; Road transport; Copper concentration; Exhaust emissions

1. Introduction

Heavy metals (HM) are known to have adverse effects on the environment and human health (Fergusson, 1990). Anthropogenic activities have drastically changed the biogeochemical cycles of HM like copper, resulting in an elevated presence and availability of these elements in ecosystems and the urban environment. Currently, a discrepancy exists between measured atmospheric deposition and the atmospheric deposition modelled using emission data as input. Ambient concentrations of metals like nickel, cadmium, chromium, zinc and

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copper are underestimated by modelled concentrations with a factor 2–4 (van Pul et al., 1998; Gusev et al., 2006; Sliggers et al., 2006). This hampers targeted policies to reduce the burden of heavy metal emission to the environment, as there is uncertainty which sources are most responsible for present day concentrations. Heavy metal reduction policies mostly focus on the so-called priority HM (Pb, Cd and Hg) as outlined in the United Nations Economic Commission for Europe (UNECE) HM Protocol (UNECE, 1998). These reduction policies simultaneously reduce emissions of other HM like copper because HM are mostly emitted from the same sources. To understand and subsequently control HM emissions, a good understanding of the sources is vital. The knowledge of remaining HM emission sources needs to be updated regularly because, e.g., important (international) point sources have been eliminated or strongly reduced over time, as was shown for copper emissions from 1900 to 1980 in the New York area and Stockholm area by Svidén et al. (2001). Denier van der Gon et al. (2005) suggested that total European copper emissions decreased from 6.1 to 2.8 ktonnes yr^{-1} over the period from 1990 to 2000. Thus, the absolute and relative contribution of source sectors may shift over time which may have important consequences for further effective reduction policies.

Furthermore, there is a growing interest in atmospheric emissions of redox-active metals like copper and iron. Redox-active metals catalyse reactions that are essential for normal nervous system function, but they also participate in the generation of toxic free-radical species. Redox-active metals may play a role in inducing oxidative stress and related diseases (Tao et al., 2003; Huang et al., 2004). Oxidant stress has recently emerged as a mechanism that may underlie the toxic effects of most forms of air pollution, including particulate matter (Kelly, 2003). In this paper, we re-assess the copper emission by road transport to air triggered by (1) the gap between measured and modelled copper concentrations in air which suggest an underestimation of the emissions, (2) the recent information on brake lining composition and brake wear that has become available since asbestos brake pads have been phased out (e.g., Westerlund, 2001; Garg et al., 2000; Sanders et al., 2003) and, (3) the possible health relevance of particulate copper emissions. Our hypothesis is that the increasing mobility in (Western) Europe is among the more important diffuse sources of HM and that proper accounting of the changes in composition of brake lining material may result in an improved inventory of copper emissions to air. Using an atmospheric chemistry and transport model we compare predicted concentrations with measured concentrations to verify if a reassessment of the road transport contribution works towards gap closure. We show that reassessment of diffuse emissions of a particular metal (in this case, copper) may be crucial in a better understanding of the sources and observed concentrations.

2. Copper emissions to air: discussion of revised estimation methodology

Parties to the convention on long-range transboundary air pollution (CLRTAP) submit total annual emission values for pollutants including HM to the UNECE secretariat. However, many reportings are incomplete (Ilyin and Travnikov, 2003). Denier van der Gon et al. (2005) made an HM emission inventory for 2000 based on emission data submitted by the Parties to the Convention complemented by default estimates to achieve completeness. Copper emissions to air for UNECE-Europe from all sources were obtained from this emission inventory and split in a contribution from road transport and other sources (Table 1). For a description of the emission inventory methodology underlying the data in Table 1 and a description of the other emission sources, we refer to Denier van der Gon et al. (2005). The road transport contribution to Cu emission consists of exhaust emissions (combustion of fuel and motor oil) and non-exhaust emissions (brake wear). The emission factors for the road transport contribution as used by Denier van der Gon et al. are briefly reviewed below.

2.1. Copper emission from fuel consumption

It is considered that the total quantity of copper present in the fuel is emitted to the atmosphere, implying no losses in the engine. This is in line with other currently used estimation methodologies (e.g., EEA (European Environment Agency), 2005). Therefore, emissions of copper can be calculated by means of the total quantity of fuels sold from the IEA statistics (IEA, 2002a, b) and the corresponding emission factor. The copper emissions from fuel consumption by road transport presented in Table 1 were calculated using a Cu content of

Table 1
European copper emission data

Country	Road transport[a] ($kg\,yr^{-1}$)	Other sources ($kg\,yr^{-1}$)	Total ($kg\,yr^{-1}$)
Albania	619	557	1176
Armenia	51	502	553
Austria	10,812	21,783	32,595
Azerbaijan	850	3918	4767
Belarus	**438**	14,034	14,472
Belgium	**13,030**	13,820	26,850
Bosnia-Herzegovina	905	8262	9166
Bulgaria	2524	16,179	18,703
Croatia	6985	2803	9788
Cyprus	945	668	1614
Czech Republic	7301	36,402	43,703
Denmark	**6038**	5608	11,646
Estonia	**951**	2531	3482
Finland	**0**	18,700	18,700
France	**81,670**	95,495	177,165
Georgia	856	1978	2834
Germany	102,940	170,329	273,268
Greece	9848	8328	18,177
Hungary	**8442**	10,288	18,731
Iceland	323	105	428
Ireland	5596	3180	8776
Italy	**2590**	69,837	72,426
Kazakhstan	2793	215,442	218,235
Kyrgyzstan	272	2133	2405
Latvia	**1024**	3071	4095
Lithuania	**5052**	1693	6745
Luxembourg	**769**	483	1252
Macedonia (Form. Yug. Rep. of)	572	2877	3450
The Netherlands	**2044**	13,493	15,537
Norway	**12,702**	6627	19,329
Poland	**2600**	371,900	374,500
Portugal	10,237	10,991	21,228
Republic of Moldova	**536**	1037	1573
Romania	4449	21,364	25,813
Russia	56,600	743,716	800,316
Slovak Republic	**2133**	21,552	23,685
Slovenia	2324	2140	4463
Spain	47,615	101,929	149,544
Sweden	**10,290**	4826	15,116
Switzerland	9119	12,522	21,641
Turkey	16,379	73,676	90,054
Ukraine	4815	193,581	198,396
United Kingdom	**584**	47,599	48,183
Yugoslavia (Fed. Rep. of)	2986	28,237	31,223
Total ($tonnes\,yr^{-1}$)	460	2386	2846

[a]Bold figures are based on official submitted data to the cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe (EMEP), all other figures estimated by Denier van der Gon et al. (2005).

$1.7\,mg\,Cu\,kg^{-1}$ fuel, taken from EMEP/CORINAIR emission inventory guidebook (EEA, 2005). The EMEP/CORINAIR emission inventory guidebook is a guidebook prepared by the UNECE/EMEP Task Force on Emissions Inventories and Projections providing a comprehensive guide to state-of-the-art atmospheric emissions inventory methodology and is published by the European Environmental Agency (EEA). Data on the content of copper in (European) road transport fuels are limited and show a substantial variation (Table 2). Therefore, a limited number of fuel samples were

collected in 2006 in the Netherlands. Fuel samples (diesel and gasoline) were extracted using an adapted scheme of Munoz et al. (2006) for determination of Cu and Pb in fuels and lubricating oils and analyzed for its copper content on an Agilent 7500 a ICP-MS equipped with low uptake nebulizer and large autosampler. These data are included in Table 2. The use of these new data would result in a much lower emission factor for copper from combustion of diesel or gasoline than the values in the EMEP/CORINAIR guidebook. However, the samples were collected in the Netherlands and may not be representative for all UNECE-Europe countries. The use of a copper content of 1.7 mg Cu kg^{-1} fuel (EEA, 2005) as was done by Denier van der Gon et al. (2005) and which underlies the data in Table 1 will be referred to as the default methodology in this paper. The use of a new emission factor based on the analysis of Dutch fuel samples will be referred to as the revised methodology for Cu emission due to combustion of road transport fuels.

2.2. Copper emission from brake wear

Brake wear of road vehicles is due to forced deceleration during which brake linings are subject to large frictional heat generation. This wear generates brake lining particles, which are partly released to the environment. Not all of the worn brake material will be emitted as airborne particulate matter. Detailed laboratory tests conducted by Sanders et al. (2003) showed that ~50% of the total wear is emitted as airborne material; the other half directly deposits on the (road) surface and the wheel of the car. A wide spectrum of formulations is applied in brake pad material, e.g., matrices of organic resins, fillers such as barium sulphate or other inorganic material, friction modifiers such as graphite, talc, antimony and fibres of steel, glass and brass (Chan and Stachowiak, 2004; Blau and Meyer, 2003). Since the phase out of asbestos brake linings, iron and copper have become the most abundant metals in brake linings, but the concentrations may vary widely between makes and models (Garg et al., 2000; Sanders et al., 2003). A compilation of data on the copper content of brake pads and linings indicates that the copper contents vary between 1% and 14% (Table 3). This is not random variation but depends on the type of brake lining material (Sanders et al., 2003). Hence, a realistic average Cu content of brake lining material must reflect the weighted average of brake lining material used in the real world. So, for example if 3/4 of the brakes would have 1% Cu and 1/4 of all brakes contain 14%, the average Cu content would be 4.25%. The Brake Pad Partnership (2006) and Sanders et al. (2003) suggest that 5% Cu content is a good estimate of the average copper content of brake lining material used in the US. However, van Hyfte (2005) with backup from a Copper Uses Task Group lead by representatives of the copper

Table 2
Copper contents of road transport fuels and motor oil

Fuel	Cu content (mg kg^{-1})	Reference
Gasoline	1.7	EEA (2005)
	0.0318	Klein et al. (2004)
	0.046 (0.016–0.102)	This study (the Netherlands)
Diesel	1.7	EEA (2005)
	0.0236	Klein et al. (2004)
	0.010 (0.005–0.020)	This study (The Netherlands)
LPG	0	
Used motor oil	34	Recalculated from Klein et al. (2004)
	8 (4–20)	This study (The Netherlands)

Table 3
Copper content of brake pads and linings

Copper content (wt%)	Remarks	Reference
1.5–2.7	HDV-Volvo	Westerlund (2001)
0.01	HDV-Scania	Westerlund (2001)
11.8	New passenger cars (1997)—front	Westerlund (2001)
9.2	New passenger cars (1997)—rear	Westerlund (2001)
7.2	Old[a] passenger cars-front	Westerlund (2001)
5.1	Old[a] passenger cars-rear	Westerlund (2001)
1.5–14.2	Based on various references	Luhana et al. (2005)
4.4	Based on 40% of sales in US in 2000	Brake Pad Partnership (2006)
7.5	Non-asbestos Organic	Recalculated from Garg et al. (2000)
7.1	Non-asbestos Organic	Sanders et al. 2003
0.6	Semi-metallic	
3.5	Low-metallic	
10	European assessment	van Hyfte (2005)

[a]Pre-1993.

industry, estimated that 10% Cu content is the average Cu content of European brake lining material. Since it largely depends on the type of brake linings used, such regional differences in the average Cu content of brake wear emissions are possible and are well within the range of 1–14% shown in Table 3. However, this difference (a factor 2) is important in our calculations and therefore we take 5% Cu content (based on the monitoring programme in the US (Brake Pad Partnership, 2006)) as a low estimate and 10% based on van Hyfte (2005) as a high estimate of the average Cu content in brake lining material. Note that the 10% value based on the study of van Hyfte (2005) may well be most representative for Europe. The study by van Hyfte is part of the draft copper Risk Assessment to the European Commission and Member States. Review and approval is expected to take until the end of 2007.

To calculate the Cu emission from brake wear to air, the above-mentioned average Cu fractions have been applied to brake wear PM10 emission factors per vehicle kilometre (mg PM10 vkm^{-1}) and combined with kilometres driven by vehicle category by country for the year 2000 from the Baseline Scenarios for the Clean Air for Europe (CAFE) Programme (Amann et al., 2005). The applied PM10 emission factors for brake wear are 3, 6, 10 and 27 mg vkm^{-1} for motor cycles, passenger cars, light duty vehicles and heavy duty vehicles, respectively (Visschedijk et al., 2004). For total Cu to air, PM10 estimates are sufficient but as we intend to use the emission estimates in an atmospheric transport model both PM10 and PM2.5 fractions were estimated because the size of the particles determines deposition rate and is therefore important to predict the ambient air concentrations and Cu deposition. As a first approximation it is assumed that PM2.5 from break wear covers 70% of the PM10 fraction (Klimont et al., 2002).

2.3. Analysis illustration revised methodology

The application of the revised methodology is illustrated in Table 4 for Albania. Table 4 shows the respective calculations for Cu emission due to road transport fuel combustion, brake wear and motor oil burning. The diesel and gasoline consumption for road transport are taken from IEA (2002a, b), the mileage data needed for the brake wear and motor oil burning are taken from Amann et al. (2005). Total amount of motor oil burned is calculated from the mileage data using the assumption of Klein et al. (2004) that 1 l of motor oil is burned for every 5000 km driven. The bold figures in Table 4 summarize the emissions from the three emission causes. This procedure is followed for all UNECE-Europe countries and the results are listed in Table 5 together with the Cu emission from other sources derived from Denier van der Gon et al. (2005).

3. Model description

We have used the LOTOS-EUROS model (Schaap et al., 2007) to calculate the copper concentrations in ambient air over Europe using meteorological data from 2001. The LOTOS-EUROS model is a 3D-chemistry transport model developed to study the formation, transport and sinks of oxidants, particulate matter and HM. LOTOS-EUROS is applied for the region that spans from 10°W to 40°E and from 35 to 70°N with a spatial resolution of $0.5 \times 0.25^{\circ}$ lon-lat, roughly corresponding to 25×25 km. The model has been applied in numerous studies for particulate matter (Schaap et al., 2004a, b, 2007).

The model input in this study is either (1) a default scenario using a gridded Cu emission map prepared by Denier van der Gon et al. (2005) based on the data in Table 1 or (2) a revised, newly constructed emission grid which is a combination of a revised road transport copper emission estimate (including fuel combustion and brake wear) described in Section 2 whilst the other sources were kept fixed at the same levels. The tracers for Cu in the model are chemically inert and deposition is modelled as fine and coarse mode particles. For a full model description, we refer to the model documentation by Schaap et al. (2007).

4. Results and discussion

A new estimate of the road transport contribution to European Cu emissions to air is made based on revised emission factors for Cu emission from road transport fuel combustion, motor oil burning and brake lining composition as discussed in Section 2. The new estimation methodology drastically revises the Cu emission from road transport for UNECE-Europe going from 0.49 (Table 1) to 1.59 or 3.16 ktonnes yr^{-1}, for a 5% or 10% Cu content in brake material, respectively (Table 5). The contribution of road transport to Cu emissions in the revised estimate is now dominated by brake

Table 4
Analysis illustration of the revised estimation methodology for Albania

Exhaust emissions

Fuel	Consumption (TJ)	Revised emission factor		Revised emission ($kg\,yr^{-1}$)
		$mg\,Cu\,kg^{-1}$ fuel	$kg\,Cu\,TJ^{-1}$[a]	
Diesel	9490	0.01	0.000231	2
Gasoline	5600	0.05	0.001116	6
Total Cu emission from road transport fuel combustion (exhaust)				8

Brake wear emissions

Vehicle type[b]	Mileage (10^6 km)	EF brake wear ($mg\,Cu\,km^{-1}$)		Emission brake wear ($kg\,yr^{-1}$)	
		Low	High	Low	High
HDV	1166	1.35	2.7	1574	3148
PC	2020	0.3	0.6	606	1212
MC	75	0.15	0.3	11	23
Total Cu from brake wear				2191	4383

Motor oil burning emissions

Vehicle type[b]	Mileage (10^6 km)	EF Cu motor oil ($mg\,Cu\,km^{-1}$)	Motor oil burning ($kg\,yr^{-1}$)
HDV	1166	0.00144	1.7
PC	2020	0.00144	2.9
MC	75	0.00144	0.1
Total Cu emission motor oil burning			5

[a]Emission factor converted using diesel 23.0769 tonne fuel/TJ fuel; gasoline 22.32205 tonne fuel/TJ fuel.
[b]HDV = heavy duty vehicle; PC = passenger car; MC = motor cycle.

wear, fuel combustion and motor oil burning have become insignificant sources (Table 5). Application of the new Cu brake wear emission estimates increases the total estimated Cu emissions (all sources) with a factor ~1.5–2 going from 2.8 ktonnes yr^{-1} (Table 1) to 4.0–5.5 ktonnes yr^{-1} (Table 5). The spatial distribution of copper emitted from other sources such as industrial emissions is taken from Denier van der Gon et al. (2005) (Fig. 1a). The results of brake wear emission calculations per country were transformed to gridded emissions by scaling the exhaust emissions (Schaap et al., 2004b) (Fig. 1b), causing the emissions to be located at the same location as emission from road transport fuel combustion. Comparison between the distributions in Fig. 1a and b illustrates that brake wear emissions dominate the total atmospheric emission in the densely populated countries of Western Europe, whereas industrial sources dominate in Eastern Europe. On a European continental scale the contribution of brake wear to atmospheric copper emissions is estimated to be 40–60%. For single countries, the contribution of brake wear emissions ranges between 10% and 90% with highest fractions for countries in Western Europe due to high road transport activity in combination with other sources being relatively reduced due to implemented policies like the HM Protocol (UNECE, 1998).

Fig. 2a–c depict the modelled copper concentrations over Europe. Fig. 2a shows the calculated annual mean copper concentration in ambient air, Fig. 2b shows the copper concentration due to other sources, and Fig. 2c the modelled copper concentration due to brake wear emissions (low emission scenario; Table 5). Hence, Fig. 2b + c equal Fig. 2a. Maximum concentrations are modelled over industrial areas (e.g., the Ruhr Area and southern Poland) and densely populated regions (e.g., the Netherlands, the Po-Valley and England).

Table 5
Copper emissions from brake wear and other sources in 2000 for UNECE Europe

Country	Road transport				Other sources[a]	Total	
	Exhaust	Brake wear (kg yr^{-1})		Burning of motor oil		Low	High
		Low	High				
Albania	8	2191	4383	5	557	2762	4953
Armenia	1	432	864	1	502	936	1368
Austria	136	25,497	50,994	98	21,783	47,514	73,011
Azerbaijan	16	11,091	22,183	24	3918	15,049	26,140
Belarus	52	11,814	23,627	32	14,034	25,932	37,746
Belgium	164	36,778	73,556	135	13,820	50,897	87,675
Bosnia-Herzegovina	15	2413	4825	7	8262	10,696	13,108
Bulgaria	40	7734	15,468	24	16,179	23,977	31,711
Croatia	44	6132	12,263	21	2803	8999	15,131
Cyprus	14	2833	5666	9	668	3525	6358
Czech Republic	115	16,978	33,956	59	36,402	53,553	70,531
Denmark	113	18,922	37,845	68	5608	24,712	43,634
Estonia	16	2720	5441	9	2531	5276	7996
Finland	106	19,394	38,788	70	18,700	38,271	57,664
France	958	205,144	410,287	750	95,495	302,347	507,491
Georgia	18	514	1027	1	1978	2511	3025
Germany	1687	273,714	547,427	930	170,329	446,659	720,373
Greece	180	27,495	54,991	98	8328	36,102	63,597
Hungary	81	15,311	30,622	49	10,288	25,729	41,041
Iceland	8	1249	2498	5	105	1366	2615
Ireland	89	18,317	36,635	65	3180	21,651	39,969
Italy	1005	190,141	380,283	695	69,837	261,678	451,820
Kazakhstan	82	5576	11,152	27	215,442	221,127	226,703
Kyrgyzstan	8	543	1086	3	2133	2686	3229
Latvia	17	2918	5836	10	3071	6016	8935
Lithuania	23	4429	8858	14	1693	6159	10,588
Luxembourg	38	8299	16,599	24	483	8845	17,144
Macedonia	9	1927	3855	7	2877	4820	6747
Moldova	3	2141	4281	7	1037	3187	5328
The Netherlands	249	48,585	97,169	182	13,493	62,508	111,092
Norway	91	14,904	29,808	55	6627	21,677	36,581
Poland	274	46,134	92,267	163	371,900	418,471	464,604
Portugal	139	28,770	57,539	113	10,991	40,012	68,782
Romania	75	13,840	27,681	50	21,364	35,329	49,170
Russia	1206	1125	2250	3	743,716	746,050	747,175
Slovak Republic	36	6987	13,975	24	21,552	28,599	35,587
Slovenia	45	6053	12,107	25	2140	8263	14,316
Spain	595	135,195	270,391	443	101,929	238,162	373,357
Sweden	224	32,995	65,990	122	4826	38,167	71,161
Switzerland	202	26,791	53,582	111	12,522	39,626	66,417
Turkey	232	53,204	106,407	127	73,676	127,239	180,443
Ukraine	122	24,329	48,658	108	193,581	218,140	242,469
United Kingdom	1226	203,808	407,615	719	47,599	253,352	457,160
Yugoslavia	49	7971	15,941	28	28,237	36,285	44,256
Total (tonnes yr^{-1})	10	1573	3147	6	2386	3975	5548

[a]Cu emissions from sources other than road transport taken from Denier van der Gon et al. (2005).

The influence of other large point sources such as the smelters in the north of Russia is also visible. Furthermore, a large number of cities can be identified. The modelled regional background ranges between 2 and 5 ng m^{-3} in central Europe, North-western Europe and Italy. In South-western Europe, Scandinavia and (south) Eastern Europe rural concentrations tend to be <2 ng m^{-3}. The

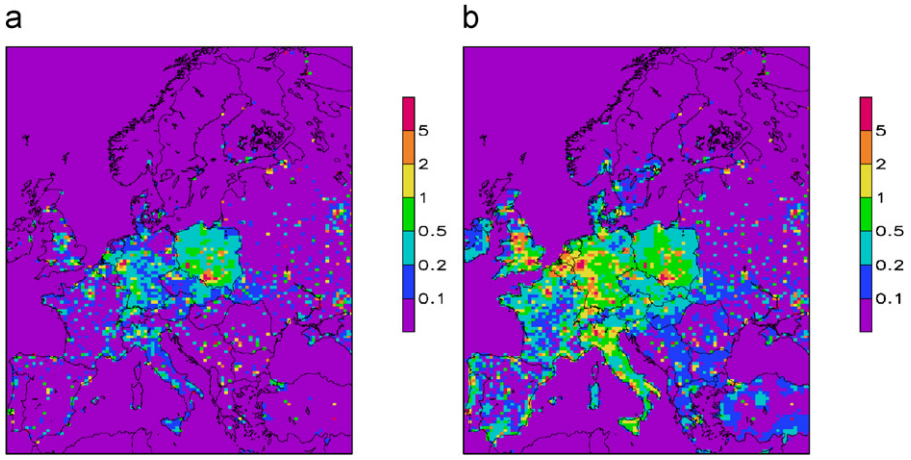

Fig. 1. (a) Default geographical distribution of Cu emissions except road transport (tonne/gridcel of 0.5–0.25°) as compiled by Denier van der Gon et al. (2005) and (b) geographical emissions of Cu with improved road transport contribution (low scenario, this work).

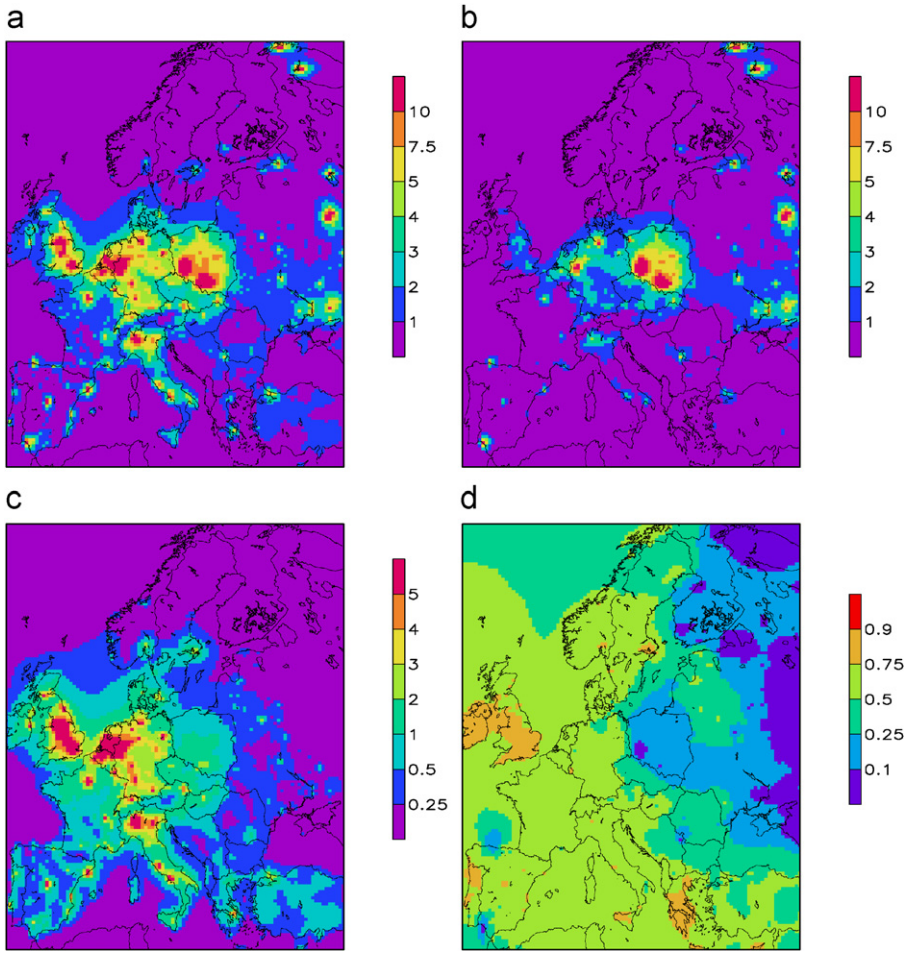

Fig. 2. (a) Total modelled copper concentration (ng m^{-3}), (b) modelled copper concentration that derives from other sources (non-road transport, (c) modelled copper concentration due to break wear (low scenario), (d) fraction of total copper concentration originating from brake wear.

contribution of brake wear to these concentrations are 50–75% in the western part of the model domain and <50% in the eastern part (Fig. 2d). These ratios reflect that even in the so-called low (but revised) brake wear emission scenario with 5% Cu content in brake lining material, brake wear is the dominant source for copper in the atmosphere in Western Europe.

The modelled concentrations with the LOTOS-EUROS model can be compared with measurements at sites in Europe which measure the Copper content of aerosol (Hjellbrekke, 2005). In Fig. 3, we compare the modelled annual average concentrations of Cu to those measured at 19 stations in the EMEP network. The concentrations calculated with the official emission database (base case, Fig. 3) underestimate the measured concentrations by about a factor 3. This phenomenon was already reported by van Pul et al. (1998) and more recently by Gusev et al. (2006) and Sliggers et al. (2006). Although we revised the combustion emission to a much lower value using our own (limited) fuel analysis data, the inclusion of brake wear emissions with a realistic present-day copper content results in a much better fit between between modelled and measured concentrations (Fig. 3). If the scatter plot is differentiated in western European sites and eastern European sites, the former yield values slightly above the 1:1 line for the low emission scenario, whereas a significant underestimation remains for the latter sites. Such a comparison for the high emission scenario yields a similar picture but, as to be expected, with higher modelled concentrations and, consequently, a significant overestimation in Western Europe. However, the scatter may also be partly caused by our assumption that brake linings have the same average composition in the whole of Europe and/or some uncertainties in the model relating to the lifetime of the brake wear particles.

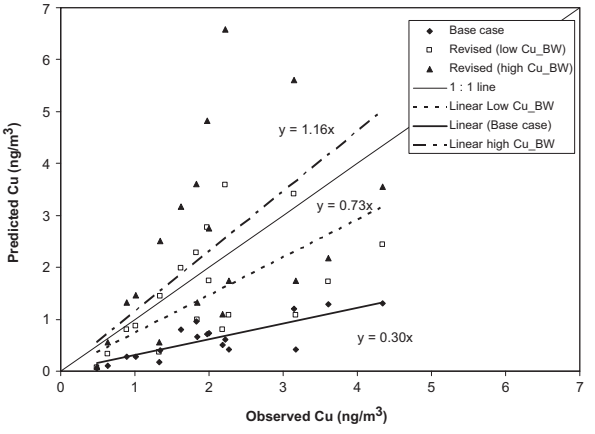

Fig. 3. Modelled versus measured concentrations in ambient air in the year 2001 using the default emission inventory (base case) and revised road transport Cu emissions with average 5% Cu in brake lining (low Cu_BW) and average 10% Cu in brake lining (high Cu_BW).

4.1. Uncertainty in the copper emission estimates and the modelled concentrations

The uncertainty in sources other than road transport is not assessed and beyond the scope of the present study. Uncertainty in the new emission estimates for road transport originates from

(1) The Cu content in road transport fuels (reflected in the Cu content range in Table 2); to reduce this uncertainty, more fuel analysis data from other UNECE countries are needed to derive a representative emission factor. The data available suggest that the value of $1.7\,mg\,kg^{-1}$ suggested by EEA ((2005) is an upper value. So, potentially road transport fuel combustion could still contribute but the emission will be dominated by the brake wear contribution.
(2) The Cu content of (average) brake lining material. The uncertainty is estimated to be at least a factor of ~2 based on estimates that include information of the brake lining manufacturing industry (5% vs. 10% Cu suggested by Brake Pad Partnership (2006) and van Hyfte (2005), respectively). Table 3 shows that the range of Cu content in brake lining material is 1–14%, so even larger regional variability may also exist due to regional/national variation in brands and compositions being used.
(3) The amount of brake wear material emitted to air. An overview of estimated air borne break wear emission factors is presented in Table 6. At first, the range in emission factors appears quite large but the higher emission factors, e.g., from Westerlund (2001) are for urban traffic. It is to be expected that break wear in the urban environment is relatively high due to congestion, traffic lights and frequent crossings. The emission factors are expressed per vkm driven and a substantial amount of total vkm driven is on highways and rural roads with much less braking involved. The other emission factors

Table 6
Brake wear PM10 emission factors and the fraction of PM10 emitted as PM4.7, PM2.5, PM1.1 and PM0.1

Vehicle class	PM10 ($mg\,vkm^{-1}$)	Fraction of PM10 (%) in				Reference
		PM4.7	PM2.5	PM1.1	PM0.1	
Motor cycles	0.5		70			Klimont et al. (2002)
	3					Visschedijk et al. (2004)
	4					Klein et al. (2004)
	3.7		40	10	8	EEA (2005)
	4					van Hyfte (2005)
Passenger cars	8					Klein et al. (2004)
	6.8					van Hyfte (2005)
	6					Visschedijk et al. (2004)
	3.6		70			Klimont et al. (2002)
	5[a]					Warner et al. (2002)
	5.3		73[b]			Garg et al. (2000)
	7.3		40	10	8	EEA (2005)
	17[c]					Westerlund (2001)
	8.1	82	38	16		US EPA (United States Environmental Protection Agency) (2003)
	8	44[b]	12.5[b]	2.5[b]		Sanders et al. (2003)
Light duty vehicles	7.5					Visschedijk et al. (2004)
	11.5		40	10	8	EEA (2005)
	10.6					van Hyfte (2005)
	10					Klein et al. (2004)
Heavy duty vehicles	32.3					Visschedijk et al. (2004)
	32		40	10	8	EEA (2005)
	84[c]					Westerlund (2001)
	22.8		70			Klimont et al. (2002)
HDV-buses	31					Klein et al. (2004)
	17.2					van Hyfte (2005)
HDV-trucks	43					Klein et al. (2004)
	26.5					van Hyfte (2005)

[a]Total wear reported by Warner et al. (2002) is $9\,mg\,vkm^{-1}$, based on Garg et al. (2000) and Sanders et al. (2003), we estimated the PM10 fraction at $5\,mg\,vkm^{-1}$.
[b]Recalculated as fraction of PM10.
[c]Urban traffic only.

represented a weighted average of driving on urban, highway and rural roads. Therefore, the data of Westerlund (2001) are not necessarily contradicting the other emission factors but they cover only part of the vkms driven, being the part with most intensive braking. If we omit these values, the average emission factors are 3.7 ± 0.6, 6.4 ± 1.7, 10.3 ± 0.4, $28.1\pm9.7\,mg\,vkm^{-1}$ for motor cycles, passenger cars, light duty vehicles and heavy-duty vehicles, respectively. Generalized one step further, the uncertainty can be estimated as ~30%. However, based on Westerlund (2001), the spatial allocation of the emissions seems not well treated at the moment and most likely a higher fraction ought to be located in the urban areas at the expense of highway and rural driving.

Overall the uncertainty surrounding the Cu emission estimate of road transport is estimated at a factor 2–3, and approximated by the low and high estimate in Table 5. The ranges between countries and regions (urban and rural environment) may be considerably larger depending on driving behaviour, fleet composition, favourite brake pad composition, etc.

An independent indication if our estimates point in the right direction can be obtained from the PM composition analyses in tunnel studies where we may assume that all PM is originating from road transport (including both exhaust and non-exhaust

emissions). The comparison should be seen as qualitative because braking may be limited in the tunnels (giving lower Cu emissions) compared to the urban environment with frequent traffic lights, traffic jams and crossroads. On the other hand, some heavy-duty vehicles will be included which may cause higher Cu emissions than passenger cars only. Emission factors for Cu in PM10 from tunnel studies range from 0.34 mg Cu km^{-1} (Maas tunnel, Rotterdam, the Netherlands (Denier van der Gon et al., 2003)) to 0.17 mg Cu km^{-1} Tingstad tunnel, Sweden (Sternbeck et al., 2002)) and 0.16 mg Cu km^{-1} (Gelezenis Vilkas tunnel, Vilnius, Lithuania (Valiulis et al. (2002)). These road tunnel studies indicate equal or slightly lower emission factors than the average Cu emission factor for brake wear from passenger cars based on our low scenario with 5% Cu content in brake pads. However, braking will be somewhat underestimated in the tunnel environment. Still, it confirms that the emission factors used here for brake wear appear to be in the right order of magnitude. By contrast, Laschober et al. (2004) report a lower Cu emission factor of 0.03 mg Cu km^{-1}. Clearly, to fully understand the range in emission factors derived from tunnel studies and interpret this material correctly, more detailed information is needed on the composition of brake lining in the particular country as well as driving/braking behaviour within the respective tunnels.

Another option to verify our hypothesis that road transport is an important source of Cu in PM10 is to investigate ambient PM10 samples closer and further away from the source. Hueglin et al. (2005) reported that the abundance of Cu is gradually decreasing from urban kerbside to urban background, near-city and rural sites, indicating that road traffic is a main source of this element. In Fig. 4, we compiled data from Switzerland (Hueglin et al., 2005) and the Netherlands (Visser et al., 2001) which contained chemical composition data for both fine and coarse PM at different locations. The pattern for both countries is very similar, showing a clear elevation of Cu in the PM mixture sampled closer to roads (Fig. 4), further confirming that road transport may significantly contribute to total Cu loading of the atmosphere. A feature from Fig. 4 is that the enrichment in Cu near roads is overwhelmingly seen in the course fraction of PM10 whereas based on Klimont et al. (2002) we had expected a large fraction in the fine fraction. This is further discussed in the next paragraph.

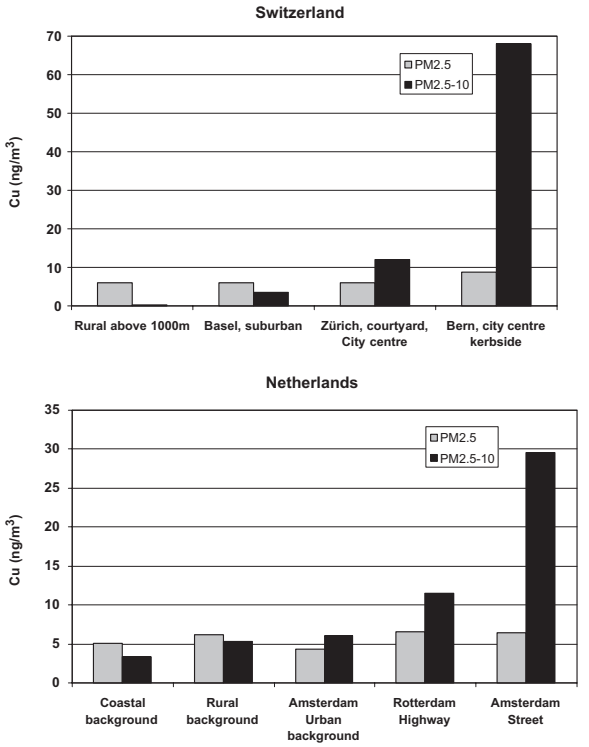

Fig. 4. Concentration of Copper in ambient PM samples at various locations in the coarse fraction (PM2.5–10) and the fine fraction (PM2.5) for Switzerland (top) and the Netherlands (bottom). (Recalculated from data by Hueglin et al., 2005 and Visser et al., 2001, respectively.)

4.2. *Uncertainty in the modelled copper concentrations due to size fractionation*

Next to uncertainty in total emission to air discussed in Section 4.1, the modelled concentrations are sensitive to the size fractionation of the emitted particles. In our first calculations, we assumed 70% of the PM10 from brake wear to be in the PM2.5 fraction (Klimont et al., 2002) but the data by US EPA (United States Environmental Protection Agency) (2003) and Sanders et al. (2003) suggest that potentially a larger fraction may be in the coarse fraction (PM2.5–10) and only ~30% of PM10 in the PM2.5 size fraction (Table 6). This will have implications for the lifetime of the Cu containing particles in the atmosphere because coarse mode particles have a higher dry deposition velocity than fine mode particles. To analyse the impact of size fractionation we repeated the simulation with a different size fractionation for brake wear; 30% in the fine mode (PM2.5) and 70% in the PM2.5–10 fraction. Overall, reversing the size fractionation

yields a 10–20% and 20–30% lower total copper concentration at the regional validation stations for the low emission scenario (Fig. 5) and high emission scenario (data not shown), respectively. The results show that it is important to know the size fractionation of the emissions and the related uncertainty is approximately ~20%.

An explanation for the enrichment of Cu in the PM2.5–10 fraction going well beyond the 70–30% ratio near busy roads may be that these particles deposit faster than PM2.5 particles. Therefore, the coarse fraction will remain more in the vicinity of the road and resuspension of these particles could be an important secondary source of copper. If so, the extreme enrichment in the PM2.5–10 fraction (Fig. 4) which is more than is to be expected based on the size distribution data (Table 5) is not necessarily contradicting.

4.3. Health relevance of copper in ambient air

The biological effects of particulate matter are mediated primarily through pro-inflammatory oxidative stress reactions involving reactive oxygen species (ROS) (Tao et al., 2003). Water soluble metals, especially transition metals such as Fe, V and Cu, are capable of producing ROS by catalyzing Fenton-type reaction (Stohs and Bagchi, 1995). Oxidative stress may be (one of) the major mechanisms causing the adverse health effects of exposure to particulate matter (Li et al., 2003) and copper is among the important redox-active metals capable of inducing such oxidative stress (Huang et al., 2004). Therefore, the Cu content in ambient air could be a valuable marker in relation to possible health effects. Further research is needed to investigate if copper from break wear is bioactive and capable of inducing oxidative stress. If copper in particulate matter proofs to be a relevant contributor to adverse health effects, there is clear potential to mitigate this effect by changing to brake lining material containing no or very little copper. Copper-free brake lining material is technically feasible and available (e.g., Sanders et al., 2003; Blau and Meyer, 2003), but the alternatives for copper in brake material need to be screened for adverse effects as well to avoid the possibility of replacing one problem with the next one.

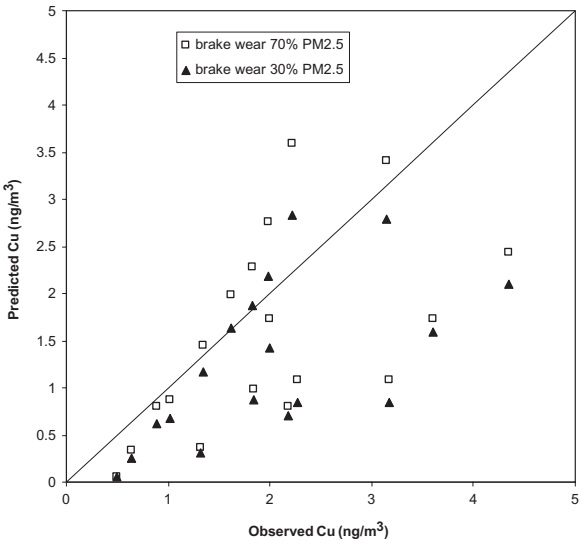

Fig. 5. Modelled versus measured copper concentrations in ambient air using the low break wear scenario with different partioning of brake wear particulates in the fine (PM2.5) fraction and coarse (PM2.5–10) fraction.

5. Conclusions

Since the phase out of asbestos brakes, brake lining material contains 1–14% Cu with an average Cu content of 5–10% in current brake linings. This makes brake wear from vehicles an important source of atmospheric (particulate) copper concentrations. It is the dominating source of copper in ambient air in Western Europe. By contrast, the currently used Cu emission factors for combustion of road transport fuels appear to overestimate copper emissions. A broader survey of actual copper contents of fuels sold in Europe is needed to give a representative new emission factor for combustion emissions from road transport. The balance of lower Cu exhaust emission and higher Cu brake wear emissions is a considerable increase in total Cu emission from road transport. Based on our revised estimates for copper emission from road transport we estimate total copper emission to air in UNECE-Europe to be 4.0–5.5 ktonnes yr^{-1} which is substantially higher than the previous estimate of 2.8 ktonnes yr^{-1}. The latter estimate is largely based on official submissions to the convention of LRTAP and, in our opinion, needs to be revised. The revised copper emissions from road transport proposed in this paper are a major step towards gap closure of predicted and observed Cu concentrations in ambient air. For most of Western Europe, brake wear emissions may be responsible for 50–75% of the total copper emissions to air.

The PM2.5 Cu concentration in Western Europe appears to be rather stable around $5\,ng\,m^{-3}$, independent of the location (Fig. 4) and is still somewhat underestimated by the model predictions. The literature review suggests that particulates emitted from brake wear are mostly in the coarse mode and this hypothesis is supported by the observed elevation of copper concentrations in the PM2.5–10 fraction going from background sites towards busy streets. Modelling results indicate that the uncertainty in predicted Cu concentrations caused by incorrect size fractionation of brake wear particulates may be ~20%. Although relevant, this is small compared to the importance of correct estimation of the copper content of brake wear material and possible regional variation therein.

Further research is needed to investigate if copper from break wear is bio-active and capable of inducing oxidative stress. If copper in particulate matter proofs to be a relevant contributor to adverse health effects, the results of this study indicate that changing to brake lining material containing no or very little copper may be a promising mitigation option to reduce exposure of the population to copper in Western Europe.

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