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Primary Emissions of Submicron and Carbonaceous Particles in Europe and the Potential for their Control

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Contents

Acknowledgments

Abstract

The interest in submicron and specifically carbonaceous particles in the atmosphere has risen recently, largely because of their potential role as climate forcing agents. Black carbon (BC) particles absorb solar radiation and are suspected to be a significant factor contributing to climate warming. Particulate organic carbon (OC), in turn, acts as a cooling substance. In principle, all of the atmospheric BC and a large part of the OC are emitted from incomplete combustion of fossil fuels and biomass. To model the climatic effects of carbonaceous aerosols it is crucial to provide robust estimates of their emission strengths. Recent measurements of atmospheric optical depth suggest that earlier BC emission inventories may lead to over-estimations of atmospheric BC over Europe. This paper describes estimates of emissions of primary submicron particles, BC and OC in Europe, applying an extended PM-module of the RAINS model.

The European emissions in 2000 are estimated at 2.8, 0.67 and 0.99 Tg for submicron, BC and OC, respectively. The main sources are exhaust emissions from traffic and residential combustion of solid fuels, which together amount to 64 percent of the submicron emissions, 85 percent of the total BC and 81 percent of the total OC. By 2010 the emissions of all three pollutants are projected to decline by about 20 percent, largely due to implementation of the 'EURO-standards' for mobile sources and fuel switching in the residential sector.

Primary Emissions of Submicron and Carbonaceous Particles in Europe and the Potential for their Control

1   Introduction

Submicron particles have a high probability to penetrate deep into the human respiratory system and thus are hypothesized to be an important contributor to health effects from air pollution, with respiratory and cardiovascular mortality as the most severe endpoints (Pope & Dockery, 1992; Dockery *et al.,* 1993; WHO, 2000; Seaton *et al.,* 1995; Laden *et al.,* 2000; Mar *et al.,* 2000; Wichmann *et al.* 2000). Submicron particles, especially in the accumulation mode with diameters ranging between 0.1-1 μm, have a long atmospheric residence time, lasting from several days to weeks, since they are not affected efficiently by removal mechanisms like diffusion or gravitational settling. At the same time, submicron particles are important cooling agents in the atmosphere. Cooling occurs directly through backscattering the incoming solar radiation as well as indirectly through acting as cloud condensation nuclei (CCN) that form clouds by growing into cloud droplets (Charlson *et al.* 2001). Clouds then reflect the radiation away from the atmosphere. The total cooling effect of aerosols is estimated to be ~1 W m^{-2} with a large uncertainty (Hansen *et al.,* 1998; Charlson *et al.,* 2001; Ramaswamy *et al.,* 2001).

In addition to their size, both the health and climate effects depend also on the chemical properties of the particles. One of the most abundant elements in atmospheric particles is carbon. Carbonaceous particles, containing elemental carbon (also often called black carbon) or organic compounds (organic carbon), are found in high concentrations especially in the submicron size range (e.g., Gray & Cass 1998; Offenberg & Baker 2000; Pakkanen *et al.,* 2000). They are often linked with adverse health effects (e.g., Mar *et al.* (2000) observed a significant association with cardiovascular mortality and elemental carbon particles).

Atmospheric black or elemental carbon is emitted in particulate form from incomplete combustion of carbonaceous material. Organic carbon particles are formed in combustion as well as from gaseous precursors through nucleation and condensation processes (secondary organic carbon) (Penner *et al.,* 1993; Hildemann *et al.,* 1994; Gray & Cass 1998; Pakkanen *et al.,* 2000). Apart from combustion, small amounts of coarse carbonaceous particles can be generated by the physical weathering of graphite-containing sedimentary rocks or exposed charcoal (Charlson & Ogren 1982). There is also evidence that natural sources like plant detritus and organic films on the ocean surface can contribute to the concentrations of organic carbon in the aerosol (Rogge *et al.,* 1993a; Seidl, 2000). Although often treated as separate components, the elemental and organic fractions are rarely found as separate individual particles in the aerosol emissions and in the atmosphere, but rather forming complex mixtures together and with other aerosol species, e.g., sulfate (Ogren 1982; Kittelson 1998). This

mixing state with non-absorbing aerosol in turn affects the optical and chemical properties of the carbonaceous aerosol.

Airborne black carbon absorbs solar radiation and thus contributes to the warming of the climate (Hansen *et al.* 2000; Andrae 2001; Jacobson 2001). The global mean radiative forcing of black carbon aerosols from fossil fuels has been estimated by IPCC at +0.2 Wm^{-2} with an uncertainty range from +0.1 to +0.4 Wm^{-2} (Ramaswamy *et al.,* 2001). The uncertainty of these estimates is high: Jacobson (2001 & 2002) discusses the possibility that the forcing could be as high as +0.54 Wm^{-2} (Jacobson 2001), whereas Penner *et al.* (2003) suggested the forcing from black carbon and organic matter to be not significantly different from zero. Following Jacobson (2001 & 2002), carbonaceous particles would make be the second most important direct-forcing component after CO_2. Considering that BC has a relatively shorter lifetime in the atmosphere than other greenhouse gases (e.g., CO_2) it has been suggested that controls of black carbon emissions could provide a faster way to combat global warming in the short-term (Hansen *et al.,* 2000; Jacobson, 2002). The exact role of absorbing aerosols in the global climatic system and global warming is still unresolved (see, e.g., Jacobson 2002; Chock *et al.,* 2003; Feichter *et al.,* 2003; Jacobson 2003a, 2003b, 2003c; Penner 2003; Penner *et al.,* 2003) and a more profound quantitative understanding is needed to formulate reliable policy recommendations (Hansen *et al.,* 2000). This also applies to the emission estimates of carbonaceous particles.

In order to better understand the health and climatic effects of submicron and carbonaceous particles it is important to know their origin. Against this background this study attempts to quantify the primary emissions of carbonaceous particles from anthropogenic sources in Europe. The overall goal is to estimate the European primary emissions of black carbon, organic carbon and submicron particles with the RAINS Europe model. Following the RAINS approach for estimating PM emissions (Klimont *et al.,* 2002), this study

  i.   conducted a literature survey to quantify the theoretical volume of uncontrolled primary emissions of submicron and carbonaceous particles (i.e., emissions at the emission source, without any emission control measures),

  ii.   identified the shares of BC, OC and PM_1 in total particulate mass of uncontrolled emissions or, if that was found impossible or unreasonable, estimated absolute emission rates of the concerned species,

  iii. determined the removal efficiencies of possible control measures devices, distinguishing BC, OC and PM_1, and

  iv.   calculated European emissions with the RAINS model. For this purpose, additional sources that were not yet included in the RAINS Europe model have been incorporated.

1.1   An Integrated Assessment Model for Particulate Matter

Over the last few years, the RAINS model has been used to address cost-effective emission control strategies in a multi-pollutant/multi-effect framework. For this purpose, the RAINS

model included the control of SO_2, NO_x, VOC and NH_3 emissions as precursors for acidification, eutrophication and ground-level ozone. In order to allow for analysis of health damage due to fine particles this framework was extended to include particulate module (Klimont *et al.,* 2002).

While a certain fraction of fine particles found in ambient air originates directly from the emissions of these substances (the "primary particles"), a second fraction is formed through secondary chemical processes in the atmosphere from precursor emissions, involving SO_2, NO_x, VOC and NH_3. Consequently, a search for cost-effective solutions to control ambient levels of fine particles needs to balance emission controls over the sources of primary emissions as well as over the precursors of secondary aerosols. Thus, the control problem can be seen as an extension of the "multi-pollutant/multi-effect" concept applied for acidification, eutrophication and ground-level ozone (Table 1.1).

Table 1.1: Air quality management as a multi-pollutant, multi-effect problem.

	SO_2	NO_x	NH_3	VOC	Primary PM emissions
Acidification	√	√	√		
Eutrophication		√	√		
Ground-level ozone		√		√	
Health damage due to fine particles	√	√	√	√	√
		via secondary aerosols			

Further, a more sophisticated assessment framework could be used for more than just balancing measures for the five pollutants to control fine particles. Such a framework could consider the possible policy objectives for fine particles together with targets for acidification, eutrophication and ground-level ozone, and thereby search for least-cost solutions to address all four environmental problems simultaneously.

The present implementation of the RAINS model contains modules to describe emissions and emission control costs for SO_2, NO_x, VOC, NH_3, and PM (distinguishing between $PM_{2.5}$, PM_{10}, and TSP). The atmospheric dispersion models linked to RAINS also include the processes leading to the formation of secondary aerosols, the dispersion of fine particles in the atmosphere and the formation of secondary aerosols from the "conventional" precursor emissions. A module has been developed to assess the health impacts resulting from a certain emission control strategy.

Since the PM control options that are already included in the RAINS model as described in Klimont *et al.* (2002) also reduce simultaneously emissions of submicron and carbonaceous particles, the control costs that are already estimated within RAINS also apply to these species and thus are not discussed in this paper. This study assesses size fractions, species-specific reduction efficiencies and source-specific emission strengths.

The present structure of the RAINS model is illustrated in Figure 1.1, where the elements required for the analysis of fine particulate matter are highlighted (Johansson *et al..*, 2000).

Economic
activities

Emission control
policies

Environmental
targets

Agriculture → NH_3 control & costs → NH_3 emissions → NH_3 dispersion

Energy use → SO_2 control & costs → SO_2 emissions → S dispersion

→ NO_x control & costs → NO_x emissions → NO_x dispersion

Critical loads f. acidification

Critical loads f. eutrophication

Transport → NO_x/VOC control&costs

VOC emissions

O_3 formation

Critical levels for ozone

Solvents, fuels, industry → VOC control & costs

Secondary aerosols

O_3 Population exposure

Other activities → PM control & costs → Primary PM emissions → Primary PM dispersion → PM Population exposure
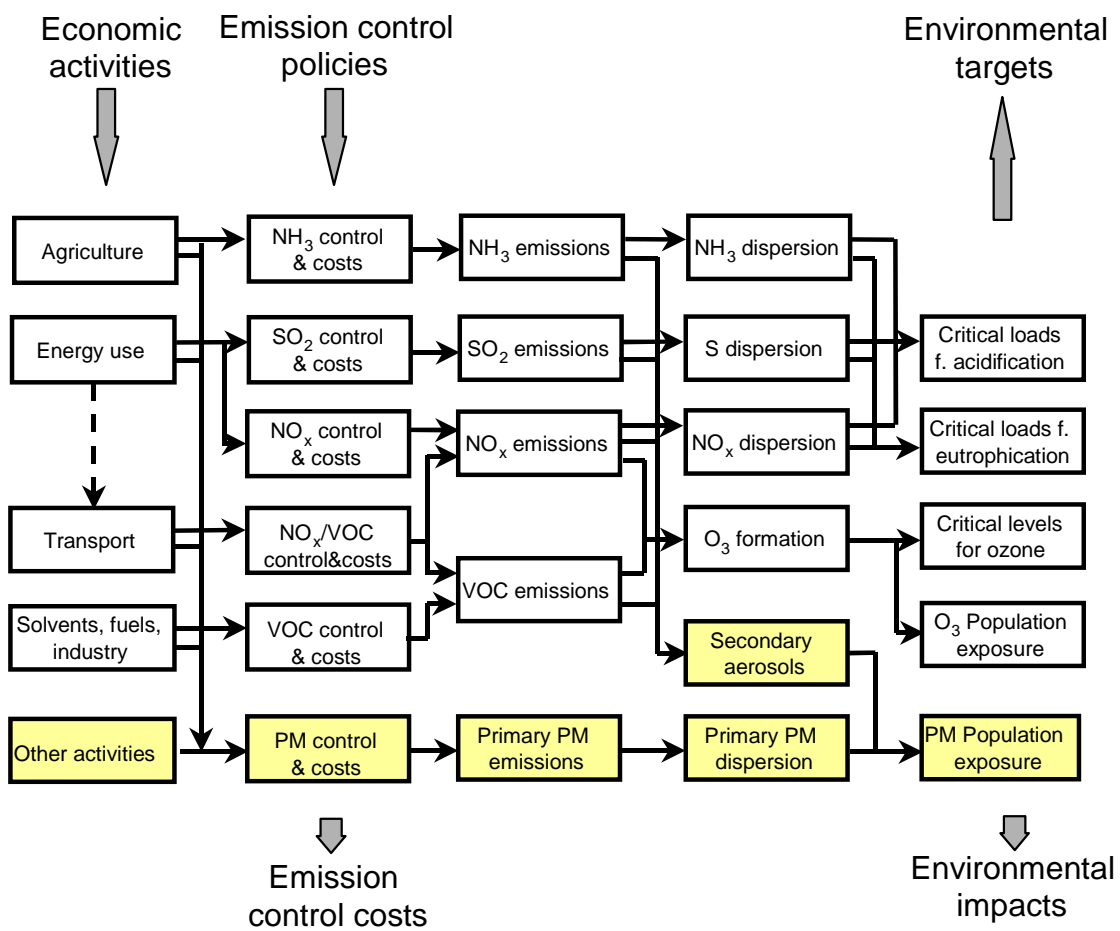
Emission
control costs

Environmental
impacts

Figure 1.1: Flowchart of the RAINS model.

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2 Measurement Methods

Measuring concentrations and chemical composition of particles differs from the identification of gaseous components. In case of particles it is important to decide first which characteristics are of interest, i.e., physical (e.g., number, size, mass, density, morphology, etc.) or chemical (e.g., elemental composition, chemical compounds etc.), before choosing a method of measurement and analysis. A more detailed discussion of the methodologies is provided, e.g., in Suess & Prather (1999) and McMurry (2000).

Physical parameters are usually measured with methods utilizing either the electrical or aerodynamical properties of the particles. The chemical analysis can be made "off-line" from a sample collected on a substrate, e.g., a filter. It can look at a bulk of particles (e.g., mass spectrometry analysis of filters) or at single particles (e.g., electron microscopy combined with x-ray analysis). Recently, methods have been developed that can analyze the composition of single particles in the air flow "on-line" (on-line mass spectrometry). For carbonaceous aerosols, both 'bulk' and 'single particle' approaches have been used. The bulk analyses are based on differences in, e.g., thermal evolution, optical properties or solvent extraction of the carbonaceous species.

Particulate size distribution is measured with several different methods depending for example on the size range of particles in focus or the concentration of interest (e.g., number or mass). They are based either on the electrical or aerodynamical properties, which vary with particle size. Electrical techniques are used for particles with negligible inertial mass. A widely used electrical method for measuring submicron number size distribution of the aerosol is the SMPS (scanning mobility particle sizer) (e.g. Morawska *et al.,* 1998; Shi *et al.,* 2000; Kayes & Hochgreb 1999a). For larger particle sizes sedimentation or inertia based methods are used. These include, e.g., APS (aerodynamic particle sizer) and different kinds of impactors for the determination of the mass size distribution of the aerosol (e.g., Kerminen *et al.,* 1997; Morawska *et al.,* 1998; Shi *et al.,* 2000). Filter measurements are used to measure particle mass within certain size ranges ($PM_{2.5}$, PM_{10}, TSP). Impactors and filters are used to collect particulate matter for chemical analysis.

The remaining sections of this chapter focus on the issues related to measuring characteristics of carbonaceous particles and discuss the definitions found in literature and used in this document.

2.1 Definitions of Carbonaceous Particles

Chang *et al.* (1982) describe elemental carbon particles as "a complex three-dimensional organic polymer with the capability of transferring electrons, rather than merely as an amorphous form of elemental carbon". Each particle has a large number of crystallites which are made of carbon layers with a graphitic hexagonal structure. These layers however have defects, dislocations and discontinuities, and thus contain sites with unpaired electrons. The sites are active to react with other molecules in the flue gas during particle formation. Such

molecules include, e.g., oxygen, hydrogen, and nitrogen, and they are incorporated into the structure. The amount of these molecules in the elemental carbon particle affects its chemical, adsorptive and catalytic behaviors and is different in different combustion conditions and for different fuels (Chang *et al.,* 1982).

In the literature the term "black carbon" is often used as a synonym for elemental or graphitic carbon or soot and vice versa (e.g., Hamilton & Mansfield 1991; Horvath 1993; Bond *et al.,* 1999; Offenberg & Baker 2000). It is important to notice that the concepts can refer to different properties of carbonaceous aerosols and that there is no exact definition of these terms. Differences arise, e.g.., from measurement methodology and light absorbing properties and are discussed in more detail by, e.g., Chow *et al.* (1993), Birch & Cary (1996), Cooke & Wilson (1996), Pakkanen *et al.* (2000), Turpin *et al.* (2000), Ballach *et al.* (2001) and Yu *et al.* (2002). The terminology presented here is partly based on the nomenclature discussed in Bond (2000).

Graphitic carbon - Graphitic carbon refers to the molecular state of carbon. In pure graphitic carbon, all chemical bonds are aromatic. Graphite has been identified to be the dominant contributor to light absorption.

Elemental carbon - The term elemental carbon (EC) is often used with thermal analysis to indicate the carbon that does not oxidize below a certain temperature (usually 550-650 C) or which is not extractable with, e.g., hydrogen peroxide or benzene.

Black carbon - In general the term black carbon (BC) or light absorbing carbon (LAC) refers to the whole light absorbing fraction of carbonaceous aerosols (Cooke *et al.,* 1996; Pakkanen *et al.,* 2000). Some large molecular organic compounds also have such properties, so in that sense one can argue that BC is not pure elemental carbon but some organic carbon is included.

Organic carbon - Organic carbon (OC) refers to the non-carbonate carbonaceous particles other than black or elemental carbon and it includes numerous organic compounds (e.g., Rogge *et al.* 1993b). The term OC actually refers to the content of carbon in the compounds. For estimating the organic compound mass concentration a multiplicative factor of 1.2-1.4 is commonly used in the literature (Turpin *et al.,* 2000).

Carbonate carbon - Carbonate carbon (or inorganic carbon, e.g., $CaCO_3$, $MgCO_3$, K_2CO_3) can be determined by measuring the CO_2 evolved upon acidification before the analysis of the other fractions (EC and OC). However, carbonate carbon usually constitutes less than five percent of the total carbon, so that the carbonate procedure is usually not applied (Chow *et al.,* 1994). In many studies the total carbon is defined as the sum of elemental and organic carbon.

Soot - Soot is formed from gaseous fuels as well as from the volatilizing components of liquid and solid fuels. Soot particles are formed through gas-to-particle nucleation and they grow in size through condensation and coagulation. Soot is also used as a general term for dark-appearing, carbon-containing compounds generated in combustion, which may be a mixture of both elemental and organic carbon fractions (see, e.g., Novakov 1982).

<u>Char</u> - Char particles are the carbonaceous particles, formed from the unburned carbon in the fuel during burning of solid fuels and heavy fuel oil. Char particles are typically in the coarse size range.

<u>Total carbon</u> - Total carbon (TC) is actually the sum of organic carbon, elemental carbon (or black carbon) and carbonate carbon. However, carbonate carbon usually constitutes less than five percent of the total carbon, so that many studies define TC as the sum of only elemental and organic carbon.

Table 2.1: Terminology used in this study for different particle species.

Terminology	Abbreviation	Description
Submicron	PM_1	Diameter less than 1 µm
Fine	$PM_{2.5}$	Diameter less than 2.5 µm
Coarse		Diameter between 2.5 and 10 µm
Large	$>PM_{10}$	Diameter larger than 10 µm
	PM_{10}	The sum of fine and coarse fractions
	TSP	The sum of fine, coarse and large particles
Black carbon	BC	Black carbon in fine particles
Organic carbon	OC	Organic carbon in fine particles
Total carbon	TC	Total carbon, sum of BC and OC

2.2 Analysis of Carbonaceous Particles (Chemical Properties)

Impactors and filters are the most widely used methods to collect particulate matter samples for chemical analysis of carbonaceous particles. The sampling method has been found to affect the accurate measurement of OC because of the interference from semi-volatile and volatile organics (Turpin *et al.,* 2000). The interaction occurs in two ways: 1) as volatilization of particulate-phase organics from the sample (negative artifacts) and 2) as adsorption of gas-phase organics, e.g., onto the filter (positive artifacts) (Turpin *et al.,* 2000).

The commonly used methods for determining the concentrations of total, black and organic carbon are based on optical properties or on the thermal evolution of the different carbonaceous species of particles. Black carbon is a very efficient light absorber and optical methods, such as integrating sphere, the aethalometer, or Raman spectroscopy, use that property to measure its concentration (e.g., Horvath 1993; Hitzenberger *et al.,* 1999; Pakkanen *et al.,* 2000). With the most frequently used optical method, the aethalometer, it is possible to measure BC concentration in real-time (Hansen *et al.,* 1984). The aethalometer converts the attenuation measurements into mass concentrations using a specific attenuation coefficient. This coefficient depends on many factors and is different in samples collected from different sources or environments (Hitzenberger *et al.,* 1999; Ballach *et al.,* 2001). If the aethalometer has not been calibrated to match the properties of the aerosol found in the area of operation, it may give biased results. Therefore comparisons with thermal methods have indicated site-dependences (Ballach *et al.,* 2001).

Thermal methods use the different volatilization temperatures of EC and OC to extract the different fractions into gaseous form, e.g., into CO_2, which is subsequently reduced to CH_4

and measured with a flame ionization detector (e.g., Ballach *et al.,* 2001; Chow *et al.,* 2001). The analysis is usually done from filter samples. With the mostly used thermal techniques it is not possible to measure in 'real-time'. Thermal methods are based on the concept to volatilize OC from a sample when heated in the absence of oxygen, whereas oxygen is required for EC combustion (Turpin *et al.,* 2000). The results from different thermal methods agree well for total carbon concentration (the sum of EC and OC), but show large disagreements in the EC and OC fractions (Countess 1990; Birch & Cary 1996; Chow *et al.,* 2001; Yu *et al.,* 2002). One analytical problem is that some organic species (e.g., vulcanized rubber) may produce pyrolytically EC (char or PEC) during the analysis procedure, depending on the thermal and atmospheric conditions in the analyzer (Birch & Cary 1996; Yu *et al.,* 2002). The PEC can then be mistakenly added to the EC fraction of the sample (Kleeman *et al.,* 1999). To correct this artifact, approaches have been developed (e.g., Chow *et al.,* 1993; Birch & Cary 1996) that combine thermal and optical methods. Measurements of either transmittance or reflectance of the filter are used to correct for PEC (Chow *et al.,* 1993; Birch & Cary 1996).

Disagreement on the delineation between EC and OC may also occur, even when an optical correction for PEC is used. This is because different protocols with different operating conditions for the individual steps of analysis have been used (Chow *et al.,* 1993; Chow *et al.,* 2001). The different protocols use, e.g., different levels of temperature and different residence times at the temperature levels. This has led to the conclusion that different methods may cause different results and that OC and EC are operationally defined (Chow *et al.,* 2001). The magnitude of this sensitivity depends on the type of aerosol particles analyzed (Chow *et al.,* 2001; Schauer *et al.,* 2003). To improve the situation, Chow *et al.* (2001) have suggested that the organic composition of the carbonaceous particles should be known in more detail and traceable standards should be made available. However, this is a major task and it is unlikely that it will be completed in the near future (Chow *et al.,* 2001).

Organic carbon can be removed from the sample by solvent extraction (e.g., extraction by an organic solvent like benzene). The OC concentration can then be determined from the solvent and the EC concentration from the original sample. Solvent extraction and analysis by gas chromatography-mass spectroscopy (GC-MS) has also enabled to identify individual organic compounds of OC (e.g., Hangebrauck *et al.,* 1964; Schauer *et al.,* 1999a; 1999b). However, with current methods it is not possible to completely resolve all of the OC mass into concentrations of individual compounds (Cadle & Groblicki 1982; Turpin *et al.,* 2000).

2.3 Discussion

Because of the methodological differences the split between OC and EC can be thought of as operational (Chow *et al.,* 1993; Birch & Cary 1996; Turpin *et al.,* 2000; Chow *et al.,* 2001). Thus, it is difficult to directly compare the results from studies conducted with different methods or even studies with the same basic methodology but with different operating conditions (Hitzenberger 1999; Chow *et al.,* 2001). Thermal methods split the carbonaceous species into elemental and organic fractions based on the thermal evolution of the compounds in the specimen, but the lineation depends on the temperature program (protocol) of the analysis. For example, Chow *et al.* (2001) reviewed several papers reporting measurements of diesel exhaust samples with thermal/optical methods using different protocols and found that

for the same samples the TC concentrations usually agreed within ±5%, whereas the EC within ±20%.

The fundamental difference between the optical and thermal methods is that the optical methods are based on optical properties and not the thermal evolution of the carbonaceous species in the specimen (Chow *et al.,* 1993; Pakkanen *et al.,* 2000; Ballach *et al.,* 2001). Optical methods may measure other light absorbing species as well as elemental carbon and therefore the term black carbon often basically refers to the total light absorbing fraction of the carbonaceous aerosol. However, as discussed in Section 2.4, the terms are also often used as synonyms.

In comparison to thermal methods, optical methods have been found to give different results in certain circumstances (Hitzenberger *et al.,* 1999; Watson & Chow 2002). Hitzenberger *et al.* (1999) observed that for pure BC aerosols the (optical) integrating sphere technique gave 21 percent higher the BC mass concentrations when compared to a thermal technique. For ambient samples the integrating sphere agreed within five percent with a thermal-optical technique. Chow *et al.* (2002) observed that, although highly correlated, the aethalometer (optical) gave consistently 20 to 25 percent higher concentrations in ambient air when compared with analyses made from filters with a thermal optical method.

For solvent extraction it is often unclear what proportion actually is extracted and included in the analysis. Cadle & Groblicki (1982) studied several different solvents for extraction of the organic carbon fraction and found out that of the solvents studied, the benzene-ethanol extraction was most efficient, but removing only 80 percent of the organics extracted by the most efficient thermal method.

The measurements found in the literature for specific components are presented in the following tables. Most of the studies used the thermal method with an optical correction, but also the other methods can be found among the references. The background documentation describing the methodology was not always sufficient to eliminate possible measurement biases. However, care was taken in considering them in the analysis that was used to derive the RAINS emission factors. In addition, it was often found that a major source of variation in emission characteristics was rather the variation in combustion conditions due to differences in, e.g., fuel characteristics, engine operation conditions, designs of the combustion devices. These factors were also carefully reviewed so that an aggregated, best estimate emission factor or emission profile could be derived.

3   Estimating Emissions of PM$_1$, BC and OC

While the general approach for estimating emissions of PM1, BC and OC follows to a large extent the methodology for estimating PM emissions applied by the RAINS model (Lükewille *et al.,* 2001 and Klimont *et al., 2002*), several modifications were necessary to accurately estimate BC and OC components. The sectoral structure for the calculation of emissions remains the same as in the current implementation of the RAINS PM module. The detailed list of distinguished activities is described in Klimont *et al.* (2002) and available from the Web application of the RAINS model (www.iiasa.ac.at/rains).

3.1   Submicron Particles (PM$_1$)

The present framework to estimate PM emissions in the RAINS model (Klimont *et al.,* 2002) was adapted to incorporate submicron particles (PM$_1$). The general concept of calculating emissions for distinguished size classes is extended to include the fraction of PM$_1$, so that now four classes are considered:

submicron fraction (PM$_1$),
fine particles (PM$_{2.5}$),
coarse fraction (PM$_{2.5}$ - PM$_{10}$) and
large particles (PM_>10 m).

The RAINS methodology includes the following three steps (Klimont *et al.,* 2002):

In a <u>first step</u>, country-, sector- and fuel-specific "raw gas" emission factors for total suspended particles (TSP) are derived (for solid fuels burned in large installation the mass balance approach considering ash content is used (see Equation 2 in Klimont *et al.,* 2002); for liquid fuels, industrial processes, residential combustion of solid fuels, and transport emission rates are derived from the literature);
In a <u>second step</u>, "raw gas" emission factors for each of the size fractions are estimated;
In a <u>third step</u>, PM emissions are calculated for the four size fractions (Equation 1):

$$E_{i,y} = \sum_{j,k,m} E_{i,j,k,m,y} = \sum_{j,k,m} A_{i,j,k} ef_{i,j,k,y} (1 - eff_{m,y}) X_{i,j,k,m} \qquad (1)$$

where:

i,j,k,m	Region, sector, fuel, abatement technology;
$E_{i,y}$	Emissions in region *i* for size fraction *y*;
A	Activity in a given sector, e.g. coal consumption in power plants;
ef	"Raw gas" emission factor;
$eff_{m,y}$	Reduction efficiency of the abatement option *m* for size class *y*, and;
X	Actual implementation rate of the considered abatement, e.g., percent of total coal used in power plants that are equipped with electrostatic precipitators.

If no emission controls are applied, the abatement efficiency equals zero (*eff* = 0) and the application rate is one (*X* = 1). In that case the emission calculation is reduced to a simple multiplication of the activity rate by the "raw gas" emission factor.

3.2 Black Carbon (BC) and Organic Carbon (OC)

For calculating BC and OC, two different approaches distinguishing stationary and mobile sources are used.

For *stationary sources*, absolute values of BC and OC emission factors rather than shares of total PM are defined for specific fuels, sectors and combustion techniques. This is based on the assumption that there is no clear relationship between BC and OC emission rates and the ash content of the fuel, but that the type of combustion installation[1] and fuel used have major influence. In principle, Equation 1 remains valid but the meaning of indices changes slightly, i.e., *y* refers to the BC and OC fraction and sector *j* is representing the type of combustion installation for stationary sources only.

Since the emission rates are 'decoupled' from the ash content and consequently independent from the estimates of TSP, PM_{10}, etc., the consistency is safeguarded by comparing the BC and OC rates with estimates of various PM fractions (see also discussion in Section 3.3.1).

For *mobile sources* reported shares of BC and OC in measured total PM, PM_1, or total carbon were used and further recalculated into share of TSP. Again, Equation 1 is used with *y* referring to BC and OC and *j* representing transport sub-sectors. Verification assured that the sum of BC and total organic matter (OM) does not exceed PM_1 or $PM_{2.5}$, where OM was estimated as OC times a factor of 1.3 to 1.7 (see discussion in Section 4.1.1.2).

3.3 Emission Control Options

In addition to the obvious "structural changes" that lead to a lower consumption of emission generating fuels, there are several end-of-pipe options for reducing particulate matter emissions. The PM removal efficiencies of these options as well as their applicability are discussed in detail in Klimont *et al.* (2002). This section lists the major categories of options distinguished and discusses the removal efficiencies related to PM_1, BC and OC for stationary and mobile sources.

3.3.1 Stationary Sources

In the interest of keeping a European-scale analysis manageable, the RAINS model considers a limited number of emission control options reflecting groups of technological solutions with similar emission control efficiencies and costs. For large boilers in industry and power stations, and for control of industrial process emissions, five options are distinguished:

- Gravity / inertial settlers;
- Cyclones (centrifugal separators);
- Wet scrubbers;
- Electrostatic precipitators;
- Fabric, packed, bed or rigid barrier filters;

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[1] The type of combustion installation is reflected by the RAINS PM sectoral structure, distinguishing between residential (fireplaces, stoves, boilers, etc.), grate, fluidized bed, pulverized coal, and wet bottom boilers.

In addition, RAINS includes a non end-of-pipe measure for industrial and residential emission sources:

- Regular maintenance of oil fired industrial and residential boilers.

For wood burning, which is a major source of PM emissions, improved burning technologies are considered for new stoves, fireplaces, etc.:

- Improved wood burning technologies, e.g., catalytic and non-catalytic inserts, primary and secondary air deflectors.

Only few studies report specific removal efficiencies of submicron and carbonaceous particles for individual control technologies. However it can be expected that the efficiencies for submicron particles are lower than for the larger size fractions, since the removal mechanisms, i.e., inertial impaction, gravitational settling and also Brownian motion are weakest in the accumulation mode, which dominates the PM_1 mass (e.g., Hinds 1999).

It is important to verify that the emission characteristics remain internally consistent even after emission controls, i.e., the $PM_{2.5}$ emissions are higher or equal PM_1 emissions. This was done in two steps: first the technology-specific removal efficiencies for PM_1, BC and OC were derived; in a second step the abated emission factors of PM_1, total carbon (TC, sum of BC and OC) and the sum of BC and OM were compared with those for fine particles. If discrepancies were found, emission factors or control efficiencies were reviewed and adjusted

The specific removal efficiencies assumed in the RAINS model for these control options are presented in Table 3.1.

Table 3.1: Removal efficiencies for PM$_1$, black carbon (BC), and organic carbon (OC) assumed in RAINS.

Control technology	Removal efficiency [%]		
	PM$_1$	BC	OC
Multicyclone	11.00	11.00	11.00
Wet scrubbers	95.00	72.36	90.00
Fabric filters	99.99	99.99	99.99
Electrostatic precipitator, 1 field	91.96	91.10	96.00
Electrostatic precipitator, 2 fields	95.40	94.05	98.00
Electrostatic precipitator, 3 fields and more	98.60	96.98	99.50
Wet electrostatic precipitator	98.86	98.00	99.70
Oil fired boilers, regular maintenance	21.52	5.00	10.00
Good practice (industrial process), stage 1 (fugitive)	20.00	5.00	10.00
Good practice (industrial process), stage 2 (fugitive)	65.33	10.00	30.00
Catalytic inserts (wood fired fireplaces and stoves)	79.79	25.00	95.00
Non-catalytic inserts (wood fired fireplaces and stoves)	62.60	5.00	35.00
New coal fired stoves, stage 1	20.00	1.00	25.00
New coal fired stoves, stage 2	42.86	5.00	55.00
New coal fired boilers in domestic sector	40.00	10.00	65.00
New biomass fired boilers, domestic (wood chips, pellets)	89.00	89.00	89.00

3.3.2 Mobile Sources

Primary particle emissions from mobile sources have two entirely different origins: exhaust, i.e., due to fuel combustion, and non-exhaust emissions, i.e., tire and brake wear and road abrasion. The options considered in the RAINS PM model for control of vehicle emissions are listed in Table 3.2 and Table 3.3.

The reduction efficiencies for PM$_1$, BC and OC in the following tables were calculated based on the PM reduction efficiencies necessary to meet the "Euro" emission standards (documented in Klimont *et al.,* 2002) and assuming shares of PM$_1$, BC, and OC in controlled PM emissions (which are different from the uncontrolled vehicles) as discussed in Section 4.1 and summarized in, e.g., Table 4.7.

Table 3.2: Assumed removal efficiencies of control options for diesel vehicles [%].

Vehicle category, control technology /EU standards [a]		PM$_1$	BC	OC
Passenger cars and light duty vehicles	Euro I – 1992 / 94	31.39	18.75	57.61
	Euro II – 1996	72.56	67.50	83.04
	Euro III – 2000	79.94	76.25	87.61
	Euro IV – 2005	85.22	82.50	90.87
	Euro V – post 2005, stage 1	97.89	97.50	98.70
	Euro VI – post 2005, stage 2	98.94	98.75	99.35
Heavy duty trucks and buses	Euro I – 1992	32.32	33.33	48.80
	Euro II – 1996	72.51	72.92	79.20
	Euro II – 1998	72.51	72.92	79.20
	Euro III – 2000	80.97	81.25	85.60
	Euro IV – 2005	95.77	95.83	96.80
	Euro V – 2008	95.77	95.83	96.80
	Euro VI – 2008 – post 2008	99.79	99.79	99.84
Vehicles in construction and agriculture	Stage 1 – 1998	43.40	43.40	43.40
	Stage 2 – 2000/02	74.45	74.45	74.45
	Stage 3A – 2006/07	74.45	74.45	74.45
	Stage 3B – 2010/11	98.20	98.20	98.20
	Stage 4	98.30	98.30	98.30
	Stage 5	98.40	98.40	98.40
Rail and inland waterways	Stage 1	33.30	33.30	33.30
	Stage 2	50.00	50.00	50.00
	Stage 3	85.00	85.00	85.00
	Stage 4	97.00	97.00	97.00
	Stage 5	97.05	97.05	97.05
	Stage 6	99.80	99.80	99.80
Maritime activities, ships (combustion modification)	Medium vessels	17.70	2.70	38.46
	Large vessels (fuel oil)	20.00	23.08	53.85
	Large vessels (diesel oil)	17.70	2.70	38.46

[a] Directive 98/69/EC (Diesel Cars and Light-Duty Trucks); Directive 88/77/EEC (Heavy- Duty Diesel Truck and Bus Engines).

Table 3.3: Assumed removal efficiencies of control options for gasoline vehicles [%].

Vehicle category, control technology /EU standards [a]		PM$_1$	BC	OC
Passenger cars and light duty vehicles (4-stroke)	Euro I	42.25	8.33	51.05
	Euro II	42.25	8.33	51.05
	Euro III	80.65	47.20	89.20
	Euro IV	80.65	47.20	89.20
	Euro V – post 2005, stage 1	81.73	50.13	89.80
	Euro VI – post 2005, stage 2	82.80	53.07	90.40
Passenger cars and light duty vehicles (GDI – gasoline direct injection engines)	Euro III	81.57	76.15	84.16
	Euro IV	81.57	76.15	84.16
	Euro V – post 2005, stage 1	82.59	77.48	85.04
	Euro VI – post 2005, stage 2	83.61	78.80	85.92
Motorcycles, mopeds and off-road engines (2-stroke)	Stage 1	57.75	35.00	71.11
	Stage 2	70.00	40.00	86.67
	Stage 3	84.00	60.00	94.07
Motorcycles (4-stroke)	Stage 1	42.25	8.33	51.05
	Stage 2	80.65	47.20	89.20
	Stage 3	81.73	50.13	89.80
Heavy duty vehicles (spark ignition engines)	Stage 1	42.25	8.33	51.05
	Stage 2	80.65	47.20	89.20
	Stage 3	81.73	50.13	89.80

[a] Directive 98/69/EC (Diesel Cars and Light-Duty Trucks); Directive 88/77/EEC (Heavy- Duty Diesel Truck and Bus Engines).

4 Emission Source Categories

This chapter provides brief characteristics of emission sources and a detailed account of literature studies reporting actual measurements of submicron and carbonaceous particles. Measurement results are reported as close as possible to the original material limiting modification of units (apart from converting miles and gallons into kilometers and liters) and avoiding recalculation of shares (e.g., to express everything as percentage of fine particles or total carbon). However, in order to derive values that can be further used in the RAINS model, the original data require "normalization". This is not always straightforward since studies represent wide temporal (from 1960s to current time) and spatial (US, Europe, Asia, and Australia) variations and results are reported in various units. For further analysis, all shares were converted into shares in total PM, making assumptions about changes in fuel efficiency between different vintages and using standard fuel parameters, e.g., density, heating value (e.g., Table 4.2). All conversions were done using original material (if available), otherwise using conversion rates of the current RAINS model and provided by the International Energy Agency (IEA). The original data, i.e., emission factors as reported in the considered studies, are provided in Annex 1 and 2 at the end of this document. The tables with recalculated values are marked accordingly.

As already discussed in Section 2, a number of measurement methods are used to estimate carbonaceous particles. Information about the method used is very important for a proper interpretation of the results and therefore it is included in the tables where literature data is compared. The abbreviations used in this document are summarized in Table 4.1.

Table 4.1: Abbreviations of carbon analysis methods used in the tables

Name	Abbreviation	Example references
Thermal methods	T	Shi *et al.,* 2000
Thermal method, modified to take into account the charring effect	T (mod.)	Muhlbaier Dasch, 1982; Muhlbaier & Williams, 1982
Thermal methods with an optical correction based on reflectance or transmittance of light	TO	Williams *et al.,* 1989ab; Chow *et al.,* 1993; Birch & Cary 1996; Ålander 2000; Chow *et al.,* 2001
Optical methods	O	Hansen *et al.,* 1984; Hitzenberger *et al.,* 1999; Ballach *et al.,* 2001
Solvent extraction	SE	Cadle & Groblicki, 1982
Electron microscopy	EM	Fisher *et al.,* 1978

4.1 Mobile Sources

Mobile sources include exhaust emissions from different types of engines as well as non-exhaust emissions like tire wear, brake lining and road wear. The exhaust emission sources have been further divided according to the fuel and engine type. In order to recalculate originally reported values (g/kg or g/km) into the RAINS units for emission factors, i.e., mg/MJ (for combustion sources), assumptions about fuel characteristics and unit fuel

consumption had to be made if the literature source had no such information. Typical values are shown in Table 4.2.

Table 4.2: Default values used in recalculation of originally reported measurements into native RAINS units.

Parameter	Unit	Fuel	
		Gasoline	Diesel
Density	[kg/l]	0.75	0.85
Heat value	[MJ/kg]	44.8	42
Fuel consumption – Light duty vehicles	[l/100km]	8 - 12	7 - 10
Fuel consumption – Heavy duty vehicles	[l/100km]	~ 40	~ 30

4.1.1 Exhaust Emissions

Exhaust emissions of diesel and spark-ignition engines have been extensively studied, and much information on size fractions and chemical composition of particulate emissions are available. Usually the emission factors are measured using driving cycles (e.g., for the USA FTP or US06 and for Europe ECE/EUDC), which simulate the typical driving conditions either in urban or highway environments with, e.g., changing speed and acceleration. Emissions have been observed to vary between different cycles (Maricq *et al.,* 1999ab; Cadle *et al.,* 2001).

4.1.1.1 Diesel Engines

Light and heavy duty diesel vehicles and off-road machinery are important sources of primary submicron and carbonaceous particles (e.g., Hamilton & Mansfield 1991; Gray & Cass 1998; APEG 1999). In western countries, they constitute a major source of black carbon (Hamilton & Mansfield 1991; Gray & Cass 1998) and one of the major anthropogenic sources of submicron particles (APEG 1999). Diesel exhaust particles are mostly submicron agglomerates of small (10-80 nm in diameter) carbonaceous particles.

Particulate emissions from diesel engines are in general higher than the emissions from spark ignition engines. However, the emission rates have decreased so that the newer diesel vehicles have significantly lower emission rates than the older ones, due to introduction of after-treatment of the exhaust gases (CONCAWE 1998; Durbin *et al.,* 1999; Yanowitz *et al.,* 2000). Apart from the age of the engine, the concentration of particles emitted from a diesel engine may be affected by several other factors. Humidity and temperature in general affect emissions (Yanowitz *et al.,* 2000), e.g., in cold conditions (cold start) emissions are higher than in warmed-up conditions. This is possibly due to the larger size of particles emitted (CONCAWE 1998). Also increasing engine load increases emissions (Kerminen *et al.,* 1997; Morawska *et al.* 1998; Burtscher 2000). High altitude has been observed to increase emissions because the lower barometric pressure lowers the effective air to fuel ratio in the engine at idle and low engine speeds. Vehicle fleets typically include so-called high emitting vehicles, which have significantly higher emissions than the fleet average. This might be the result of, e.g., poor maintenance of an engine.

Diesel exhaust particles are mainly submicron and most of the mass emitted is found in the mode between 0.01-1 micrometers (Lighty *et al.,* 2000). Also a nanoparticle mode is found,

which has the largest number concentration but represents only little of the emission mass. Yanowitz *et al.* (2000) studied the difference in emission concentrations between two- and four-stroke diesel engines. The difference was statistically not significant, yet they stated that four-stroke engines can produce lower PM emissions.

The submicron mode, which dominates emissions from diesel engines, consists primarily of BC and OC (Lowenthal *et al.*, 1994; Kerminen *et al.*, 1997; Cadle *et al.*, 1999; CONCAWE, 1998). In general, diesel engines emit a larger BC fraction (BC/OC usually >1) than gasoline engines (BC/OC <1), although there is considerable variation between individual vehicles (Burtscher *et al.*, 1998; Gillies & Gertler, 2000). Burtscher *et al.* (1998) observed that the BC content of particles from a diesel engine increases with increasing load.

The type of engine and the control technologies used affect the emissions characteristics. In diesel engines exhaust filters (or traps) and catalysts may be used to reduce emissions (Kittelson, 1998). The control devices can also affect the chemistry of the emissions. Kerminen *et al.* (1997) measured the same vehicle with and without a catalytic converter. The catalytic converter lowered particulate emissions by 10 to 30 percent and removed OC more efficiently than BC. OC may have been removed better because smaller particles with higher OC to BC ratios penetrate the converter more easily or because the converter removed condensable organics from the exhaust thus lowering the amount of organics condensing into the particulate phase after the converter. There is some indication that the gasoline direct injection technique (GDI) also lowers the OC fraction compared to a port fuel injection (PFI) engine (Lappi *et al.*, 2001b).

A summary and discussion of the emission factors and shares of submicron, BC and OC particles in total PM for diesel light and heavy duty vehicles is provided in the following sections.

Light Duty Vehicles (LDV)

This category includes passenger cars and light duty trucks up to 3.5 t GWV. Table 4.3 shows emission factors for submicron PM for LDV. All three studies (Williams *et al.*, 1989b; CONCAWE 1998; Norbeck *et al.*, 1998a) give similar estimates for no-control vehicles, i.e., around 80 to 100 mg/MJ. In terms of g/km (see ANNEX 1 Mobile Sources) the differences (from 0.324 in Norbeck *et al.* (1998a) to around 0.22 in both CONCAWE (1998) and Williams *et al.*, 1989b) can be explained by different vehicle ages and fuel consumptions. A comparison with the current RAINS TSP values shows that the reported PM_1 represents about 80 to 90 percent of TSP. The reviewed studies (Table 4.4) show similar ranges of PM_1, i.e., shares of 86 to 93 percent of PM_1 in TSP. Based on the analysis of both absolute numbers and shares reported, a PM_1 share in TSP of 90 percent was assumed.

For controlled vehicles, the emission factors for PM_1 vary between 17 to 33 mg/MJ with an average of 25 mg/MJ. Comparison to the uncontrolled emission factor (~90 mg/MJ) indicates a reduction efficiency of about 72 percent.

Table 4.3: Emission factors of PM_1 for light duty diesel vehicles [mg/MJ] [R].

Source	PM_1	Remarks
Norbeck *et al.,* 1998a ; Durbin *et al.,* 1999	107	US, models mainly from the 1980s
CONCAWE, 1998	33	ECE+EUDC cycles
	79	DI, without catalyst
Kerminen *et al.* 1997	19	no catalyst, FTP-cycle
	17	catalyst, FTP-cycle
Williams *et al.,* 1989b	79	g/kg, Australia, models 1978-1986

[R] RECALCULATED – Original values can be found in the Annex (Table A 1)

Table 4.4: Summary of PM_1 shares in TSP for light duty diesel vehicles [%].

Source	PM_1	Remarks
Norbeck *et al.,* 1998a; Durbin *et al.,* 1999	93.1	US models mainly from the 1980s, FTP-cycle
PART5 (US EPA)	86	percent of PM_{10}
Williams *et al.,* 1989b	86	Australia, models 1978-1986
CONCAWE, 1998	86.3	ECE+EUDC cycles
	82.0	DI, without catalyst

For BC emissions from uncontrolled vehicles (Table 4.5) the picture is fairly consistent, although there are only few studies that could be used (Williams 1989b and Norbeck 1998a). The emission factor for individual vehicles varies between 20 and 100 mg/MJ with an average in both studies of approximately 50 mg/MJ. Comparing this value to the RAINS TSP numbers gives a share of about 40 to 60 percent of TSP. Converting all reported shares (Table 4.6) relative to TSP (assuming that TC share is on average about 80 percent - if not given in a specific study), a range between 35 to 84 percent is observed. However, the higher shares of BC (above 70 percent) are typically for more modern vehicles (studies from 1999 and 2000), while the lower values (below 50 percent) reported refer to only two vehicles. All compared studies used the TO measurement method to determine BC, giving an average BC share of 60 percent in total PM.

Lambrecht and Höpfner (2000) indicate that for vehicles equipped with advanced emission control technology BC the emission factor does not change with the introduction of oxidation catalysts. However, the new technologies that are required to comply with EURO I, II, III, etc. might result in overall lower emissions of PM with a higher share of BC (Table 4.6). This share is estimated at about 75 percent in TSP. This is also confirmed by Kerminen *et. al* (1997) and Ålander (2000).

The average values reported for OC differ significantly, although only few measurements were found, i.e., Williams *et al.* (1989b) about 21 mg/MJ and Norbeck *et al.* (1998a) 51 mg/MJ (Table 4.5). However, especially the second study indicates a very large spread of OC shares in PM for individual vehicles, so that the range reported by Williams *et al.* (1989b) sits well inside it. Comparing these average emission rates to the RAINS TSP factors results in OC shares in TSP of 45 and 20 percent for Norbeck *et al.* (1998a) and Williams *et al.* (1989b), respectively. The reported average OC shares (Table 4.6) are fairly consistent, i.e., between 20 and 30 percent in TSP. Results for particular vehicles and tests combinations (speed/load) show a significantly larger spread, ranging from 15 to 60 percent. In this study it

was assumed that OC represents 23 percent of total PM emissions from uncontrolled light duty vehicles (Table 4.7).

The emissions of organic compounds are expected to decline with the introduction of oxidation catalysts (Lambrecht and Höpfner, 2000). The results of Kerminen *et. al* (1997) and Ålander (2000) indicate lower OC shares in controlled PM exhaust from diesel vehicles. For this study, an OC share (in total PM) of 15 percent was assumed for LDVs equipped with oxidation catalysts and other PM control technologies (Table 4.7).

Table 4.5 also includes results from a tunnel study (Israel *et al.,* 1996). The measured BC and OC are significantly lower than in other studies. One of the possible explanations is a significant share of gasoline vehicles (characterized typically by much lower emissions) passing the tunnel and it is possible that this study might not be representative for light duty diesel cars. Therefore it was not used for deriving numbers for the purposes of RAINS.

Table 4.5: Emission factors of BC and OC for light duty diesel vehicles [mg/MJ] [R].

Source	BC	OC	Remarks	Method
Norbeck *et al.* 1998a ; Durbin *et al.* 1999	52	51	US, models mainly from the 1980s	TO
Israel *et al.,* 1996	4	3	Tunnel measurements	T
Williams *et al.,* 1989b	52	21	Australia, models 1978-1986	TO

[R] RECALCULATED – Original values can be found in the Annex (Table A 2)

Table 4.6: Summary of BC and OC shares in TSP for diesel light duty vehicles [%]

Source	BC	OC	Remarks	Method
US studies				
Cadle *et al.,* 1999	58	42	% of TC, summer and winter shares	TO
	65	35	UDDS & FTP cycles in high altitude (1600 m)	
Gillies & Gertler, 2000	66 [a]	19 [a]	% of $PM_{2.5}$, CE-CERT-database	TO
Norbeck *et al.,* 1998a ; Durbin *et al.,* 1999	50 [a]	23 [a]	Mainly 1980s models, FTP-cycle	TO
Watson *et al.,* 1990	~80	~20	% of $PM_{2.5}$, FTP-cycle in high altitude (1600 m)	TO
Williams *et al.,* 1989b	56.8	23.2	Australia, models 1978-1986	TO
European studies				
Kerminen *et al.,* 1997	75	25	% of TC, FTP-cycle	T
	69	31	% of TC, non-catalyst FTP-cycle	T
Lambrecht & Höpfner, 2000	46-84			(b)
Ålander, 2000	72-85	15-28	% of TC, 1997 TDI engine with oxidation catalyst (higher load decreased fraction of OC), results without artifact correction	TO
	41-78	22-59	% of TC, 1988 diesel car, results with artifact correction	

[a] Calculated from the share of total carbon and BC:OC ratio.
[b] This study reviews other measurements and the range given for BC represents six studies done between 1988 and 1999 where vehicles of different age (1978-98) and type of control were tested.

Table 4.7: Shares and ranges[2] of values of BC, OC and PM$_1$ as used in the RAINS model.

	Share in TSP [%]			Value ranges [mg/MJ]		
	BC	OC	PM$_1$	BC	OC	PM$_1$
No Control	60	23	90	51 – 77	20 – 29	77 – 115
Controlled [a]	75	15	95	25 – 37	5 – 8	32 – 48

[a] Although the given shares are assumed for all control technologies, the value range refers to an example for the EURO I standard only.

Heavy Duty Vehicles (HDV)

Table 4.8 provides PM$_1$ emission factors for HDV vehicles. For uncontrolled engines the emission factors (converted into per energy units) vary largely between about 21 mg/MJ (Norbeck *et al.,* 1998b; only light heavy duty vehicles) and 38 mg/MJ (Hildemann *et al.,* 1991) up to 125 mg/MJ Williams *et al.* (1989b). The latter, however, reported a large deviation between individual vehicles, i.e., from 40-400 mg/MJ or 40-170 mg/MJ when high emitters were excluded. It has to be noted that the measurements by Williams *et al.* (1989b) were made from an agglomeration/settling duct to simulate the effect of emissions on visibility. The agglomeration duct allows the bigger particles to settle out and the fine particles to agglomerate into the accumulation mode. This can lead to an overestimation of the PM$_1$ share and possibly also the share of OC due to condensation of organics.

Taking the lower middle of the range of emission factors from Williams *et al.* (1989b) and excluding the high emitters gives an average emission factor of 65 mg/MJ. Since Hildemann *et al.* (1991) reported 38 mg/MJ, based on these numbers the average emission factor for PM$_1$ is estimated to be 52 mg/MJ. A comparison of this number with the current RAINS emission factor for total PM (about 60 mg/MJ) results in a PM$_1$ share in TSP of about 87 percent. The shares of PM$_1$ in PM emissions found in the reviewed studies (Table 4.9) varied from 82 to above 90 percent, confirming that the derived share of 87 percent (in TSP) seems to be a good estimate for PM$_1$.

The controlled emission factors for submicron particles emitted by heavy duty vehicles range from about 7 mg/MJ (Norbeck *et al.* 1998b), 12 mg/MJ (Shi *et al.,* 2000; Ojanen *et al.,* 1998) to 21 mg/MJ (Schauer *et al.,* 1999b). From the description of the tested vehicles in the above studies it was concluded that they can be considered representative for EURO I to EURO II PM emission levels. The TSP control efficiency for EURO I and II HDV vehicles in RAINS are estimated at 35 and 74 percent, respectively, resulting in country-specific TSP emission factors (controlled) from 11 to 35 mg/MJ. Lack of information about the actual level of control in the measurements and their relationship to EURO I and EURO II makes it difficult to relate the current RAINS values to these measurements. However, assuming that vehicles tested in Shi *et al.* (2000) and Ojanen *et al.* (1998) resemble EURO II standards allows the conclusion that the PM1 fraction is exceeding 90 percent. Similar fractions were reported by Norbeck *et al.* (1998b) and Shi *et al.* (2000) in their size distribution measurements for

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[2] Ranges rather than single numbers are given as RAINS includes country-specific emission factors for PM emissions; the same applies to other vehicle categories.

vehicles from the mid 1990's (Table 4.9). Based on this discussion, a share of 92 percent of PM_1 in TSP is assumed in RAINS for controlled heavy duty vehicles.

Table 4.8: Emission factors for PM_1 for diesel heavy duty vehicles [mg/MJ] [R]

Source	PM_1	Remarks
Hildemann *et al.,* 1991	38	PM_2, US models 1987
Lowenthal *et al.,* 1994	58	$PM_{2.5}$, US without particulate trap
	12	with particulate trap
Schauer *et al.* 1999	21	$PM_{1.8}$, medium duty, 1995 models
Norbeck *et al.,* 1998b	21	US 1982-1996 medium- and light heavy duty
	32	Pre-1992 models, without oxidation catalyst
	7	Models 1994-1996, with oxidation catalyst
Williams *et al.,* 1989b	160	TSP, Australia, 1978-1986 models, averages with and
	125	without the high emitter
Shi *et al.* 2000	12	Mainly submicron, US 1995 certified test engine
Ojanen *et al.* 1998	11	TSP, European

[R] RECALCULATED – Original values can be found in the Annex (Table A 3)

Table 4.9: Summary of PM_1 shares in TSP (unless otherwise stated) for diesel heavy duty vehicles [%].

Source	PM_1	Remarks
APEG, 1999	85	of PM_{10}
	94	of $PM_{2.5}$
Norbeck *et al.,* 1998b	93.5	US models 1982-1996
	95	Pre-1992 models, without oxidation catalyst
	91	1994-1996 models, with oxidation catalyst
PART 5	86	of PM_{10}
Shi *et al.,* 2000	>90	US 1995 certified test engine
Williams *et al.,* 1989b	82	Australia, 1974-1985 models

For BC the average uncontrolled emission factors (for pre-1990 vehicles without oxidation catalyst) range from 15 mg/MJ to 49 mg/MJ (Hildemann *et al.,* 1991; Lowenthal *et al.,* 1994; Norbeck *et al.,* 1998b; Williams *et al.,* 1989b, Table 4.10). Based on the average values from the studies, an emission factor of 30 mg/MJ is applied to represent the unabated BC emissions from heavy duty vehicles. A comparison with the current TSP emission factor in the RAINS model yields a share of 40 to 60 percent of TSP.

Converting all given shares (Table 4.11) relative to TSP shows a range from 22 percent (Shi *et al.,* 2000) up to 65 percent (Gillies & Gertler 2000). Excluding the studies reporting controlled emissions from medium and light HD vehicles (Schauer *et al.* 1999 and Norbeck *et al.* 1998b), the average share emerges at approximately 45 percent for BC in TSP. The evaluation of reported emission factors, however, results in a share of 50 percent. Taking into account that studies based on data of more vehicles (e.g., Gillies & Gertler 2000) have a tendency to give higher shares for BC, it was decided to use in RAINS the middle of the range, 48 percent BC in TSP, for uncontrolled HDV. All studies used thermal-optical (TO) measurement method to determine BC.

Two studies reported controlled BC emission factors (Norbeck *et al.,* 1998b and Schauer *et al.* 1999). They measured medium and light HDVs and observed values around 6 mg/MJ (Norbeck *et al.,* 1998b; Schauer *et al.,* 1999). Comparing these values with the average controlled TSP emission factors in RAINS, a share of 50 percent of BC in TSP was derived. It should be noted, however, that these numbers might not represent the average HDV fleet and should be further reviewed when additional studies are available.

Table 4.10: Emission factors for BC and OC for diesel heavy duty vehicles [mg/MJ] [R]

Source	BC	OC	Remarks	Method
Hildemann *et al.,* 1991	15	12	PM_2, US models 1987	TO
Israel *et al.* 1996	22	13	TSP, Europe tunnel measurements	T
Lowenthal *et al.,* 1994	30	21	$PM_{2.5}$, US, without particulate trap	TO
	2	8	with particulate trap	
Schauer *et al.* 1999	6	4	$PM_{1.8}$, medium duty, 1995 models	TO
Norbeck *et al.,* 1998b	15	8	TSP US medium- and light heavy duty	TO
	18	8	Models pre 1992, without oxidation catalyst	
	6	1	Models 1994-1996, with oxidation catalyst	
Williams *et al.,* 1989b	63	89	TSP, Australia models ranging 1974-1985, averages with and without the high emitter	TO
	49	69		
Kirchstetter *et al.,* 1999	31	12	$PM_{2.5}$, US tunnel measurements	TO
Miguel *et al.,* 1998	34		$PM_{1.3}$, US Tunnel measurements	TO
Shi *et al.* 2000	3	4	TSP, US 1995 certified test engine, 1600 and 2500 rpm	T
	5	4		

[R] RECALCULATED – Original values can be found in the Annex (Table A 4)

An evaluation of the results reported by Norbeck *et al.* (1998b) suggests that the more modern light/medium heavy duty vehicles equipped with oxidation catalysts had higher shares of BC in total carbon (63-93 percent). Using a share of 70 percent of TC in emissions as reported by Shi *et al.* (2000) to approximate BC in emissions observed by Norbeck *et al.* (1998b) results in an average share of 57 percent of BC in PM. Schauer *et al.* (1999) and Shi *et al.* (2000) both report lower shares of BC in emissions, about 30 to 45 percent, respectively. However, they both state that up to 30 percent of the mass of emissions remains unexplained for their chemical species; one possible explanation might be water that is retained in the samples despite desiccation. Scaling up the shares reported by Schauer *et al.* (1999) and Shi *et al.* (2000) results in a range from 40 to 60 percent of BC in PM emissions. A share of 50 percent of BC in TSP is used for controlled emissions in RAINS.

The reported OC emission factors for uncontrolled HD vehicles (Table 4.11) ranged from about 10 mg/MJ (Hildemann *et al.,* 1991; Norbeck *et al.,* 1998b) to 69 mg/MJ (Williams *et al.,* 1989b). However, in the study by Williams *et al.* (1989b) sampling was done from an agglomeration/settling duct and an enhanced condensation of organics may has affected the share of OC in emissions. Giving less weight to the result from Williams *et al.* (1989b), an average of 20 mg/MJ was derived. This estimate is also supported by Lowenthal *et al.* (1994) reporting an emission factor of 21 mg/MJ, and by tunnel measurements (Kirchstetter *et al.,* 1999; Israel *et al.,* 1996) reporting values between 12 and 13 mg/MJ. It is also in line with the BC emission ratio (BC/OC = 30/20 = 1.5), since all of the studies, except Williams *et al.*

(1989b), reported BC/OC ratios larger than 1, i.e., 1.2 to 2.6. Comparing the derived emission rate for OC (20 mg/MJ) with the current average TSP value in the RAINS model (about 60 mg/MJ) gives a share of 33 percent.

The fraction of OC observed in the studies varied from 16 to 45 percent when converted into shares of TSP. All studies reported a high variation between individual vehicles. Taking these into account, the average share (excluding light and medium HD) is estimated at 27 percent. Taking further into account that the analysis of the emission factors reported in the literature gave the share of 33 percent (see discussion above), a share of 30 percent of OC in TSP is used for uncontrolled emissions from HDV.

Table 4.11: Summary of BC and OC shares in TSP (unless otherwise stated) for diesel heavy duty vehicles [%].

Source	BC	OC	Remarks	Method
Gillies & Gertler, 2000	54	30	of TC, US SPECIATE-database	Several
	75	19	US NFRAQS-database	TO
Hildemann et al., 1991	40.5	32.6	of PM_2, US models 1987	TO
Kirchstetter et al., 1999	51	20	of $PM_{2.5}$, US tunnel measurements	TO
Lowenthal et al., 1994	51	37	of $PM_{2.5}$, US without particulate trap	TO
	17	68	with particulate trap	
Norbeck et al., 1998b	64.0	36.0	of TC, US models 1982-1996	TO
	53.0	47.0	Pre-1992 models, without oxidation catalyst	
	80.7	19.3	Models 1994-1996, with oxidation catalyst	
Schauer et al., 1999	30.8	19.7	of $PM_{1.8}$, medium duty, 1995 models	TO
Shi et al., 2000 *(US 1995 certified test engine)*	33.9	20.4	1600 rpm, 100% load	T
	25.9	37.2	1600 rpm, 50% load	
	24.6	48.1	1600 rpm, 25% load	
	51.5	20.4	2600 rpm, 100% load	
	47.3	24.1	2600 rpm, 50% load	
	35.2	41.6	2600 rpm, 25% load	
Watson et al., 1994	32.9	40.1	of $PM_{2.5}$, US PHDIES-profile	TO
Williams et al., 1989b	32.8	45.2	of TC, Australian buses and trucks, models 1974-1985	TO

The studies by Norbeck et al. (1998b) and Schauer et al. (1999) were used to derive OC emission factors for controlled HDVs. They reported emission rates from 1 mg/MJ (Norbeck et al., 1998b) to 4 mg/MJ (Schauer et al., 1999). The average of these values represents about 24 percent of the controlled TSP emission factor in RAINS. These studies and also Shi et al. (2000) report shares of OC in PM emissions. Based on Shi et al. (2000), the TC share was estimated at about 70 percent. This share was used also for converting OC percentage reported by Norbeck et al. (1998b) to refer to TSP. The resulting range of OC in TSP was 14 to 35 percent, with an average of 24 percent. Since the analysis of the measured emission factors resulted in a similar percentage, this share is used in RAINS to represent OC in emissions from controlled HDV (Table 4.12).

Information about the share of TC in PM emissions is also available and the discussion in this section compares the derived shares with the observations presented in the studies. Based on the derived average emission rates for uncontrolled vehicles and comparing with the RAINS estimates of TSP and $PM_{2.5}$, the TC (the sum of BC and OC) constitutes about 78 percent of TSP and about 81 percent of fine particles. The BC/OC ratio is about 1.6. This is consistent with the available literature, which reports BC and OC representing typically 70 to 90 percent of fine particles with BC/OC ratios ranging from 1.2 to 2.6.

For vehicles equipped with emission controls, the estimated TC constitutes about 74 percent of TSP with a BC/OC ratio of about 2.1. This is in the middle of the large range quoted in the literature. E.g., Shi *et al.* (2000) reports the TC share varying from 54 to 77 percent of PM emissions and the BC/OC ratio from 0.5 to 4.2. The lower share of TC in PM for controlled vehicles (e.g., 74 for controlled versus 78 percent for uncontrolled) might be explained by a more efficient removal of organic compounds compared to inorganic material. Also a number of studies (e.g., Norbeck *et al.,* 1998a; 1998b) report typically higher shares of OC for higher particulate emitting vehicles.

Table 4.12: Shares and ranges of values of BC, OC and PM1 as used in the RAINS model.

	Share in TSP [%]			Value ranges [mg/MJ]		
	BC	OC	PM_1	BC	OC	PM_1
No Control	48	30	87	24 – 34	15 – 21	43 – 61
Controlled [a]	50	24	92	16 – 23	8 – 11	30 – 42

[a] Although given shares are assumed for all control technologies, the value range refers to an example for the EURO I standard only.

4.1.1.2 Spark-ignition Engines

Although diesel engines emit higher concentrations of particles than spark-ignition engines, the vehicle kilometers traveled by spark-ignition engines can exceed that traveled by diesels. The situation varies between countries, but the emissions from gasoline powered engines can make a significant contribution to ambient concentrations (Ristovski *et al.,* 1998; Kayes *et al.* 1999a). As for diesel engines, the emissions are mainly submicron and consist of carbonaceous particles with the BC/OC ratio usually lower than one (Ristovski *et al.,* 1998; CONCAWE, 1998; Norbeck *et al.,* 1998c; Maricq *et al.,* 1999b; Gillies & Gertler 2000).

Several parameters affect particle formation in spark-ignition engines (Maricq *et al.,* 1999b). Similarly to diesel vehicles, later models usually emit less PM than earlier ones. Ristovski *et al.* (1998) studied the number concentrations and size distributions of gasoline powered (both catalyst and non-catalyst) cars and LPG powered passenger vehicles. They found a relationship between emissions and the age/generation of the vehicles, with lower emissions for the later models.

The different fuel types used in spark ignition engines, e.g., leaded, unleaded, CNG, LPG, can have a large effect on emission levels and chemistry. Durbin *et al.* (1998) concluded that the emissions from engines fueled with CNG and methanol fuel were comparable to those of their gasoline counterparts. For leaded fueled cars Ristovski *et al.* (1998) reported an order of

magnitude higher number concentrations than for unleaded and LPG powered vehicles. Higher emissions are also observed in terms of particle mass; Hildemann *et al.* (1991) measured five times higher mass emissions of particles for cars using leaded fuel. They also reported that cars using unleaded fuel emitted a higher share of elemental carbon, but only half as much on an absolute basis (in mass emissions rate).

Another factor that significantly affects emissions is the engine technology. Hall & Dickens (1999) studied gasoline direct injection (GDI) engines and found that the number of particles emitted was much higher than in FPI (fuel port injection) gasoline engines, more in line with diesel engines both in number and size. Lappi *et al.* (2001a, 2001b) reported preliminary results from the measurements of BC and OC in particulate emissions from a GDI engine with average BC/OC ratio exceeding one; this measurement is similar to those of diesel engines and FPI gasoline engines equipped with state-of-the-art abatement.

Two-stroke gasoline engines are reported to have considerably higher emissions than four-stroke engines (Berdowski *et al.,* 1997). The two-stroke exhaust particles have been identified as unburned lubrication oil droplets and unburned fuel with the particle number concentration peaking at around 0.1-0.2 m (Patschull & Roth, 1995). Ulrich *et al.* (1992, cited by Berdowski *et al.,* 1997) reported 10 to 20 times higher emissions from an East European two-stroke engine compared to typical West European cars. Also increasing load increases particle emissions (Patschull & Roth, 1995).

The effect of the operating conditions of the engine and the effects of fuel, oil and catalyst parameters have been studied, e.g., by Kayes & Hochgreb (1999a; 1999b; 1999c).

A more detailed discussion and a summary of the emission factors and shares of PM1, BC and OC particles in PM for gasoline light duty vehicles are presented in the following sections.

Light Duty Gasoline Vehicles (LDG)

Because most of the measurements performed for non-catalyst cars use leaded fuel, no conclusive data for unleaded-non-catalyst combinations were found. However emission factors of fine and submicron particles for leaded gasoline from light duty vehicles were measured[3] by Williams at al. (1989a) and Hildemann *et al.* (1991) (Table 4.13). They report emission rates from about 14 to 18 mg/MJ for submicron and PM_2 particles, respectively.

Williams *et al.* (1989a) reported detailed measurements made for many vehicles using leaded fuel. The share of submicron particles varied from 75 to 97 percent with an average of 85 percent. However, they indicated that the submicron share might be overestimated due to the settling of particles in the duct. Ganley and Springer (1974) gave an average of 75 percent varying for different cycles, with lower values for steady state conditions. Berdowski *et al.* (1997) reported a share of 72 percent of $PM_{2.5}$ in PM_{10} (after US EPA). Based on the above discussion a share of 75 percent of PM_1 in TSP was derived and used in RAINS for vehicles operated with leaded fuel. Using this share and the RAINS TSP emission factor gives a PM_1 emission rate of 15.3 mg/MJ. This is also in line with the range of emission rates observed.

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[3] Results of other studies of PM emissions from vehicles run on leaded fuel were also reviewed.

In order to estimate emissions from vehicles equipped with control techniques, the measurement results were grouped (where possible) by vintage, i.e., pre-1985, 1986-91, and post 1991 models. The first category was not used for deriving numbers for the RAINS model, as it mostly includes vehicle technology that is not representative for the present European conditions. The latter two categories served to develop average emission factors for early catalyst cars (TWC) and modern vehicles, where catalysts are supplemented with other improvements such as engine modifications (TWC-plus).

Table 4.13: The emission factors of PM_1 for light duty gasoline engines [mg/MJ] [R].

Source	PM_1	Remarks
Unleaded fuel		
Cadle *et al.,* 2001	1	FTP-cycle, US 1990 or later, oxygenated fuel
	2	REP05-cycle, 1990 or later, oxygenated fuel
Hildemann *et al.,* 1991	3	PM2, US (catalyst) unleaded
Norbeck *et al.,* 1998a ; Durbin *et al.* 1999	6	US, FTP-cycle, pre 1981
	8	1981-85 models
	3	1986-90 models
	0.4	1991-97 models
Norbeck *et al.,* 1998c	4	US, Unified cycle, six pre 1987 vehicles
	0.6	Four 1989-1994 models
CONCAWE, 1998	0.6	ECE+EUDC cycles, European
Direct injection engine		
Hall & Dickens, 1999	2	ECE+EUDC-test, European
Kwon *et al.,* 1999	3-5	Total PM, a mix of FTP and EURO III cycles
	5	Average for the EURO III
Lappi *et al.,* 2001b	1-5	ECE+EUDC-test
Two-stroke		
Patschull & Roth, 1995	154-2009	6.3 kW, single cylinder two-stroke [a]
Leaded fuel		
Hildemann *et al.,* 1991	18	PM2, six US non-catalyst, leaded fuel (0.07-0.09 g Pb/l)
Williams *et al.,* 1989a	14	Australia, 22 SI-vehicles models 1965-1983 using leaded fuel (0.4 g Pb/l)

[R] RECALCULATED – Original values can be found in the Annex (Table A 5)
[a] Observed mass concentrations: ~0.5-6.5 g/m^3

For TWC vehicles, the collected evidence suggests an average value of around 3 mg/MJ for PM_1. This is based to a large extent on studies from the United States (Norbeck *et al.,* 1998a & 1998c; Durbin *et al.,* 1999, excluding the very old [pre-1985] and new [post 1991] vehicles) (Table 4.13). In addition, an improvement in fuel efficiency from about 15 liters/100 km in the beginning of the 1980's to about 12 liters in the beginning of the 1990's was assumed. Based on the studies by Norbeck *et al.* (1998a & 1998c), who also report PM_1 shares (Table 4.14), a share of 84 percent of PM_1 in TSP was derived.

For TWC-plus vehicles, the results from CONCAWE (1998), Cadle *et al.* (2001) and Norbeck *et al.* (1998a & 1998c) were included. The reported values for modern (end of 1990's) gasoline vehicles are significantly lower than measurements for the other vintages. For example, Cadle *et al.* (1999 & 2001) reported two to four times lower emission factors for

vehicles from the 1990's. Other studies confirm low emissions for this category of vehicles with an estimated average PM_1 emission factor of about 1 mg/MJ. The share of PM_1 in TSP for TWC plus vehicles was estimated at 86 percent, based on results from Norbeck *et al.* (1998c) and Cadle *et al.* (2001) (Table 4.14).

Table 4.14: Summary of the shares of PM_1 in TSP for light duty gasoline engines [%].

Source	PM_1	Remarks
Unleaded fuel		
Cadle *et al.*, 2001	92.2	FTP-cycle, US 1990 or later model year, oxygenated fuel
	83.6	REP05-cycle, US
Norbeck *et al.*, 1998a	89.2	1972-85 models, US
	85.6	1986-90 models, US
Norbeck *et al.*, 1998c	84.6	FTP, pre 1975 models, US
	82.5	1975-80 models, US
	88.8	1981-85 models, US
	84.1	1986-90 models, US
	85.1	1991-96 models, US
APEG 1999	85	Percent of PM_{10}, Europe
Direct injection engine		
Lappi *et al.*, 2001b	80-90	Dilution tunnel measurements, Europe
Leaded fuel		
APEG 2000	65	Percent of PM_{10}, Non-catalyst, Europe
Williams *et al.*, 1989a	85	Australia, 22 SI-vehicles models 1965-1983 using leaded fuel (0.4 g Pb/l)

The assessment of PM emissions from GDI engines is based on the measurements reported by Hall and Dickens (1999), Kwon at al. (1999) and Lappi *et al.* (2001a, 2001b). Hall and Dickens (1999) concentrated on number and size distribution measurements, but also report PM mass. They conclude that number and size distributions of GDI engines resembles that of a modern diesel engine, but the total mass is significantly lower. The reported emission factors show a wide spread with an average at the lower end of the range of TWC gasoline vehicles as reported by the studies listed in Table 4.13. The two other studies showed higher PM emissions from GDI engine when compared with FPI gasoline engines. Kwon et al (1999) tested a vehicle using both European and US test cycles and showed a spread between 3 and 5 mg/km with an average for the European test of about 5 mg/MJ. Lappi *et al.* (2001b) measured a similar range (1 to 5 mg/MJ) using the ECE/EUDC-cycle for a GDI engine. They also measured mass size distributions and reported that, in tests with a dilution tunnel, 80 to 90 percent of the mass was in the submicron range. Considering all three studies, an average TSP emission factor of about 5 mg/MJ has been derived. Applying the middle range reported by Lappi *et al.* (2001b) for dilution tunnel measurements gives an 85 percent share for PM_1 in TSP.

Table 4.15: The emission factors of BC and OC for light duty gasoline cars [mg/MJ] [R].

Source	BC	OC	Remarks	Method
Unleaded fuel				
Cadle *et al.,* 1999	3.5	11.5	FTP-cycle, pre 1981 models, US	TO
	2.5	4.3	1981-85 models, US	
	1.0	2.2	1986-90 models, US	
	0.9	2.0	1991-96 models, US	
	9.2	56.6	High emitters	
Cadle *et al.,* 2001	0.5	0.4	FTP-cycle, 1990-,oxygenated, US	TO
	0.6	0.7	REP05-cycle	
Hildemann *et al.,* 1991	0.7	1.7	PM_2, catalyst, unleaded, US	TO
Norbeck *et al.,* 1998a	1.0	3.7	FTP-cycle, pre 1981 models, US	TO
	1.6	4.3	1981-85 models, US	
	0.6	1.7	1986-90 models, US	
	0.2	0.1	1991-97 models, US	
Norbeck *et al.,* 1998c	0.5	2.9	Unified cycle, 1979-87, US	TO
	0.2	0.1	1989-94, US	
Sagebiel *et al.,* 1997	2.3	7.0	Normal emitters 1976-90, US	TO
	6.6	68.2	High emitters 1976-90, US	
	2.8	9.2	Normal emitters 1976-86, US	
	1.5	3.7	Normal emitters 1986-90, US	
Schauer *et al.,* 2002	0.2	1.0	$PM_{2.5}$, 1981-1994, catalyst, US	TO
	2.5	148.2	non-catalyst, 1969-1970, high emitters, US	
Kirchstetter *et al.,* 1999	0.8	1.2	$PM_{2.5}$, tunnel measurements, 98% gasoline vehicles, US	TO
Miguel *et al.,* 1998	0.7		$PM_{1.3}$, Tunnel measurements, ~1990, 98% gasoline LDVs, US	TO
Direct injection engine				
Lappi *et al.,* 2001	0.4-2.5	0.2-0.8	$PM_{2.5}$, 50 km/h, Europe	TO
Leaded fuel				
Hildemann *et al.,* 1991	1.2	7.7	PM_2, non-catalyst, leaded (0.07-0.09 g Pb/l), US	TO
Williams *et al.,* 1989a	0.7	4.5	Australia, 1965-1983, leaded (0.4 g Pb/l)	TO

[R] RECALCULATED – Original values can be found in the Annex (Table A 6)

No conclusive data on BC emission rates for unleaded-non-catalyst combinations was found. For leaded fuel, the measured/estimated BC mass emissions are broadly comparable to that of the TWC vehicles. However due to significantly higher total PM emission rates for leaded fuel, i.a. depending on the lead (Pb) content in fuel, the carbonaceous shares are different. The emission rates reported in Hildemann *et al.* (1991) and Williams *et al.* (1989a) give an average of about 1 mg/MJ. Comparing this number to the total PM in RAINS, 20.4 mg/MJ gives a BC share of about five percent. The analysis of the studies reporting shares of TC, OC, BC (see discussion below on derivation of OC emission factors and shares for leaded fuel) confirms the BC share derived above.

The estimate of the BC emissions from TWC vehicles requires adjustments to reflect changes in fuel efficiency for different vintages (see discussion in the PM_1 section). The reported BC emissions are between 1 and 2 mg/MJ. Following the same methodology as for PM_1 and OC

(using the same studies as for the OC), an average emissions factor of 0.9 mg/MJ was derived. Comparing this with the TSP estimate for TWC vehicles of about 3.6 mg/MJ (discussed in Klimont *et al.,* 2002) gives a BC share of 25 percent in PM. This compares well with the reported shares (Table 4.16 and Table 4.17) that fall typically between 15 and 28 percent in total PM with only few measurements beyond that range.

A similar analysis for TWC-plus vehicles results in an average BC emission rate of 0.5 mg/MJ. This represents about 42 percent of the PM emission factor presently included in RAINS and is consistent (although not the same) with the reported estimate of the share of BC in total PM. For modern (post 1991) gasoline vehicles, the shares of BC and OC change so that BC/OC ratio is larger than one, approaching the ratio that is reported for diesel vehicles (see Norbeck *et al.,* 1998a & 1998c). Norbeck *et al.* (1998c) indicated that this might be due to lower OC emissions as a result of the oxidation over the catalyst, a phenomenon also observed for diesel vehicles with oxidation catalysts. Cadle *et al.* (1999) observed a similar trend (especially measurements done in summer) for modern vehicles although the BC/OC ratio remained lower than one. The average of the reported BC shares is 46 percent in total PM (Table 4.16 and Table 4.17). The estimated share is consistent with the absolute values for emission factors reported above; a share of 44 percent was eventually assumed in RAINS.

Table 4.16: Summary of the shares of BC and OC in PM for light duty gasoline engines [%].

Source	BC	OC	Remarks	Method
Unleaded fuel				
Gillies & Gertler, 2000	28.8	35.2	of $PM_{2.5}$, SPECIATE-database	Unknown
	31.9	53.1	DRI-database	TO
	33.8	51.2	NFRAQS-database	TO
	45.8	32.2	CE-CERT-database	TO
Hildemann *et al.,* 1991	22.6	50.1	of PM_2	TO
Kirchstetter *et al.,* 1999	33	50	of $PM_{2.5}$, 98% gasoline powered	TO
Schauer *et al.,* 2002	10.3	43.7	of $PM_{2.5}$, catalyst 1981-1994, US	TO
	1.4	83.9	Non-catalyst high emitters, models 1969-1970, US	TO
Watson *et al.,* 1994	13.5	30.1	of $PM_{2.5}$, PHAUTO-profile	TO
Leaded fuel				
Gillies & Gertler, 2001	14.4	49.6	of $PM_{2.5}$, SPECIATE-database (leaded, 0.5gPb/l)	Unknown
Hildemann *et al.,* 1991	8.01	65.5	of PM2, non-catalyst, leaded fuel (0.07-0.09 g Pb/l), US	TO
Williams *et al.,* 1989a	4	27	of TSP, Australia, 1965-83; leaded (0.4 g Pb/l)	TO

Only one study (Lappi *et al.,* 2001a & 2001b) reported measurements of carbonaceous particles for vehicles with a gasoline direct injection engine (Table 4.15 and Table 4.17). The carbonaceous emission profile from a GDI engine seems to resemble that of diesel engines with a BC/OC ratio larger than one. For BC, a wide emission range was reported, i.e., 0.4 – 2.5 mg/MJ, with more values in the upper end of the range. Lappi *et al.* (2001a & 2001b) also performed simultaneous measurements with a FPI vehicle that showed consistently lower mass concentrations of BC. In order to estimate the BC share, the BC and OC shares in TC reported in that study were converted to refer to total PM by assuming a typical TC share for

gasoline engines of about 75 percent of TSP (Norbeck *et al.,* 1998a). This leads to a BC share in TSP of about 53 percent. Applying this to the TSP emission factors of RAINS gives a BC emission rate of about 2.6 mg/MJ, which is broadly in the range reported by Lappi *et al.* (2001a). It is important to note that the emission rates for GDI vehicles refer to a controlled engine complying with EURO III standards.

Table 4.17: Summary of the shares of BC and OC in TC for light duty gasoline engines [%].

Source	BC	OC	Remarks	Method
Unleaded fuel				
Cadle *et al.,* 1999	23.6	76.4	pre-1981, FTP-cycle, TC 77% of PM_{10}	TO
	33.1	56.9	1981-85 models	
	30.2	69.8	1986-90 models	
	34.4	65.6	1991-96 models	
	14.0	86.0	High emitters	
Cadle *et al.,* 2001		36	1990 or later, FTP-cycle, US	TO
		45	REP05-cycle	
Norbeck *et al.,* 1998a	21	79	pre-1981, TC 71% of TSP	TO
	27	73	1981-85 models	
	30	70	1986-90 models	
	63	27	1991-97 models	
Norbeck *et al.,* 1998c	28.5	71.5	pre-1987, FTP-cycle, US	TO
	60.6	39.4	1989-1994	
Sagebiel *et al.,* 1997	24	76	1976-90, normal emitters, TC 98.9% of PM_{10}	TO
	19	81	1976-90, high emitters, TC 72.5% of PM_{10}	
	22	78	1976-85, normal emitters	
	30	70	1986-90, normal emitters	
Direct injection engine				
Lappi *et al.,* 2001	70.6	29.4		TO

There are only a small number of studies reporting measurements of emissions of carbonaceous particles from non-catalyst vehicles and they have only limited applicability to the European situation since most of them have been conducted for vehicles are pre-1981 US vehicles. Schauer *et al.* (2002) measured OC emissions for two old vehicles including one European (Volkswagen; 1970 model year) reporting very high emissions of 0.2 g/km (~60 mg/MJ). These results were not used for the purposes of this study.

Two studies reporting OC emission factors from vehicles using leaded fuel were found (Hildemann *et al.,* 1991; Williams *et al.,* 1989a). The average emission rate for 22 vehicles reported by Williams *et al.* (1989a) is lower (4.5 mg/MJ) than the value reported by Hildemann *et al.* (1991) (8 mg/MJ; emission factor corrected for the possible condensable OC). However, Williams *et al.* (1989a) reported a large variation between individual vehicles ranging from 1.7 up to 10.3 mg/MJ. Based on these two studies, an OC emission factor for leaded fuel of 6.2 mg/MJ is assumed, which makes up about 30 percent of the TSP emission rate used in RAINS.

Only few studies report shares of OC in emissions from vehicles using leaded fuel. Converted to shares of TSP, they range from 27 percent (Williams, 1989a) to 42.2 percent (Gillies & Gertler, 2001), with Hildemann *et al.* (1991) reporting a 36.6 percent share (corrected for possible gas phase adsorption). The average of these studies gives a share of 35 percent of OC in TSP. However, the actual share is most likely lower since one of the studies (Gillies & Gertler, 2001) included also vehicles running on unleaded fuel. In the absence of lead particles the emissions typically have a higher share of TC in emissions. This is confirmed by Williams *et al.* (1989a). The high TC share reported in Hildemann *et al.* (1991) (above 70 percent) can be explained by the low lead content of the fuel and a possible impact of gas phase adsorption on measured organic carbon. Based on the available information it was possible to adjust the values reported in Hildemann *et al.* (1991), but not those from Gillies and Gertler (2001), so that the latter study is excluded from the analysis. The estimated average OC share of 32 percent compares very well with the share in TSP estimated from the absolute OC and PM emission rates, i.e., 30 percent (see discussion above). Finally, an average of two shares, i.e., 31 percent, is applied.

To account for the changing share of OC in PM emissions due to controls, vehicles were split into 'TWC' and 'TWC-plus' categories (see definitions in the preceding sections). In general, emissions of OC are expected to decline with the introduction of oxidation catalysts. Based on the results reported in Sagebiel *et al.* (1997), Norbeck *et al.* (1998a & 1998c), Cadle *et al.* (1999), Kirchstetter *et al.* (1999) and Schauer *et al.* (2002) for TWC vehicles (models 1986-91 and adjusting for fuel efficiency changes where appropriate), an average emission factor of 1.6 mg/MJ was derived. This represents about 44 percent of total PM. Using results reported in the above studies and additionally from Gillies & Gertler (2000) and Watson *et al.* (1994), an average share of 45 percent of OC in TSP was derived. This compares well with the estimate based on absolute emission factors. For TWC vehicles a share of 44.5 percent of OC in TSP is introduced to RAINS.

Based on the results reported in Cadle *et al.* (2001) and Norbeck *et al.* (1998a & 1998c) for vehicles registered after 1991 (TWC-plus), an average emission factor of 0.3 mg/MJ was derived. This is about 28 percent of total PM in RAINS and is in fair agreement with the shares reported in the studies by Cadle *et al.* (1999 & 2001) and Norbeck *et al.* (1998a & 1998c). Considering all of the above, a share of 32 percent of OC in total PM was derived. With additional information from other studies reporting emission factors and shares, an average of 30 percent was estimated.

Only one study (Lappi *et al.,* 2001a & 2001b) reports measurements of OC for GDI cars (Table 4.15 and Table 4.17). A wide range (0.2 – 0.8 mg/MJ) is quoted. As for BC, simultaneous measurements of an FPI engine showed consistently lower mass of OC. However, the difference is much smaller than for BC. Lappi *et al.* (2001a & 2001b) reported shares of BC and OC in TC, but no TC content of the emissions. A typical TC share in TSP for a gasoline engine is estimated at 75 percent based on Norbeck *et al.* (1998a). Following that assumption, an average share of 22 percent of OC in PM was derived.

Two-stroke Gasoline Engines

Two-stroke gasoline engines are often mentioned as a large source of particulate matter emissions, especially in urban areas where motorcycles and mopeds equipped with these engines represent a significant proportion of vehicle fleet. Typically, their poor emission performance is brought up when air quality issues in Asian cities are discussed, but there are also a number of European countries where the contribution of two-stroke vehicles to emissions of various air pollutants is important. Until recently, however, more research has been done on emissions of gaseous compounds rather than particulate matter. Therefore, it has been difficult to develop a reliable picture of the magnitude of PM emissions, their size distribution and chemical speciation from these sources.

Two studies reporting TSP emissions from two-stroke engines were found. Patschull & Roth (1995) studied a small engine under varying operating conditions in a laboratory. Kojima *et al.* (2000) reviewed several measurements of PM for scooters and motorcycles in the US and Asia. For uncontrolled vehicles, emission factors range from about 20 to 3000 mg/MJ, partly reflecting the wide spread of vintages in the analysis i.e., from 1970's (SRI, 1973; Danielson, 1978; Smith, 2000 – who tested a 1974 motorcycle), to late 1990's models (e.g., Kojima *et al.,* 2000). However, other very important factors affecting emissions are operating conditions like load and speed and oil to gasoline ratio used in the fuel. The influence of changes in the above factors on emission levels is reported to be similar in a number of studies (Patschull and Roth, 1995; Kojima *et al.,* 2000). For example, an increase in the oil to gasoline ratio from 1:100 to 1:50 nearly doubles the emissions of PM, while changing ratio to 1:25 causes further PM increase by up to about 40 percent. Consequently the highest emissions measured refer to highest lubricant share in fuel and high load, i.e., PM emissions of 2000-3000 mg/MJ (Patschull and Roth, 1995). It is concluded that such high emissions are not representative for the average European fleet, which is also confirmed by other studies (see Kojima *et al.,* 2000), which determined emission factors for older engines from 100 to 400 mg/MJ and for new non-catalyst scooters and motorcycles from 20 to 60 mg/MJ. In this study a TSP emission factor of 200 mg/MJ is assumed for a reference uncontrolled two-stroke vehicle. This factor is somewhat lower than the average of reported measurements for 1970's motorcycles, but significantly higher than the current RAINS value of about 120 mg/MJ (Klimont *et al.,* 2002).

For modern scooters and motorcycles, Kojima *et al.* (2000) reports significant reductions in PM emissions both for catalyst and non-catalyst vehicles when compared to the older generation of engines. For non-catalyst late 1990's models, the reported values vary from 20 to 60 mg/MJ for motorcycles and about 50 mg/MJ for scooters, which is considered to be more representative for the European fleet of two-stroke road vehicles. These measurements were done for a lubricant content of two percent (manufacturer recommended value). However, considering that in real life the lubricant content will vary, typically being too high and thus resulting in higher PM emissions (see discussion above), a 30 percent higher value (65 mg/MJ) is assumed, indicating an improvement of about 67.5 percent over the reference vehicle.

For catalyst-equipped scooters, a value of about 20 mg/MJ is reported (Kojima *et al.,* 2000). Compared to the previously discussed non-catalyst motorcycles the new generation is

typically equipped with a mechanical lubrication system, which should keep the oil to gasoline ratio at the recommended level (in fact, it is often lower, i.e., down to one percent owing to new lubricant formulations) and therefore the emission factor is not adjusted for that. However, oxidation catalysts installed on motorcycles and scooters have a relatively short lifetime, reported to be as low as 6,000 to 15,000 km, although it is expected that newer catalysts will last for at least 30,000 km (Kojima *et al.,* 2000). This has a potentially strong implication on emissions of PM, which will rapidly increase with a catalyst failure. Assuming a certain rate of premature failure and that a certain percentage of the vehicle stock will not get a timely replacement of catalyst, the PM emission factor for the first generation catalyst vehicles is increased up to 40 mg/MJ. It was also assumed that the newer generations of catalysts would achieve PM emission rates of 20 mg/MJ.

In order to assess emissions of submicron particles, the results from Patschull and Roth (1995) and Smith (2000) were used. Patschull and Roth (1995) reported number size distributions and observed a number concentration peak at about 0.1 μm. This, however, does not allow drawing clear conclusions about the mass size distribution, especially because the measurement system used in this study (DMPS – Differential Mobility Particle Sizer) operates in a size range of 0.01 – 1 μm. Smith (2000) measured only 5 to 22 percent of PM_{10} mass smaller than 0.3 μm. These results were interpreted and it was estimated that about 50 percent of the total mass is smaller than PM_1.

Because a large proportion of particles emitted from two-stroke engines are unburned oil droplets (Kojima *et al.,* 2000), a large share of the emissions must be carbonaceous. Smith (2000) used solvent extraction to remove organics from PM_{10} filter samples and observed a decrease of 98 to 99 percent in mass. This was assumed to represent the OM content of the PM_{10} aerosol. In order to estimate the OC share, a factor of 1.3 was used, i.e., a ratio of OM to OC typical for combustion (Stelson and Seinfeld, 1981). Considering that the share of PM_{10} in TSP is about 90 percent it was concluded that the share of OC in total particulate mass is about 67.5 percent. No studies about BC content were found, but drawing on the results of Smith (2000) the BC emissions can be estimated as small. A share of five percent of BC in TSP is considered representative, and on that basis the numbers presented in Table 4.18 were derived.

Table 4.18: Shares and emission rates of BC, OC and PM$_1$ as used in the RAINS model

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM$_1$	BC	OC	PM$_1$
Four-stroke						
No control – leaded gasoline	5	31	75	0.69	4.28	10.4
No control – unleaded gasoline	15	50	80	0.99	3.3	5.28
No control – LPG, CNG	15	50	80	0.3	1.0	1.6
TWC [a]	25	44.5	84	0.9	1.6	3.03
TWCplus [b]	44	30	86	0.52	1.0	1.02
GDI [c]	53	22	85	2.6	1.1	4.2
Two-stroke						
No control	5	67.5	50	10	135	100
I-stage	10	60	65	6.5	39	42
II-stage (catalyst)	15	45	75	6	18	30
III-stage (catalyst)	20	40	80	4	8	16

[a] Refers to pre-2000 catalysts (EURO I & II).
[b] Refers to post-2000 catalysts (EURO III & IV).
[c] Complying with EURO III standards

4.1.1.3 Off-road Vehicles

Use of off-road vehicles extends from small-scale equipment employed in agriculture to large marine vessels and thus many types of fuels as well as engines are used. Since the range of applications is so large, it is obvious that the emission characteristics vary, too. However, there are not many studies with quantitative data characterizing size distribution or chemical speciation of PM emissions from off-road vehicles.

Lyyränen *et al.* (1999) studied emissions from typical medium-speed diesel engines used in off-road applications both on land and the sea. The engines tested varied from a small, auxiliary diesel engine to a large, power plant type engine and they all used heavy fuel oil. They observed a bimodal mass size distribution with the main mode below 0.1 μm and a second mode at about 10 μm. The mode around 10 μm consisted of particles formed through the incomplete combustion of fuel oil droplets or of particles re-entrained from the combustion system. The main mode consisted of spherical primary particles formed through nucleation. The authors reported that 60 percent of the total particle mass was under 0.4 μm. Lloyd´s Register (1995) reported a preliminary evaluation of the emissions of some organic species (PAHs) and heavy metals for ships running with diesel and fuel oil.

For land-based machinery very few studies with appropriate data were found. There were no studies reporting emission factors for PM$_1$ and only one report where BC and OC emission rates were presented for diesel engines used in tunnel construction (Mayer, 1999 – VERT project) (Table 4.19). However these values seem to be very low when compared with the total emission of PM reported in other studies (Klimont *et al.,* 2002) and it was decided that they are not used before the full documentation of the VERT project is available (only the summary paper was available for this review). This led to the point where no specific data on the species of interest was available. The RAINS database includes data on total PM emissions drawing on the Berdowski *et al.* (1997) report that refers to the AP-42 (US EPA, 1995). The AP-42 was thus revisited for possibly other new material available on off-road

machinery. US EPA is in the process of reviewing their own background studies and some new documents where total emissions of PM are reported were identified.

Eventually, it was concluded that Berdowski *et al.* (1997) still is the only study giving applicable PM emission rates for "land-based" off-road machinery powered with fuel oil and thus the information from that study was used. A PM_1 share of 60 percent was assumed based on Lyyränen *et al.* (1999) (Table 4.20). The shares of BC and OC were assumed the same as for shipping (fuel oil).

Table 4.19: The emission factors of BC and OC for off-road engines [mg/MJ] [R].

Source	BC	OC	Remarks	Method
Land-based				
Mayer *et al.,* 1999	7.8	1.1	Construction site diesel engines	Unknown

[R] RECALCULATED – Original values can be found in the Annex (Table A 8)

To estimate emissions from shipping this review relies on the Lloyds' Register (1995) study where total PM emissions were reported for ships running on diesel and fuel oil. The results of Lloyds' Register (1995) were found to be in agreement with Kean *et al.* (2000), the US EPA off-road model NONROAD (US EPA, 1991 – AP-42 5th Edition) and the averages estimated for the Netherlands by van den Brink (1996). Eventually, Lloyds' Register (1995) was used since it tested a large number of vessels and it is the most recent study reporting actual measurements. In order to derive PM_1 emission rates (for diesel vessels), size profiles reported by Lyyränen *et al.* (1999) for fuel oil were interpreted and the shares for on-road heavy duty vehicles were used (Table 4.20). The shares of BC and OC for vessels running on diesel were assumed the same as for off-road machinery. For medium and large ships burning fuel oil the BC/OC ratio was adjusted to 1.5 after Álander (2000), taking into account char formation when burning heavy fuel oil (Flagan and Seinfeld, 1988). The total carbon share in PM (65 percent) is in the range given in studies listed in Table 4.46.

Off-road diesel vehicles are split into several categories (Table 4.21). Data from old (AP-42, US EPA, 1991) and new US EPA (Beardsley and Lindhjem, 1998) reports as well as Kean *et al.* (2000) were reviewed. The latter two studies report values in the same range and total PM emission factors for specific categories were derived based, to large extent, on Kean et al (2000). Since no information on size distribution was found, the share of PM_1 as assessed for heavy duty trucks (Table 4.20), i.e., 87 percent, was assumed to represent the PM_1 emissions from off-road diesel vehicles and was used also to develop the emission factors in Table 4.21.

No specific data on BC and OC emission factors or shares for off-road diesel engines was found. There are several similarities between heavy duty and off-road engines, but the typical operating conditions usually vary, which most probably affects the BC/OC ratio (Shi *et al.,* 2000; Lambrecht and Höpfner, 2000). Shi *et al.* (2000) measured BC and OC emitted from a diesel test engine under changing operating conditions, i.e., load and rpm. The conditions that represent best emissions from an off-road engine were assumed to be similar to the average of the tests with 50 percent load reported in that study. Resulting BC and OC shares in total PM are 37 and 31 percent, respectively. However, since some of the measured OC might originate from condensation of semi-volatile organic compounds (Shi *et al.,* 2000; Hildemann *et al.,* 1991), a correction factor needs to be applied. Hildemann *et al.* (1991) suggests that for heavy

duty diesel trucks up to about 30 percent of observed OC might result from gas-phase adsorption. Taking into account that the variability in OC measurements reported in Shi *et al.* (2000) compensate partly for that effect, a correction factor of 15 percent was assumed. Consequently, the shares used in RAINS for off-road diesel engines are 37 and 26 percent for BC and OC, respectively (Table 4.21).

Further, the shares of BC and OC for rail and construction machinery were modified based on the data from Shi *et al.* (2000). For rail, it was assumed that typical operating conditions would be characterized by somewhat higher rpm, leading to a different BC/OC ratio than for other off-road engines. A similar correction for the impact of condensation on OC was assumed as above and BC and OC shares of 45 and 23 percent of total PM were derived. For construction machinery, a higher average load as well as slightly higher rpm than other off-road machinery, e.g., tractors, was assumed. With about 75 percent load and an average engine speed above 2000 rpm, the share of BC and OC are estimated at 44 and 20 percent, respectively.

Table 4.20: Shares of PM_1, BC and OC of TSP for off-road vehicles [%].

Source	BC	OC	PM_1	Remarks	Method
APEG, 1999			23	% of PM_{10} (fuel oil, diesel, gasoline)	-
			85		
			85		
Lyyränen *et al.,* 1999			60	$PM_{0.4}$, small to large scale engines, heavy fuel oil	-
Shi *et al.,* 2000 *(US 1995 certified test engine)*	25.88	37.23		1600 rpm, 50% load	T
	33.87	20.44		1600 rpm, 100% load	
	47.30	24.06		2600 rpm, 50% load	
	51.52	20.38		2600 rpm, 100% load	

For off-road four-stroke gasoline engines, data reported by US EPA (1991) and Beardsley *et al.* (1999) were used. There is great variation in emission rates (from about 7 to 150 mg/MJ), the lower values typically for new types of engines that need to comply with the forthcoming US legislation (Beardsley *et al.,* 1999). The values given in US EPA (1991) and Beardsley *et al.* (1999) relate to PM_{10} and were scaled to TSP assuming a PM_{10} share in total PM of 90 percent. Emission factors for CNG and LPG four-stroke vehicles were developed using data in Beardsley *et al.* (1999). The assumptions made to estimate average emission rates for total PM from off-road sources are discussed in more detail in Klimont *et al.* (2002). The shares of PM_1, BC and OC are based on the shares estimated for gasoline cars in Section 4.1.1.2.

For off-road gasoline two-stroke engines, emission factors reported in US EPA (1991) and Beardsley *et al.* (1999) were used. Since the values reported in these studies relate to PM_{10}, a similar adjustment as for the two-stroke engines was made. The share of PM_1, BC and OC are based on the shares estimated for the on-road two-stroke engines.

Table 4.21: Shares and emission rates of BC, OC and PM$_1$ used in the RAINS model for off-road machinery.

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM$_1$	BC	OC	PM$_1$
Land based machinery						
Fuel oil	39	26	60	58.5	39	90
Diesel – Agriculture	37	26	87	58	41	137
Diesel – Construction	44	20	87	65	30	129
Diesel – Rail	41	23	87	44	25	93
Diesel – Inland shipping	37	26	87	43	30	102
Diesel – Other	37	26	87	49	35	116
Gasoline 4-stroke	15	50	80	5	17	27
CNG, LPG 4-stroke	15	50	80	0.6	2.1	3.4
Gasoline 2-stroke	5	67.5	50	21	286	212
Marine						
Fuel oil – medium vessels	39	26	70	49	33	88
Fuel oil – large vessels	39	26	50	49	33	63
Diesel	37	26	87	11	7	25

4.1.2 Non-exhaust Sources

Apart from the exhaust emissions, mobile sources emit particulate matter from tire, brake and the road surface wear. The particles from tire wear and road surface abrasion are mainly in the coarse fraction (Rautenberg-Wulff *et al.,* 1995; Kunz *et al.,* 2001), while over half of particulate matter from break lining wear is estimated to be in the fine mode (Garg *et al.,* 2000). Road surface wear is very difficult to measure and no emission factors specifically from road abrasion were found. The emissions from roads are either calculated from the loose dust (silt) content of the roads (US EPA 1998) or by using, e.g., tracer techniques (Claiborne *et al.,* 1995; Venkatram 2000). The results represent the total particulate matter that is re-suspended from the road surface, and include also particles from other sources than road abrasion (Rogge *et al.,* 1993b).

All the non-exhaust sources emit carbonaceous particles, since the materials they are made of include carbon. For brake wear, Garg *et al.* (2000) measured an average share of 18 percent of carbonaceous particles in total particulate mass. Hildemann *et al.* (1991) measured a carbonaceous share of 14 percent in fine particles from brake wear, with three percent elemental and 11 percent organic carbon. Hildemann *et al.* (1991) measured also the carbonaceous species from tire wear; 51 percent of the fine PM was carbonaceous with 36 percent of organic carbon and 15 percent elemental carbon.

Particles from road abrasion may include carbonaceous material originating from the bitumen of the asphalt. Hildemann *et al.* (1991) reported 15 percent share of carbonaceous species in the fine paved road dust with one percent elemental and 14 percent organic carbon. Chow *et al.* (1994) found similar results, i.e., three percent EC and 20 percent OC in paved road PM$_{10}$-dust. They also measured a 3.2 percent share of PM$_1$ in TSP. The samples for both studies were collected from the road surfaces so the share might not represent the actual

carbonaceous content of particles from road abrasion. The shares may be over-estimations due to possible influence of motor vehicle emissions, including brake wear, tire wear and oil drips (Chow *et al.,* 1994).

A recent study from the Swiss Environmental Agency (BUWAL, 2002) explored emissions from rail, paying more attention to non-combustion related sources, i.e., brake and rail wear. They found about half of the emitted mass in the PM_{10} fraction. This study does not provide a size distribution (beyond 10 µm) of the emission sources, but their concentration measurements in the vicinity of rail tracks and at the railway station suggest a relatively low share of submicron particles originating from these sources. Their chemical analysis of PM samples shows that a large proportion of particles are iron oxide. There is no information about emissions of carbonaceous particles.

Brake Lining Wear

The size fraction distribution of PM emissions from this source was given in several studies (Cha, 1983; US EPA, 1995 (PART5); APEG, 1999; Garg *et al.,* 2000). The estimated share of PM_1 in TSP varied from eight percent in APEG (1999) to 52 percent in Garg *et al.* (2000). The work by Garg *et al.* (2000) was used for this analysis since it is more recent and includes measurements for the current type of brake pads used as well as an assessment of carbonaceous particles. Applying the share of PM_1 reported in Garg *et al.* (2000) to the current RAINS estimates of total PM (Klimont *et al.,* 2002), an emission factor for PM_1 was derived. It was assumed that the size distribution given in Garg *et al.* (2000) applies to all types of vehicles, including heavy duty trucks. This implies change of the RAINS $PM_{2.5}$ emission factor for this category, which so far relied on the approximate share of $PM_{2.5}$ in PM_{10} for this source of 30 percent as quoted in Dreiseidler *et al.* (1999) (after Rautenberg-Wulff, 1998, a tunnel study). This share was changed to about 70 percent for RAINS, which results in an overall $PM_{2.5}$ share in TSP of about 58 percent (larger than 52 percent associated with PM_1 as reported in Garg *et al.* (2000).

Shares of BC and OC from wear of brake linings were reported by Hildemann *et al.* (1991) (in PM2) and Garg *et al.* (2000) (in total PM). For BC, both studies give about the same value, i.e., one percent in TSP, while for OC they vary between 5.4 percent in Hildemann *et al.* (1991) and between 16 and 20 percent for different pads in Garg *et al.* (2000). Relying on the more recent study (Garg *et al.,* 2000), an average of 18 percent is used (all values refer to total PM). Using the shares discussed above, emission factors for PM1, BC and OC were derived (Table 4.24). They compare well with the measurements reported by Garg *et al.* (2000).

Tire Wear

As discussed in Klimont *et al.* (2002), there are only few studies that report size fraction distributions, especially the shares of submicron particles for tire wear. Based on APEG (1999), Berdowski *et al.* (1997) and US EPA (1995 – PART5), a share of one percent of PM_1 in TSP was derived. However, considering more recent studies (e.g., Weingartner *et al.,* 1997; later version of PART5 model), where lower values of $PM_{2.5}$ were measured (see also the discussion in Klimont *et al.,* 2002), a share of 0.5 percent for PM_1 was assumed for this source.

Only Hildemann *et al.* (1991) reported BC and OC for tire wear. Typically, tire rubber consists of about 30 percent EC and 60 percent OC (Hildemann *et al.,* 1991; Israel *et al.,* 1994; van den Brink, 1996) and therefore it is reasonable to expect that most of the emitted particles will contain large proportions of them. It is assumed that the shares of BC and OC in PM_2 as measured by Hildemann *et al.* (1991) remain constant across the size range. However, because the main interest of this study is in the size fraction that will remain airborne for longer periods, the shares are calculated assuming that all the carbonaceous PM is emitted as PM_{10} (current RAINS estimates 10 percent in TSP). This leads us to use shares of 1.5 percent for BC and 3.6 percent for OC in TSP.

Table 4.22: Summary of PM_1, BC and OC emission factors for non-exhaust sources [mg/km].

Source	BC	OC	PM_1	Remarks	Method
Break-lining					
Garg *et al.,* 2000	0.034	0.61	1.77	Small cars	TO
	0.052	0.94	2.70	Large cars	
	0.088	1.6	4.58	Large pickup truck	
Tire wear					
APEG, 1999 & Berdowski *et al.,* 1997			7	Derived from PM_{10} reported in TNO (1997) assuming PM_1 share (10 %) after APEG (1999)	-

Road Abrasion

From the results reported by Chow *et al.* (1994), a PM_1 share of three percent in TSP was derived for the RAINS model. The shares of BC and OC reported in Hildemann *et al.* (1991) and Chow *et al.* (1994) refer to particles vacuumed from the road surface and they probably include particles from other sources than road abrasion, such as motor vehicle emissions, tire and brake wear. This could lead to an overestimation of BC and OC (Chow *et al.,* 1994), which makes it difficult to apply these shares for the calculation of road abrasion emission rates. Relating BC and OC shares to TSP in both discussed studies makes them broadly comparable, i.e., giving approximate shares of about 1-3 and 10-15 percent for BC and OC in PM_{10}, respectively (assuming that the BC and OC shares remain nearly constant in all size ranges and that PM_{10} represents roughly 50 percent of TSP). Taking into account the possible overestimation due to the inclusion of other sources (see discussion above), the BC and OC share in TSP were estimated at one and five percent, respectively. Similar ranges of BC and OC in abrasion dust were reported by Kupiainen *et al.* (2002), where BC shares lower than one percent and for OC a range between 3-7 percent of PM_{10} were measured.

Table 4.23: Summary of the shares of PM_1, BC and OC for non-exhaust sources [%].

Source	BC	OC	PM_1	Remarks	Method
Brake lining					
APEG, 1999			10	% of PM_{10}	-
Hildemann *et al.,* 1991	2.61	10.7		% of PM_2 (light duty truck)	TO
Garg *et al.,* 2000	1	16-20	52	% of TSP	TO
PART5			16		-
Tire wear					
APEG, 1999			10	% of PM_{10}	-
Hildemann *et al.,* 1991	15.3	36.0		% of PM_2	TO
Road abrasion					
Chow *et al.,* 1994	~3	20	3.2	% of TSP, BC & OC: % in PM_{10} paved road dust	TO
Hildemann *et al.,* 1991	1.06	13.5		% of PM_2, paved road dust, street samples	TO
Kupiainen *et al.,* 2002	<1	3-7		Refers to PM_{10}	TO

Table 4.24: Shares of BC, OC and PM_1 in TSP and emission factor values assumed in the RAINS model

	Share in TSP [%]			Emission factors [mg/km]		
	BC	OC	PM_1	BC	OC	PM_1
Brake lining						
Light duty vehicles	1	18	52	0.044	0.792	2.29
Motorbikes	1	18	52	0.006	0.108	0.312
Heavy duty vehicles	1	18	52	0.275	4.95	14.3
Tire wear						
Light duty vehicles	1.5	3.6	0.5	0.992	2.38	0.331
Motorbikes	1.5	3.6	0.5	0.423	1.015	0.141
Heavy duty vehicles	1.5	3.6	0.5	6.312	15.15	2.104
Road abrasion						
Light duty vehicles	1	5	3	0.15	0.75	0.45
Motorbikes	1	5	3	0.06	0.3	0.18
Heavy duty vehicles	1	5	3	0.76	3.8	2.28

4.2 *Stationary Combustion Sources*

Combustion processes in general are major emission sources of submicron and carbonaceous particles (APEG 1999; Penner *et al.,* 1993; Gray & Cass 1998). Combustion sources that contribute to ambient concentrations of particles are stationary boilers and furnaces, stationary and mobile internal combustion engines, fugitive emissions from industrial processes, domestic burning, open burning and accidental fires. Although the emissions from the different installations strongly depend on the composition of the fuels and on combustion conditions, the principles governing the formation of particles are similar (Lighty *et al.,* 2000; Simoneit 2002). Here only the basics of particle formation during combustion are presented.

The emission characteristics of individual applications or fuels are discussed in more detail further in the text.

The smallest particles (nucleation mode) are formed from volatilized material through gas-to-particle conversion, and they later grow by coagulation or surface growth into the "accumulation" mode (Lighty *et al.,* 2000). The vapors may also condense on already existing, larger particles. All these processes may occur simultaneously (Shi & Harrison, 1999) and are affected by combustion conditions, which vary greatly between different applications. Coarse particles are solid or liquid and are produced from the inorganic material of from fuel that is not directly vaporized at the combustion temperature (Lighty *et al.,* 2000). The formation of submicron particles during the combustion process depends on the presence of volatile material in the fuel and on the combustion temperature. If the fuel contains many highly volatile compounds that are not combusted, large amounts of submicron particles may be formed.

Fuel properties and the combustion process govern also the relative shares of inorganic and organic fractions in the primary particles from combustion sources. In general the particles that are formed during the combustion of gaseous or liquid fuels are mainly carbonaceous with a large fraction in the submicron size range, whereas a high share of particles from solid fuel (coal, biomass and waste) burning often originates from the incombustible, inorganic material that is found in coarse sized particles (Burtscher, 2000). The emission profile for the burning of solid fuels is highly dependent on the combustion process. For example, in small-scale burning where the temperatures are low and the combustion is inefficient, many organic compounds may vaporize and later condense forming submicron particles with a high share of organics. In high temperature applications, the combustion is efficient and hardly any carbonaceous particles are present in the emissions.

Carbonaceous particles are produced either through chemical reactions and gas to particle transition at higher temperatures, involving pyrolysis (soot or black carbon) or through condensation at lower temperatures (organic carbon) (Lighty *et al.,* 2000). For black carbon, the net emission starts to increase with increasing temperature, reaches a maximum and then drops as the temperature increases further (Bond *et al.,* 1999). The diameter of the primary black carbon particles is between 0.02 and 0.1 μm. Especially in their purest form, black carbon particles are solid and chemically inert under atmospheric conditions and the only modifications and removal processes are physical in nature, e.g., coagulation affecting the size distribution in the atmosphere, as well as dry and wet deposition affecting the removal (Charlson & Ogren, 1982). In addition to the small submicron soot/black carbon particles, also coarse elemental carbon particles can be produced during combustion. The bigger particles, also known as char, are formed from the non-combusted carbonaceous material of the fuel and have a diameter of 1 to 50 μm. Char is basically formed only when solid fuels or heavy fuel oil is burned; its share in emissions depends on the fuel properties and the combustion process.

4.2.1 Solid Fuels

4.2.1.1 Coal

Coal is a combination of organic material and inorganic mineral matter. Coals are ranked according to the alteration in their natural metamorphosis. Lignite or brown coal is in the early stages of coalification and has smaller carbon content than bituminous (soft coal) or anthracite coals (hard coal). Anthracite has more fixed carbon than the others and is considered a high-ranking coal. The particulate emissions from coal combustion depend on the rank of the coal, the type and size of the boiler, the combustion conditions, control technologies in use and the level of equipment maintenance (US EPA, 1998). The low ranked coals have more mineral matter and thus usually emit more particles than higher ranked coals.

Coal is burned in stoves, boilers and furnaces of different type and size. For different applications the combustion conditions are different and thus the particulate emissions may vary significantly. Published emission data, however, exists only for a few types of sources, mostly for high technology coal burning in big units (Wehner *et al.,* 1999).

Both coarse and fine particles are formed in the combustion of coal. Supermicron (over 1 µm in diameter) particles are formed from the noncombustible material in the coal and often have a spherical shape because of high combustion temperatures (Fisher *et al.,* 1978; Kindatrenko *et al.,* 1994; Xie *et al.,* 1994). Submicron particles are formed through the vaporization and condensation of elements (McLennan *et al.,* 2000). They are usually aggregates of primary particles with a diameter of 10 to 50 nm. In general, the submicron particles comprise only few percent of the mass emissions, but dominate the number concentration (McElroy *et al.,* 1982; Wehner *et al.,* 1999). Carbonaceous particulate emissions from coal combustion consist of supermicron char particles remaining from the incomplete combustion of the coal as well as of submicron soot particles (Griest & Tomkins, 1984; Lighty *et al.,* 2000).

In high technology applications like pulverized coal combustion (PC) and fluidized bed combustion (FBC), the emissions of elemental and organic carbon are small because of the high combustion temperatures, oxidizing conditions and long residence times (Ohlström *et al.,* 2000). In pulverized coal combustion, the combustion temperature is higher (1500-1700 ºC) than in fluidized bed combustion (700-900 ºC) (Ohlström, 1998). This difference in combustion temperature and the air supply are reported to impact particle formation. In fluidized bed combustion, the volatilization of ash takes place to a lesser extent (due to the lower temperature) and less submicron particles are formed (Moisio, 1999).

The high technology burning is common for power plant applications, but much of the smaller scale burning in the industry and in domestic heating occurs in stoves and furnaces (at the bottom of the furnace or on a grate). For small-scale burning of coal there are only a few studies available (see Bond *et al.,* 1999; Wehner *et al.,* 1999). However, in some areas it can be an important source contributing both to particle exposure and climatic forcing (Ohlström *et al.,* 2000; Bond *et al.,* 1999; Wehner *et al.,* 1999). The low emission height and the absence of emission control devices increase the exposure risk of population (Ohlström *et al.,* 2000). Also the emissions of soot may be high because of the varying combustion conditions (Ohlström 1998; Bond *et al.,* 1999).

Power Plants and Industry

A number of studies reported PM size distributions or emission factors of PM_1 for power plants and industrial combustion applications (Table 4.25 and Table 4.26). Table 4.26 lists shares of submicron particles measured in several studies. Eliminating the measurements referring to installations with abatement, a good agreement between studies for the same type of combustion was found. For FBC, an average was taken based on the measurements reported in two studies[4] (Cheng *et al.,* 1985 and Lind *et al.,* 1996) since the third study (Murthy *et al.,* 1979) characterizes a small test installation where flue gases were pre-treated (cyclone battery). The average shares of PM_1 in TSP for PC, FBC and grate firings are presented in Table 4.34. Applying these estimated PM_1 shares of the combustion technologies to the current RAINS TSP estimates for individual countries and comparing the results with the actual emission factors reported (Table 4.25) showed good agreement.

Table 4.25: Summary of the emission factors of PM_1 for coal burning in power plants and industry [mg/MJ].

Source	PM_1	Remarks
Power generation		
APEG, 1999; Berdowski *et al.,* 1997	5.7 / 51.3	Abated emissions. Brown coal (Western Europe / Eastern Europe)
	1.9 / 70.3	Abated emissions. Hard coal (Western Europe / Eastern Europe)
US EPA, 1998	25*A	Unabated emissions, A=coal ash weight percent (e.g. if 3.4%, then A=3.4), lignite, boilers
	6.2*A	Bituminous, wet bottom
	4.4*A	Bituminous, dry bottom
	3.4*A	Anthracite, dry bottom
Cheng *et al.,* 1985	35.1	FBC, before the baghouse, bituminous
Murthy *et al.,* 1979	73.9	FBC, after cyclones
Utility boilers & industrial combustion		
APEG, 1999; Berdowski *et al.,* 1997	35	Abated emissions. Brown coal
	10 / 52	Hard coal (Western Europe / Eastern Europe), Western Europe - abated emissions.
US EPA, 1998	25*A	Lignite, spreader stoker, A=coal ash weight percent
	73	Bituminous, spreader stoker
	2.2	Bituminous, cyclone furnace

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[4] These studies reported shares of PM1 in PM10.4-11.4 μm. We derived the shares assuming that PM11 represents around 30% of TSP (Moisio, 1999).

Table 4.26: PM$_1$ shares in TSP for coal combustion in power plants and industry [%].

Source	PM$_1$	Remarks
Power generation		
APEG, 1999	19	% of PM$_{10}$, *abated*
Carr & Ensor, 1981	2	% of PM$_{20}$ (percentages at the *ESP inlet and outlet*)
	20	subbituminous 520 MW unit
Ehrlich *et al.,* 2001	52	Brown coal, 180 MW power station, *ESP and scrubber*
	47.7	Brown coal briquettes, 146 MW power station (operating 114 MW), *ESP and desulphurization*
	25.5	Lignite, 119 MW power station, *ESP, desulph. and de-NOx*
US EPA, 1998	6	Pulverized lignite, boilers, *unabated*
	4	Pulverized bituminous, wet bottom, *unabated*
	2	Bituminous, dry bottom, *unabated*
	2	Anthracite, dry bottom, *unabated*
McElroy *et al.,* 1982	1.5	% of PM$_{20}$ (*unabated, baghouse, ESP*)
	2	Utility boilers, bituminous and subbituminous
	20	
	0.3	360 MW, *unabated*
	0.2	540 MW
	1.3	520 MW
	2.2	113 MW
	0.9	360 MW
	0.5	25 MW
Ondov *et al.,* 1978	4	% of PM$_{30}$, 750 MW (*in-stack of the ESP, at the outlet of the mist eliminator of the scrubber*)
	20	
Cheng *et al.,* 1985	4.3	% of PM$_{11}$ (*unabated, baghouse*), bituminous, FBC
	18	
Lind *et al.,* 1996	<1	% in PM$_{10.4}$, 80 MW, *upstream of an ESP*, bituminous, FBC
Murthy *et al.,* 1979	9	FBC, *after cyclones*
Utility boilers & industrial combustion		
APEG, 1999	10	% of PM$_{10}$
US EPA, 1998	5	Lignite, spreader stoker
	5	Bituminous, spreader stoker
	5	Bituminous, cyclone furnace

Emissions of BC and OC from large-scale combustion of coal depend highly on the combustion performance. Also the type of coal can affect the share of unburned carbon in emissions (Shibaoka, 1986). The unburned carbonaceous fraction in emissions seems to vary largely. E.g., Shibaoka (1986) and Veranth *et al.* (2000) reported TC shares up to 48 percent in fly ash samples (Table 4.27). Shibaoka (1986) also reported that when the TC share was over five percent in TSP, large (coarse mode) char particles dominated the emissions. In addition, studies that measured carbonaceous shares in different size ranges observed BC and OC also in coarse particles, which indicates the presence of char particles in emissions (Engelbrecht *et al.,* 2002; Fisher *et al.,* 1979; Griest & Tomkins, 1984; Olmez *et al.,* 1988). Such large particles have short atmospheric lifetime and usually deposit near the emission source and thus are not relevant for radiative forcing. Therefore measurements with TC shares

over five percent were excluded from this study. If a study reported carbonaceous emissions in different size classes, the numbers referring to BC and OC in fine particles were used.

Table 4.27: Summary of the TC shares for coal combustion in power plants and industry [%].

Source	TC	Remarks	Method
Power generation			
Murthy *et al.,* 1979	2.4	in PM$_{1-10}$, *after cyclones*	Unknown
Querol *et al.,* 1995	0.7	in fly ash, 1054 MW power plant, subbituminous/bituminous coal	Elemental analyzer
Shibaoka, 1986	2.3-25.5	pulverized combustion, bituminous coal	Unknown
Veranth *et al.,* 2000	1-48	in fly ash (9 samples), 30 kW low-NO$_x$ laboratory furnace, bituminous coals	T
	< 3	in fly ash, lignite	
	7-32	in fly ash (4 samples), power plants, bituminous coals, *samples collected from gas cleaning devices*	
Utility boilers & industrial combustion			
Hurt & Gibbins, 1995	5-7.8	TC (residual carbon) in fly ash samples, various boiler types burning US bituminous coals, *samples from particulate control devices (primarily ESP)* or *high volume sampling at the economizer outlet.*	Unknown

All the studies that dealt with BC and OC emissions from large-scale applications (Hangebrauck *et al.,* 1964; Fisher *et al.,* 1978 and 1979; Henry & Knapp, 1980; Griest & Tomkins, 1984; Olmez *et al.,* 1988; Pinto *et al.,* 1998; Watson *et al.,* 2001) reported only abated emissions (Table 4.29). It should be noted that the control technologies may alter the chemical composition of emissions. For example, it is well known that the efficiency of the inertia based methods (cyclones, fabric filters) differs as a function of particle size. Thus, particles with a specific composition may be enriched in the controlled emissions if they are concentrated in a specific size class where the abatement efficiency is low. For example, if the carbonaceous particles are more common in the accumulation mode, they may be more abundant in the emissions after the control device than before it. The electrical properties of the particles also depend on the chemical composition and therefore the electrostatic precipitators (ESP) may work differently for particles with different chemistry.

Since no studies were found reporting removal efficiencies specifically for the carbonaceous fractions and since all available studies reported BC and OC profiles only in abated emissions, they were converted to represent unabated emissions using the current RAINS reduction efficiencies and information from Smith (1987) and Soud (1995) about the control efficiencies for submicron particles. Also the shares referring to fine particles were converted to refer to TSP using the RAINS size fractions. Most of the studies that were included in the analysis reported low fractions of BC and OC in emissions, usually below one percent when related to TSP. The numbers in the original studies are discussed below, and the final shares introduced in the RAINS calculations are presented in Table 4.34.

For *pulverized combustion of brown coal* only two studies provide shares of carbonaceous species (Pinto *et al.,* 1998; Veranth *et al.,* 2000). Veranth *et al.* (2000) observed less than three percent of TC in TSP (fly ash samples from a low-NO$_x$ laboratory furnace). Pinto *et al.*

(1998) reported zero percent of BC and 7.5 percent of OC in $PM_{2.5}$. The RAINS shares were developed based on Pinto *et al.* (1998).

For *pulverized combustion of hard coal* BC shares were measured between 0.24 and 1.17 percent in fine particles with an average of 0.6 percent (Fisher *et al.,* 1978 and 1979; Henry & Knapp, 1980; Griest & Tomkins, 1984; Olmez *et al.,* 1988; Watson *et al.,* 2001). Three of these studies (Griest & Tomkins, 1984; Olmez *et al.,* 1988; Watson *et al.,* 2001) reported also data about OC in fine particles that ranged from 'not detected' to around three percent with an average of 0.9 percent. The averages were used in generating the numbers introduced to RAINS. For wet bottom boilers no specific data were found and therefore the same "dry to wet boiler" ratio (0.5) as for PM_1 was assumed. No data were found about carbonaceous emissions from burning of coal in *fluidized bed boilers* (FBC) and it is assumed that BC comprises approximately one percent of abated $PM_{2.5}$ and that negligible amounts of OC are emitted.

Two studies address burning of coal in *stokers* (Hangebrauck *et al.,* 1964, Ge *et al.,* 2001). For industrial installations, Hangebrauck *et al.* (1964) reported OC fractions in TSP varying for different types of installations, i.e., 0.3 percent for chain grate stoker, 1.4 percent for spreader stoker and 1.1 percent for underfeed stoker. Ge *et al.* (2001) reported BC and OC shares in PM_{10} and $PM_{2.5}$ emissions of a stoker/chain watertube boiler equipped with a cyclone. The BC and OC shares in their measurements were 12 percent and 2 percent in fine particles, respectively. Adjusting the results of the above studies with current RAINS numbers (i.e., control efficiency for cyclone and share of $PM_{2.5}$ in TSP) to represent unabated TSP, average values of 0.15 percent of OC and 0.3 percent of BC in TSP were introduced for grate firing of hard coal in RAINS. Comparing the resulting emission factors with the original studies shows good agreement. There were no studies available for brown coal burned in industrial stokers. The TC share was assumed to be fairly similar as for burning of hard coal, i.e., about 0.5 percent in TSP, but with slightly less BC (0.1 percent) and more OC (0.4 percent). The difference is thought to represent a higher content of volatiles in brown coal, when compared to hard coal burned in similar conditions.

Table 4.28: Summary of the emission factors of BC and OC for coal combustion in power plants and industry [mg/MJ].

Source	BC	OC	Remarks	Method
Power generation				
Hangebrauck *et al.,* 1964		1.8-2.8	Pulverized, *sampling in the stack*	SE
Utility boilers/industrial combustion				
Ge *et al.,* 2001	3.7	1.2	In PM_{10}, stoker/chain watertube boiler, bituminous, *cyclone*	TO
	0.11	0.65	Briquette coal	
Hangebrauck *et al.,* 1964		1.7	Chain grate stoker, *in stack*	SE
		0.47	Spreader stoker	
		2.3-3.9	Underfeed stokers	

Table 4.29: Summary of the shares of BC and OC for coal combustion in power plants and
industry [%].

Source	BC	OC	Remarks	Method
Power generation				
Engelbrecht *et al.*, 2002	0.2	4.6	% of PM_{10} and of $PM_{2.5}$, in *stack measurements*	TO
	0.4	8.7		
Fisher *et al.*, 1978	0.24		% of $PM_{2.2}$, 750 MW, *sample after ESP*	EM
Fisher *et al.*, 1979	<0.3		% of TSP	T
	0.27		% of $PM_{2.2}$, *sample after ESP.*	
Griest & Tomkins, 1984	11.6	0.87	% of total stack ash (PM_{150})	See article
	1.79	0.16	Power plants, two samples of *stack ash*	
	0.81	0.31	% of $PM_{2.3}$ fraction (see above)	
Hangebrauck *et al.*, 1964		0.3-0.7	% of TSP, *in stack measurement*	SE
Henry & Knapp, 1980	1.88	<0.1	Average % of 5 fly ash samples and without the highest share, *abated*	T
	0.60			
Olmez *et al.*, 1988	0.89	Not detected	% in fine, coarse and PM_{10} particles (24% of the mass in the fine fraction), 300MW power plant, *after ESP.*	T
	2.0			
	1.7			
Pinto *et al.*, 1998	0	7.5	% of $PM_{2.5}$, power plant, high sulfur lignite, *in stack measurements*	TO
Watson *et al.*, 2001	8.08	2.24	% of $PM_{2.5}$, power plants burning bituminous coal, *abated*	TO
	1.17	2.63		
	4.30	34.1		
	0.39	0.49		
	1.70	11.7		
Utility boilers & industrial combustion				
Ge *et al.*, 2001	6	2	% of PM_{10} and of $PM_{2.5}$ stoker/chain watertube boiler, bituminous, *cyclone*	TO
	12	2		
	0.1	0.6	% of PM_{10} and of $PM_{2.5}$ briquette coal	
	0.4	1.8		
Hangebrauck *et al.*, 1964		0.3	% of TSP, chain grate stoker, *in stack*	SE
		1.4	spreader stoker	
		1.1-3.6	underfeed stokers	

The uncontrolled BC and OC emission factors for large scale industrial combustion
installations assumed in RAINS (Table 4.34) are derived based on the estimated shares in
TSP and a typical (average of country-specific values for a given installation) TSP emission
characteristic; in that way decoupling them from the ash content of the fuel.

Small Combustion Sources

Small combustion sources are split in the RAINS model into fireplaces, stoves, single-family
house boilers and medium size boilers, for the latter two distinguishing between manual and
automatic fuel feed system (Klimont *et al.*, 2002).

The emissions of submicron particles from hand-fed *stoves* are characterized by a high share
of fine particles (Macumber and Jaasma, 1982). The ash content has a secondary effect on

particulate emissions from residential size coal fired equipment; the primary factors influencing PM emissions are coal volatile matter content and the design of the combustion equipment (Hughes and DeAngelis, 1982; Bond, 2000). For hard coal, Streets *et al.* (2001) used in their inventory a PM_1 share of 80 to 90 percent in TSP. Macumber and Jaasma (1982) reported 93 percent of $PM_{1.5}$ indicating, however, that the test did not include the start-up of the stove and was probably not long enough to obtain a representative number of the very large particles emitted. On the other hand, US EPA (1998) suggested that the emission characteristics for hard coal underfeed stoker (21 percent of PM_1 in TSP) could also considered as representative for hand-fired units. Considering this aspect and the fact that the upper limit in Streets *et al.* (2001) relies on Macumber and Jaasma (1982) as well as scaling down the share reported by Macumber and Jaasma (1982), the share of PM_1 in total PM is estimated at 70 percent for hard coal burned in stoves. No studies reporting size distributions of PM emissions from brown coal stoves were found. Ehrlich *et al.* (2001) reported size distribution for stoves burning brown coal briquettes, and Bond (2000) gave a specific PM_1 emission factor for lignite briquettes (263 mg/MJ). Based on this information a 69 percent share of PM_1 in TSP is estimated.

A number of studies reporting submicron PM emissions from *medium size residential coal combustion boilers* were found, giving both absolute numbers (Table 4.30) as well as shares of PM_1 in either TSP or PM_{10} (Table 4.31). For brown coal, the studies from US EPA (1998) and Bond *et al.* (1999) were used and a share of 4.5 percent of PM_1 in TSP was derived. For hard coal, the study from US EPA (1998) was used resulting in the share of five percent.

No studies reporting submicron emissions from *single house boilers* were available and therefore an assumption was made based on the information about total carbon in particulate emissions. Since TC in emitted PM was estimated to be 78 percent (see discussion further in the text) and it was assumed that most of PM_1 is carbonaceous, a PM_1 share of 80 percent was used for single house boilers burning hard coal, i.e., slightly above the share of total carbon.

Table 4.30: Summary of the emission factors of PM_1 for coal combustion in small combustion sources [mg/MJ].

Source	PM_1	Remarks
APEG, 1999	57.6 / 102.4	Hard coal, residential combustion (Western Europe / Eastern Europe)
Bond *et al.,* 1999	112.5	Lignite, small plant (2MW) with condensable PM
	62.5	Lignite, small plant (2MW), without condensable PM
Bond, 2000	390	Bituminous, residential stove, ash 4.6%
	260	Lignite briquettes, residential stove, ash 10.2%
US EPA, 1998	44	Bituminous, top loading stokers
	71	Bituminous, bottom loading stokers

Only few studies reporting shares of BC and OC from burning of coal in residential *stoves* were found. Engelbrecht *et al.* (2002) measured burning of bituminous coal (hard coal) in South Africa. They observed shares from 10 to 11 percent for BC and from 70 to 72 percent for OC in PM_{10}. Additionally, Watson *et al.* (2001) reported 26 percent of BC and 69 percent of OC in a composite $PM_{2.5}$ sample from three stoves and one fireplace, while Hangebrauck *et al.* (1964) measured about 17 percent of OC in TSP (equals to an emission factor of

94 mg/MJ) for a hand-stoked residential furnace burning hard coal. It is important to note that Hangebrauck *et al.* (1964) used a different measurement method (benzene extraction) than other studies (thermal-optical methods). In order to make them comparable an attempt was made to correct the Hangebrauck *et al.* (1964) for potentially lost OC. The correction is based on Cadle & Groblicki (1982), who indicated that a similar solvent extraction method as used by Hangebrauck *et al.* (1964) captured approximately 80 percent of OC.

Table 4.31: Summary of the shares of PM_1 in TSP for coal combustion in small combustion sources [%].

Source	PM_1	Remarks
APEG, 1999	32	% of PM_{10}
Bond *et al.,* 1999	12	% of PM_{10}, without condensable PM
		Lignite, small plant (2MW)
Ehrlich *et al.,* 2001	63.1-76.6	Brown coal briquettes, iron stove (6 kW), unabated
US EPA, 1998	12	Bituminous, top loading stokers
	21	Bituminous, bottom loading stokers
		May also be used for uncontrolled hand-fired units
Macumber & Jaasma, 1982	93	$PM_{1.5}$ in total PM
		Hand-fired residential stove, bituminous

The estimates of BC emission factors for *stoves* rely on the shares reported in the studies discussed above. One of encountered difficulties was that none of the papers reported total emissions of PM. Based on the characteristic of fuels given in the studies it is concluded that Watson *et al.* (2001) refers to a fuel that is assumed to be representative for the European situation, while Engelbrecht *et al.* (2002) (high ash, high sulfur bituminous coal) is on the high end of emission factors applicable to Europe. Based on this assumption, and taking the confidence ranges given by the authors into consideration, a range of BC emission factors from 42 to 167 mg/MJ was derived. This is in line with the range given by Streets *et al.* (2001), where for domestic coal stoves emission factors between 4 and 144 g/MJ were presented. For RAINS, a value of 130 mg/MJ is assumed, which represents about 26 percent of the TSP. Expressed as a percentage of $PM_{2.5}$, the BC emission factor makes up about 32 percent, which is broadly in agreement with Watson *et al.* (2001). No data for brown coal stoves was found. Based on studies for small boilers, where typically the share of BC is lower for brown coal combustion than for hard coal (see below), a BC share of four percent in TSP for brown coal stoves is derived. Using the current emission factors in RAINS this translates into approximately 24 mg/MJ.

For hard coal burned in *stoves*, the OC shares in TSP showed a wide variation (about 21-64 percent). However, since the total PM emissions and size fraction distributions varied between the investigated installations, the range of calculated emission factors was smaller with an average value of 200 mg/MJ. For stoves burning brown coal only one study (Pinto *et al.,* 1998) was found. They reported shares of OC in particle emissions from hand-stoked stoves in the Czech Republic. The average share of OC in $PM_{2.5}$ was about 65 percent, which translates into 52 percent of TSP using the current size fraction distribution of emissions in RAINS. This is at the higher end of the reported shares for hard coal stoves (bituminous coal). With the current RAINS numbers an emission factor of 312 mg/MJ is derived.

Only one study (Hangebrauck *et al.,* 1964) reported emissions of OC from *single house boilers* burning hard coal. However, the value is very low (about 3 mg/MJ) especially when compared with stoves. Pinto *et al.* (1998) reported carbonaceous fractions in emissions from brown coal burned in hand fired stoves. Since no other studies were found with measurements from small domestic combustion, the shares from Pinto *et al.* (1998) were used. However, it was assumed that the high temperature phase emission profile with six percent of BC and 62 percent of OC in $PM_{2.5}$ represents better emissions from single house boilers. These shares were scaled to relate to TSP, using the current RAINS size profile, resulting in 4.8 percent of BC and 50 percent of OC. Applying these shares to the TSP emission factor in RAINS gives 29 mg/MJ and 300 mg/MJ for BC and OC, respectively, for brown coal burned in single house boilers.

Simoneit (2002) argued that, as for wood burning, the heat intensity and the duration of smoldering and flaming conditions determines the distributions and ratios of the directly emitted vs. altered compounds present in coal smoke. Rau (1989) has shown that for wood stoves hot burning vs. cool burning results in a smaller share of total carbon in emitted PM as well as in a higher share of black carbon in total carbon. These findings were used to derive shares of BC and OC for small *manually fed single house boilers*, starting from ratios found for stoves and assuming that stoves represent cool burning and boilers hot burning conditions. This resulted in BC and OC shares of 43 and seven percent for hard coal burned in single house boilers. However, the resulting emission factor for OC is very low and falls out of range of reported values for similar types of installations; compare e.g., Bond *et al.* (2004). Thus it was scaled up to approximately the same level as BC, i.e. of 35 percent. Applying these percentages to the TSP emission factors in the current RAINS database gives 215 mg/MJ for BC and 175 mg/MJ for OC from hard coal. For automatic boilers (SHB_A), it was assumed that owing to the improved combustion efficiency (compared with the manually operated boiler), the share of OC would drop to 10 percent while BC increases slightly (in relative terms) to 45 percent. The emission factors estimated with these assumptions are 67.5 and 15 mg/MJ for BC and OC, respectively.

Hangebrauck *et al.* (1964), Bond *et al.* (1999) and Ge *et al.* (2001) measured carbonaceous emissions from *medium sized boilers*. Bond *et al.* (1999) reported a BC (graphitic carbon) share below two percent in PM_{10} for a small plant (2 MW) burning brown coal, which translates into an emission factor of about 2.25 mg/MJ. The BC to OC ratio is assumed to be similar as for brown coal burned in industrial (grate) boilers, with OC roughly twice the BC, resulting in an emission factor of about 5 mg/MJ. These emission factors are introduced in RAINS for medium sized boilers burning brown coal.

Ge *et al.* (2001) measured carbonaceous emissions from hard coal burned in an industrial boiler. BC and OC emission factors were 3.7 and 1.2 mg/MJ, respectively (Table 4.28). Also Hangebrauck *et al.* (1964) reviewed OC emissions from an underfeed stoked hard coal boiler that was used for school heating. They measured 3.6 percent of OC in TSP. Correcting this value for possibly unaccounted carbon from the solvent extraction method (Cadle & Groblicki 1982, see discussion above) results in an emission factor of about 5 mg/MJ. The above measurements were used for deriving the RAINS emission factors; for BC an emission factor of 4 mg/MJ is introduced based on the measurements by Ge *et al.* (2001), for OC an emission

factor of 2 mg/MJ was derived relying on both Ge *et al.* (2001) and Hangebrauck *et al.* (1964).

Table 4.32: Summary of the emission factors of BC and OC for coal combustion in small combustion sources [mg/MJ].

Source	BC	OC	Remarks	Method
Bond *et al.,* 1999	<2.25		Lignite, small plant (2MW), with condensable PM	O
Hangebrauck *et al.,* 1964		93.8	Hand-stoked coal burners	SE

Table 4.33: Summary of the shares of BC and OC for coal combustion in small combustion sources.

Source	BC	OC	Remarks	Method
Bond *et al.,* 1999	<2		% of PM_{10}, small plant (2MW), lignite (filter with condensable PM)	O
Engelbrecht *et al.,* 2002	10.1	70.0	% of PM_{10}	TO
	9.5	70.8	% of $PM_{2.5}$, residential stoves, bituminous coal, South Africa	
	11.0	72.0	% of PM_{10}	
	1.6	16.8	% of $PM_{2.5}$, residential braziers, bituminous coal, South Africa	
Hangebrauck *et al.,* 1964		17	% of TSP, hand-stoked coal burner *sampling points located in the stack*	SE
Hughes & DeAngelis, 1982			TC ~80% of TSP, residential underfeed stoker, bituminous and subbituminous coal.	SE
Mumford *et al.,* 1987		50-90	% of PM_{10}, indoor open fire (unvented coal combustion), bituminous coal	SE
Pinto *et al.,* 1998	2.0	68	% of $PM_{2.5}$, hand fired stove (home heating), smoldering phase, high sulfur lignite	TO
	6.2	62	% of $PM_{2.5}$, hand fired stove (home heating), high temperature phase, high sulfur lignite	
Watson *et al.,* 2001	26.1	69.5	% of $PM_{2.5}$, 3 stoves and 1 fireplace, bituminous coal	TO

Table 4.34: Shares and ranges of emission rates of BC, OC and PM_1 (unabated) as used in the RAINS model for coal combustion.

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM_1	BC	OC	PM_1
Power plants and industry						
Brown coal (PC)	0	0.625	5	0	100	150-1250
Brown coal, peat (grate)	0.1	0.4	5	4.5	18	40-400
Hard coal (PC), dry bottom	0.0315	0.043	2	2	3	50-200
Hard coal (PC), wet bottom	0.0630	0.086	4	1.2	1.6	70-80
Hard coal (FBC)	0.0521	0.01	0.8	4	1	20-100
Hard coal (grate)	0.3	0.15	5	6	3	40-200
Domestic combustion						
Boiler (brown coal, peat) –MB_A			4.5	2.25	5	15-400
Boiler (brown coal, peat) –MB_M			4.5	2.25	5	15-400
Boiler (brown coal) – SHB_M	4.8	50	54	29	300	324
Boiler (hard coal) – MB A			5	4	2	30-130
Boiler (hard coal) – MB M			5	4	2	30-130
Boiler (hard coal) – SHB A	45	10	80	67.5	15	120
Boiler (hard coal) – SHB_M	43	35	80	215	120-175	280-400
Stove (brown coal)	4	52	69	24	312	414
Stove (hard coal)	26	40	70	130	140-200	245-350

4.2.1.2 Wood and Biomass

Wood and biomass burning is believed to be an important source of submicron and carbonaceous particles (Wolff *et al.,* 1981; Rau, 1989; Hildemann *et al.,* 1994; Ohlström, 1998). Particulate emissions from biomass burning are determined by the composition of the fuel and by the physical and chemical processes during combustion (Andrae & Merlet, 2001; Simoneit, 2002).

It is obvious that the emission characteristics vary between the different types of biomass (Simoneit, 2002). Also the sources range from open area sources like natural wildfires or agricultural waste burning on fields to controlled burning in different combustion devices. The range of burning devices in turn stretches from large scale power plants to residential fireplaces (Rau, 1989; US EPA, 1998; Ohlström, 1998; Purvis *et al.,* 2000). Recently, there has been more interest in using renewable biomass also for large scale energy production.

The shares of black and organic carbon from wood burning depend mainly on the combustion temperature (Rau, 1989). The temperature in turn depends primarily on air supply, but also on the burn cycle, the stove design and on the amount, species and moisture content of the wood (Butcher & Sorenson, 1979; Muhlbaier Dasch, 1982; Muhlbaier & Williams, 1982; Rau, 1989; Hildemann *et al.,* 1991; Ohlström, 1998; Fine *et al.,* 2002). Organic carbon is dominant for burning in cool conditions, which is characteristic, e.g., for small scale applications. These volatilized organics are also a major source of submicron particles and since the ash content of the wood is not very high, the emissions are dominated by small submicron particles. In higher temperatures, the share of black carbon rises and becomes dominant (Rau, 1989).

If the combustion temperature is considerably higher (e.g. in large scale power plants), elements vaporize and later nucleate, also forming submicron particles (Valmari *et al.,* 1998; Valmari *et al.,* 1999). With efficient combustion also the carbonaceous shares are low. Several biomass fuels contain significant proportions of volatile alkali metal salts, which are easily vaporized during combustion. This may lead to higher mass concentrations of fine particles than, e.g., during large scale coal combustion (Christensen *et al.,* 1998; Valmari *et al.,* 1998).

A number of biomass fuel parameters, e.g., moisture content, tree species, etc. will affect the amount of emissions. For example, several studies (e.g., Muhlbaier Dasch, 1982; Muhlbaier & Williams, 1982; Hildemann *et al.,* 1991 and Fine *et al.,* 2002) have reported that emissions from hardwoods (e.g. poplar, white ash etc.) have lower shares of BC and higher shares of OC than softwoods (e.g. pine). Butcher & Sorenson (1979) showed that higher wood moisture content resulted in higher emissions of benzene extractable organics.

Submicron Emissions from Burning of Wood and Biomass

For *fireplaces* only one study was found reporting specifically PM_1 emission factors. Purvis *et al.* (2000) gave a composite emission factor of 422 mg/MJ for wet and seasoned oak (hardwood) and douglas fir (softwood). An approximate share of submicron particles in fireplace emissions was estimated in the same paper at approximately 70 percent in TSP. This share was introduced into RAINS. The country specific range is from 525 to 700 mg/MJ, with most of the values in the lower end of the range. This is broadly in line with the measurements done by Purvis *et al.* (2000).

For domestic *stoves* and *boilers* the RAINS estimate was based on Baumbach *et al.* (1999), who reported a range from 70 to 95 percent of PM_1 in TSP for wood burning. Additionally, a presentation given by Houck *et al.* (2001) showed a typical size distribution from residential wood combustion with 92 percent in the submicron fraction. As the lower number in Baumbach *et al.* (1999) represents better small-scale installations and not necessarily devices used in the domestic sector, a value from the upper range of the shares, 92 percent, was introduced to RAINS, both for domestic stoves and single house boilers.

Two studies showed emission factors that were assumed to be broadly representative for *medium sized boilers* in industry (grate) and residential sector (medium sized boiler with automatic fuel feeding). US EPA (1998) reported 90-160 mg/MJ for boilers using wood and bark as fuel (Table 4.35). AP-42 (US EPA, 1998) reports PM_1 a share of 67 percent. A similar value (70 percent.) was measured by Baumbach *et al.* (1999). It was assumed that the share presented US EPA (1998) is applicable to medium-sized boilers in the residential sector (67 percent). Using this share and the current RAINS number for TSP to calculate the emission factor for industrial boilers (grate) gives about 160 mg/MJ, which is at the higher end of the emission factors reported by US EPA (1998). The average of the emission factors from US EPA (1998) gives 50 percent of PM_1 in TSP for industrial boilers when compared to the emission factor currently in RAINS. The lower share of PM_1 is assumed to be more representative for industrial burning, where often some additional fuels might be used together with wood and biomass. Using these shares and the current TSP value in RAINS (50 to 100 mg/MJ for medium sized residential boilers and 240 mg/MJ for grate firing) gives a

range of about 33 to 120 mg/MJ, which is in line with the PM_1 emission factors reported by US EPA (1998). These shares were introduced to RAINS.

Table 4.35: Summary of the emission factors of PM_1 for wood burning [mg/MJ] [R].

Source	PM_1	Remarks
Bond, 2000	194	firewood, residential stove
US EPA, 1998	163	boilers, wood/bark-fired
	116	
	94.6	
Purvis *et al.,* 2000	422	fireplaces, wet/seasoned oak/douglas fir

[R] RECALCULATED – Original values can be found in the Annex (Table A 10)

Table 4.36: Summary of the shares of PM_1 in total particulate matter for wood burning [%].

Source	PM_1	Remarks
Baumbach *et al.,* 1999	95	% of $PM_{11.29}$, domestic heating stoves
	70	small installations (<1MW)
US EPA, 1998	67	% of TSP, boilers, wood/bark-fired
	88	% of $PM_{2.5}$
Latva-Somppi *et al.,* 1998	2.7	BFB, abated (gravitational), paper mill waste sludge
	3.4	CFB, abated (cyclone)
Purvis *et al.,* 2000	~70	Fireplaces (burning wet/seasoned oak/douglas fir)
Valmari *et al.,* 1998	10.7	650 (the convection path)
	18.1	150 (after convection path)
		CFB, willow, abated (cyclone)
Wagner *et al.,* 1991	77.9	$PM_{1.2}$ in $PM_{23.5}$, fireplace Guayule extruded logs, ~50% by weight paraffin wax (during 3 combustion modes: flaming, flaming/smoldering, smoldering)
	76.4	
	40.7	

No specific PM_1 emission factors for large scale combustion sources were available, but two studies reported shares of submicron particles in emissions from combustion of wood and biomass in power plants with fluidized or bubbling beds. Valmari *et al.* (1998) measured 11 to 18 percent of particle mass in the submicron size range. Whereas Latva-Somppi *et al.* (1998) reported an approximate three percent share of PM_1 in TSP for paper mill waste sludge. Based on these studies a share of five percent is introduced to RAINS[5].

Carbonaceous Emissions from Burning of Wood and Biomass

This section reviews the studies that report emissions of BC and OC from burning of wood and biomass. It also describes the values used in RAINS and how they were derived. No studies that measured carbonaceous emissions from large scale combustion were found, but several studies address emissions from small scale burning in, i.e., fireplaces and stoves. Emission characteristics from fireplaces as well as domestic burning in stoves and boilers are

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[5] Currently RAINS does not distinguish between different types of combustion installations for large boilers and therefore it is not possible to specify separately shares for FBC and grate combustion for power plants and industrial boilers. It is envisaged that the model will be extended in the near future to allow for this.

discussed in separate sections. The latter includes also a paragraph about power plants and industry.

Fireplaces

Five studies reported BC emission factors for burning of wood in *fireplaces* (Cooper, 1980; Muhlbaier Dasch, 1982; Muhlbaier & Williams, 1982; Hildemann *et al.,* 1991, and Fine *et al.,* 2002). Muhlabaier & Dasch (1982), Muhlbaier & Williams (1982), Hildemann *et al.* (1991) and Fine *et al.* (2002) found that tree species affect emissions, with higher emissions for softwoods than for hardwoods. The variation between the reported emission factors was high: 5-50 mg/MJ for hardwood and 15-186 mg/MJ for softwood. One explanation for the large variation can be the different size of the measured particles. Studies measuring BC in fine particles (Hildemann *et al.,* 1991 and Fine *et al.,* 2002) showed lower emissions (5-17 mg/MJ hardwood; 15-41 mg/MJ softwood) than the studies that measured BC in TSP (24-50 mg/MJ hardwood; 81-186 mg/MJ softwood) (Muhlbaier Dasch 1982 and Muhlbaier & Williams 1982). This indicates that there may be BC emissions ("char") also in the larger size fractions of the particles as in the case of coal. Cooper (1980) reported an emission factor of 69 mg/MJ for both hard- and softwoods.

A similar difference between hard- and softwoods as in the emission factors was observed also in the shares. The share of BC was lower in emissions from combustion of hardwood than softwood. The shares for hardwood were between one and eight percent of TSP and for softwood between approximately five to 36 percent (Muhlbaier and Dasch, 1982; Muhlbaier & Williams 1982; Rau, 1989; Hildemann *et al.,* 1991; Watson *et al.,* 2001 and Fine *et al.,* 2002). For softwoods only one study (Hildemann *et al.,* 1991) reported a BC share below 10 percent and the range without that study was 12 to 36 percent.

The tree species did not affect the emissions of OC from fireplaces, nor was any size dependency observed. Emission factors ranged between 160 mg/MJ and 390 mg/MJ (Cooper, 1980, Muhlbaier Dasch, 1982, Muhlbaier & Williams, 1982, Hildemann *et al.,* 1991 and Fine *et al.,* 2002) (Table 4.37). The shares between hard- and softwoods were similar, which was already indicated by the emission factors. Most of the studies were consistent: Muhlbaier and Dasch (1982), Muhlbaier & Williams (1982), Rau (1989), Hildemann *et al.* (1991) and Watson *et al.* (2001) reported shares of OC in TSP varying from 38 to 52 percent. However, Fine *et al.* (2002) reported higher shares, 65 to 75 percent. The numbers reported by Hildemann *et al.* (1991) and Fine *et al.* (2002) were converted to refer to TSP assuming 88 percent of $PM_{2.5}$ in TSP.

Table 4.37: Summary of the emission factors of BC and OC for wood burning in fireplaces [mg/MJ] [R].

Source	BC	OC	Remarks	Method
Andrae & Merlet, 2001	36.9	250	Biofuel burning	Unknown
Cooper, 1980	68.8	249	Fireplaces	Unknown
Muhlbaier, 1981	50	300	hardwoods	T
	87.5	219		
	50	375		
	60.6	819		
	62.5	681		
	22.5	238		
	68.75	256		
	81.25	256		
	481.3	325	softwoods	
	87.5	244		
	168.8	250		
Fine et al., 2002	14.4	361	In $PM_{2.5}$, fireplace combustion, hardwoods (yellow poplar, white ash, sweetgum, mockernut hickory)	TO
	13.2	158		
	5.9	173		
	5.1	316		
	41.4		softwoods (loblolly pine, slash pine)	
	14.2			
Hildemann et al., 1991	42.5	393	In PM_2, fireplaces, softwood	TO
	17.3	160	Hardwood	
	93.8	428	synthetic log	
Muhlbaier Dasch, 1982	186	214	Residential fireplaces, softwoods, 12 tests	T (mod.)
	50.0	288	hardwoods, 24 tests	
	141	459	synthetic logs, 3 tests	
Muhlbaier & Williams, 1982	81.3	175	Residential fireplaces, softwoods, 4 tests	T (mod.)
	24.4	294	hardwoods, 6 tests	
	219	106	synthetic logs, 3 tests	

[R] RECALCULATED – Original values can be found in the Annex (Table A 9)

Based on these studies, average shares and absolute emission factors for BC and OC were derived assuming that the shares of hardwood and softwood used are 70/30 (not verified with data). The resulting average shares are 10 and 50 percent for BC and OC, accordingly (resulting in a TC share lower than PM_1). The average emission factors (assuming use of hardwood and softwood as above) derived from the studies are about 76 mg/MJ and 300 mg/MJ for BC and OC. Comparing these numbers with the RAINS emission factors derived from the above shares reveals a good agreement for BC (RAINS country specific emission factors range between 75 and 100 mg/MJ) and a larger RAINS numbers for OC, i.e., ranging from 350 to 500 mg/MJ, but still within the range reported in the literature. Additionally, adding up the BC and OC RAINS emission factors to get TC and comparing it with the current RAINS TSP emission factor (750 mg/MJ) results in a share of about 60 percent, which is in line with the TC shares reported in the reviewed studies (Table 4.38).

Table 4.38: Summary of the shares of BC and OC in total particulate matter for wood burning in fireplaces [%].

Source	BC	OC	Remarks	Method
Fine *et al.,* 2002 [a]	3.4	84.9	% of PM$_{2.5}$, fireplace combustion, hardwoods (yellow poplar, white ash, sweetgum, mockernut hickory)	TO
	6.4	76.8		
	2.7	78.8		
	1.2	74.2		
	17.9	100.4	% of PM$_{2.5}$, fireplace combustion, softwoods (loblolly pine, slash pine)	
	14.2	100.6		
Hildemann *et al.,* 1991	5.23	48.4	% of PM$_2$, fireplaces, softwood	TO
	2.86	48.4	Hardwood	
	12.5	57.0	synthetic log	
Muhlbaier Dasch, 1982	33	38	Residential fireplaces, softwoods, 12 tests	T (mod.)
	8	46	hardwoods, 24 tests	
	15	49	synthetic logs, 3 tests	
Muhlbaier & Williams, 1982	36	40	Residential fireplaces, softwoods, 4 tests	T (mod.)
	5.1	50	hardwoods, 6 tests	
	55	26	synthetic logs, 3 tests	
Rau, 1989	10	52	Residential fireplaces, hardwood and softwood	TO
Watson *et al.,* 2001	12.4	51.4	% of PM$_{2.5}$, residential stoves and fireplaces, softwoods	TO

[a] For OC the results include adsorption of gas-phase organics onto the quartz-fiber filter (more explanation in the original paper)

Stoves and Boilers

For *domestic stoves and boilers* only one BC emission factor, 43 mg/MJ, was found in a study by Cooper (1980). BC shares were available from Rau (1989) and Watson *et al.* (2001). Rau (1989) observed a connection between the emission shares and combustion temperature: The share of BC in TSP rose with temperature from five percent during cool phase up to 16 percent during hot phase for hardwoods and from five percent up to 38 percent for softwoods. Watson *et al.* (2001) reported 12 percent BC in TSP for burning of softwood.

Cooper (1980) and Butcher & Sorenson (1979) reported emission factors for OC from *domestic stoves and boilers,* showing a large variation from 70 mg/MJ to 390 mg/MJ (or even 1013 mg/MJ). The range is to large extent a result of varying combustion conditions (see, e.g., Butcher & Sorenson 1979). As for the shares of OC, Butcher & Sorenson (1979) reported 47 to 67 percent of OC in PM emissions from combustion of hardwoods, and Watson *et al.* (2001) 51 percent from combustion of softwoods. Rau (1989) observed a decreasing share of OC with increasing combustion temperature, from 57 percent in cool phase down to 14 percent in hot phase for hardwoods, and from 51 percent down to 20 percent for softwoods.

Table 4.39: Summary of the emission factors of BC and OC for wood burning in stoves [mg/MJ].

Source	BC	OC	Remarks	Method
Andrae & Merlet, 2001	36.9	250	Biofuel burning	Unknown
Cooper, 1980	43.0	249	Wood burning stoves	Unknown
Environment Australia, 2002	39.4	118.8	hardwood (Eucalyptus)	T
	200	387.5	softwood	
Butcher & Sorenson, 1979		68.1	Small wood stove burning oak (draft setting/fuel moisture: full/23.8%, 0.5/23.8%, 0.25/8.7%, 0.25/23.8%)	SE
		183		
		129		
		1013		
		392	Small wood stove burning pine (burning conditions: ¼ draft, 42.4% fuel moisture)	

Table 4.40: Summary of the shares of BC and OC in total particulate matter for wood burning in stoves [%].

Source	BC	OC	Remarks	Method
Industrial boilers				
US EPA, 2002	2.2	5.5	% PM_{10}, wood-fired boiler with cyclone (profile 11801)	
(SPECIATE v3.2)	4.6	7.3	With wet scrubber (profile 12704)	
Domestic Stoves and boilers				
Butcher & Sorenson, 1979		47.2	Small wood stove burning oak	SE
		56.2	(draft setting/fuel moisture: full/23.8%; 0.5/23.8%; 0.25/8.7%; 0.25/23.8%)	
		48.7		
		66.5		
		60.4	Small wood stove burning pine (burning conditions: 0.25 draft, 42.4% fuel moisture)	
Environment Australia, 2002	14	42	hardwoods	T
	20	39	softwoods	
US EPA, 2002	4.5	38.7	Woodstove, burning pine (profile 42101)	
(SPECIATE v3.2)	7.2	29.2	Oak (profile 42103)	
	6.4	35.9	Average of all fuels (profile 42102)	
	14.3	48.9	Residential woodstove (profile 42104)	
	7.9	45.4	(profile 42105)	
	10.1	47.2	(profile 42106)	
Rau, 1989	5	51	Woodstoves, cool burning of softwood	TO
	5	57	cool burning of hardwood	
	38	20	hot burning of softwood	
	16	14	hot burning of hardwood	
Watson et al., 2001	12.4	51.4	% of $PM_{2.5}$, residential stoves and fireplaces, softwoods	TO
Ålander, 2000	~60	~40	% of TC, small domestic boilers, spruce chips	TO

For *stoves,* a similar procedure as for fireplaces was followed to develop emission factors for RAINS. Assuming equal use of hardwood and softwood results in an average BC share of about 15 percent in TSP while for OC a share of about 45 percent could be derived. Using these shares and the current RAINS numbers and calculating the BC and OC emission factors for stoves gives country specific range from 75 to 105 mg/MJ and 225 to 315 mg/MJ.

Reviewing available emission factor data shows a large variation between hardwood and softwood. Deriving averages (assuming equal use of hard and softwoods) gives about 80 mg/MJ for BC and 346 mg/MJ for OC, however, the latter average includes a very high number reported by Butcher & Sorenson (1979) (Table 4.39). Eliminating it results in a value of 258 mg/MJ for OC and consequently a comparison of reported absolute numbers with values assumed in RAINS shows generally good agreement.

For *single house boilers,* in the absence of available studies, the shares of BC and OC were derived based on the hot burning phase from stove measurements (Rau, 1989). Rounded average numbers are 30 and 20 percent for BC and OC, respectively. The same BC/OC ratio is reported by Ålander (2000). The current RAINS data distinguishes between manually and automatically fed boilers, and it is reasonable to assume that the combustion conditions and thus the emission profiles differ between them. It can be expected that combustion in automatically fed boilers is more efficient. It was assumed that in the manually fed boilers the emission profile is more comparable with stoves and thus has a higher share of OC. Since there were no measurements available, a profile with 30 percent of BC and 45 percent of OC was assumed for manually fed single house boilers. The shares for automatically fed boilers were estimated to be 35 percent for BC and 25 for OC. The BC was assumed to be slightly higher and the OC slightly lower than in the manually fed boilers as an indication of the more efficient combustion. These shares are broadly in line with the hot burning phase measurements for wood stoves from Rau (1989).

Similarly as for single house boilers, RAINS distinguishes between manual and automatic feeding also for *medium sized boilers*. Since no measurements of carbonaceous species were found, a similar pattern as for single house boilers was used for deriving BC and OC. For manually fed medium sized boilers the carbonaceous fractions (and thus the combustion conditions) were assumed to be similar as for automatically fed single house boilers with 35 percent of BC and 25 percent of OC.

The automatically fed boilers are assumed to be fairly similar to boilers used in industrial applications (grate in RAINS). For industrial scale boilers (grate) the SPECIATE emission profiles were used to derive BC and OC. The resulting shares are four percent for BC and six percent for OC, which gives 9.6 mg/MJ and 14.4 mg/MJ for BC and OC, respectively. For domestic boilers slightly lower combustion efficiency was assumed with 15 percent shares for both BC and OC.

For fluidized bed combustion of wood the share of PM_1 is very low, so it is expect that the share of TC will not be higher. A large fraction of the submicron particles can be volatile alkali metal salts, and thus a very low share of carbonaceous particles, around one percent, was assumed.

Table 4.41: Shares and ranges of emission factors of BC, OC and PM_1 as used in the RAINS model for wood and biomass combustion

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM_1	BC	OC	PM_1
Power plants and industry						
FBC	0.5	0.5	5	1.2	1.2	12
Grate	4	6	50	9.6	14.4	120
Domestic combustion						
Boiler – MB_A	15	15	67	7.5	7.5	33.5
Boiler – MB_M	35	25	67	35	25	67
Boiler – SHB_A (pellet boilers)	35	25	92	17.5	12.5	46
Boiler – SHB_M	30	45	92	75-100	112-158	230-320
Stove	15	45	92	75-105	225-315	460-640
Fireplace	10	50	70	75-100	350-500	525-700

4.2.1.3 Waste Incineration

The formation mechanism of particles in waste incineration is similar to that observed for other solid fuels such as coal. The combustion conditions and thus the emissions depend on several factors ranging from incinerator design to the type of waste burned. This applies to both the chemical composition and size range of the particulate emissions. High levels of chloride for example can lead to increased formation of submicron particles. Otherwise the submicron fraction is formed through vaporization and condensation/nucleation (Hangebrauck *et al.,* 1964; US EPA, 1998; Lighty *et al.,* 2000).

Table 4.42: Summary of the emission factors of PM_1 and OC for waste incineration [mg/MJ][R].

Source	OC	PM_1	Remarks	Method
Hangebrauck *et al.,* 1964	2.61		Large units, incineration	SE
	0.55			
	2.42		Small units, incineration	
	13.2			
US EPA, 1998		82	Medical waste	
		47	Sewage sludge, multiple hearth incinerator	
		60	Sewage sludge, electric infrared incinerator	

[R] RECALCULATED – Original values can be found in the Annex (Table A 11)

Table 4.43: Summary of the shares of PM_1, BC and OC in total particulate matter for waste incineration [%].

Source	BC	OC	PM_1	Remarks	Method
APEG 1999			73	% of PM_{10}	-
Hangebrauck *et al.,* 1964		0.32		250 ton/day	SE
		0.15		50 ton/day, large units, incineration	
		1.3		5.3 ton/day	
		4.4		3 ton/day, small units, incineration	
US EPA, 1998			35.4	Medical waste	
			1.2	Sewage sludge, multiple hearth incinerator	
			6	Sewage sludge, electric infrared incinerator	
Olmez *et al.,* 1988	3.5	0.57		% in fine particles ($PM_{2.5}$), municipal incinerator, measured from the breach before the stack, unabated emissions	T
	2.3	2.5		% in coarse particles (2.5<PM<10)	
	3.4	0.8		% in PM_{10}	
Pinto *et al.,* 1998	18	56		Hospital incinerator (Teplice, Czech Republic)	TO

The numbers for RAINS were derived based on BC and OC shares in fine particles reported by Olmez *et al.* (1988). Converting them to relate to total particulate mass gives 0.9 percent of BC and 0.15 percent for OC. These shares are introduced to RAINS, while it has to be noted that they are very uncertain and might not represent all possible waste types. Only a limited number of studies reporting submicron emissions from waste incineration were found and currently a lower share, 17 percent, than for fine particles is assumed. This and the resulting emission factors are broadly in line with the values for medical waste reported by US EPA (1998) and APEG (1999) when converted to refer to total particle mass.

Table 4.44: Shares of BC, OC and PM_1 in TSP as used in the RAINS model for waste incineration

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM_1	BC	OC	PM_1
Power plants and industry	0.9	0.15	17	1.29	0.21	24
Small combustion	0.9	0.15	17	4.55	0.74	85

4.2.2 Liquid Fuels and Natural Gas

Particulate emissions from burning of liquid fuels depend, similarly to solid fuels, on combustion conditions and fuel type, e.g., the ash content of the fuel. The ash content is, however, much lower than that of solid fuels, which makes the share of inorganic particles smaller. The major categories of fuel oil are distillate oils and residual oils. Residual oil is also known as heavy fuel oil and it is produced from the residue remaining after the lighter fractions like distillate oil or light fuel oil have been removed from the crude oil in the refining process (US EPA 1998; Lighty *et al.,* 2000).

4.2.2.1 Heavy Fuel Oil

For heavy fuel oil, particulate emissions are influenced by the ash and sulfur content of the oil. The emissions are composed of three basic types of particles, i.e., submicron carbonaceous particles, ash residues and residues of the fuel spray droplets, called cenospheres (Goldstein & Siegmund, 1976). Ash and the carbon-rich cenospheric particles are coarse and may account for a major part of the mass emitted. However, owing to their relatively short atmospheric lifetime, they are not of primary interest for this analysis. They are both highly dependent upon fuel composition. Especially small boilers burning residual oil can have a large mass fraction in the coarse mode, composed largely of cenospheres. In bigger boilers, combustion is more efficient, so that the carbon content is lower and almost all emitted particles are in the fine or submicron mode (Goldstein & Siegmund, 1976; Lighty *et al.*, 2000). For heavy fuel oil, the emission factors and the shares of black carbon, organic carbon and submicron fractions found in the literature are shown in Table 4.45, Table 4.46 and Table 4.47.

Table 4.45: Summary of the PM1 emission factors for heavy fuel oil combustion [mg/MJ]

Source	PM_1	Remarks
APEG, 1999; TNO, 1997	3.92	public power generation
	2.10	industrial combustion
	1.15	small combustion
Bond, 2000	0.75	small plant (2MW), residential
	1.50	(*normal, warmup, overall emission factor*)
	1.25	
Goldstein & Siegmund, 1976 [a]	9.46	50 hp package boiler, low sulfur (0.5%S) fuel
	14.2	high sulfur (2.2%S) fuel
US EPA, 1998	10.1*A [b]	utility boilers
	9.20*A	industrial boilers
	3.58*A	commercial boilers

[a] original values 30 and 45 mg/SCM (mg/standard cubic meter), respectively; [b] No 4 oil: A=0.84, No 5 oil: A=1.2, No 6 oil: A=1.12*S+0.37, where S is the weight% of sulfur in the oil

Table 4.46: Summary of the PM1 shares in total particulate matter for heavy fuel oil combustion [%]

Source	PM_1	Remarks
APEG, 1999	56	% of PM_{10}, public power generation
	42	industrial combustion
	23	small combustion
Bacci *et al.*, 1983	85	% of $PM_{2.5}$, power plant
Buerki *et al.*, 1989	15.5	% of $PM_{11.3}$, small industrial boiler
Ehrlich *et al.*, 2001	49.9-64.3	10 MW boiler (operating 5-8.5 MW), abated with additive
Goldstein & Siegmund, 1976	~60	50 hp package boiler low sulfur (0.5%S) fuel
	~25	high sulfur (2.2%S) fuel
US EPA, 1998	39	Utility boilers
	36	Industrial boilers
	14	Commercial boilers

Submicron shares for heavy fuel oil burned in power plants, industry and residential sector were derived based on the PM_1 fractions found in the literature (Table 4.46). The resulting numbers are 40, 30 and 15 percent in TSP, respectively.

Table 4.47: Summary of the shares of BC and OC in total particulate matter for heavy fuel oil combustion. (HF) [%]

Source	BC	OC	Remarks	Method
Goldstein & Siegmund, 1976			Total carbon 60% of TSP	Unknown
Henry & Knapp 1980	23.8 12.5	<0.1	Power plants, (average of 6 fly ash samples, average without highest value)	T
Lighty *et al.,* 2000			TC >75% of TSP, (from Miller *et al.,* 1998), small boilers	Unknown
Olmez *et al.,* 1988 [a]	7.7	2.7	% in $PM_{2.5}$ (fine mass 93% of PM_{10}), 395 MW power plant, in stack measurements, *after ESP*	T
	21	Not detected	% in coarse particles (2.5<PM<10)	
	8.6	2.5	% in PM_{10}	
	0.22	0.75	% in $PM_{2.5}$ (fine mass 96% of PM_{10}), 660 MW power plant (operating 460 MW), duct measurements, *after cyclone*	
	1.0	Not detected	% in coarse (2.5<PM<10)	
	0.25	0.72	% in PM_{10}	
US EPA, 2002 (SPECIATE v3.2 [b])				
Oil fired power plants, unabated				
Profile 11507	12.8	5.0	% in $PM_{2.5}$ (fine mass 94% of PM_{10})	
	18.7	44	% in coarse particles	
	13.2	7.3	% in PM_{10}	
Profile 11508	7.7	3.2	% in $PM_{2.5}$ (fine mass 94% of PM_{10})	
	21	12	% in coarse particles	
	8.4	3.7	% in PM_{10}	
Profile 11509	0.22	1	% in $PM_{2.5}$ (fine mass 96% of PM_{10})	
	1.1	26	% in coarse particles	
	0.26	2	% in PM_{10}	
Oil fired boiler, unabated				
Profile 13504	8.69	8.96	% in $PM_{2.5}$ (fine mass 65% of PM_{10})	
	80.2	5.6	% in coarse particles	
	33.6	7.8	% in PM_{10}	
Wolff *et al.,* 1981	11.5	24.5	Utility and industrial boilers, (see references in Wolff *et al.* 1981)	Unknown

[a] Power plants burning No. 6 fuel oil; [b] Not including profiles that refer to Henry & Knapp, 1980

The emission shares of BC and OC for heavy fuel oil burning in industry and power plants were derived by taking the averages of all available measurements for fine fraction and converting them to refer to TSP using the current $PM_{2.5}$ share in RAINS (60 percent). The shares introduced in RAINS are 4.3 percent for BC and 1.9 percent for OC. There were no studies available reporting measurements representing residential burning of heavy fuel oil.

Therefore, the OC value (0.375 mg/MJ) used by Bond *et al.* (2004) and the current RAINS $PM_{2.5}$ emission factor of 10 mg/MJ were used to derive the share of OC. Combining these values leads to an estimated one percent of OC in TSP. In order to derive BC shares and emission factors, information available in the SPECIATE 3.2 database (US EPA, 2002) and Bond *et al.* (2004) was used. An average share of 3.5 percent was derived, which leads to a BC emission factor of about 1.3 mg/MJ, which is slightly higher than that reported by Bond *et al.* (2004), i.e., about 1 mg/MJ.

4.2.2.2 Light Fuel Oil

Particles that are formed during combustion of light fuel oil are found in fine and coarse modes. They are mainly carbonaceous, but may contain inorganic components, e.g., sulfates (Sabbioni & Zappia, 1992; Lighty *et al.,* 2000). The ash content of the distillate fractions is, however, much smaller than that of residual oil. Distillate oils are often used for small-scale domestic heating, where emissions are usually uncontrolled. The emission factors of black carbon, organic carbon and submicron fractions in fine particles are shown in Table 4.48 and Table 4.50.

Table 4.48: Summary of the emission factors of PM_1, BC and OC for combustion of light fuel oil [mg/MJ]

Source	BC	OC	PM_1	Remarks	Method
APEG, 1999; Berdowski *et al.,* 1997			1.26	public power generation	
			0.85	industrial combustion	
			42.5	small combustion	
Hangebrauck *et al.,* 1964		3.4-13.2		small units	SE
		1.3		large units (steam atomized)	
		3.1			
Hildemann *et al.,* 1991	2.71	0.45		PM_2, industrial scale boiler	TO
US EPA, 1998 [a]			0.571	industrial boilers	
			2.52	commercial boilers	

[a] original values 0.0204 and 0.09 kg/1000 l, respectively

Table 4.49: Summary of PM1 shares in total PM for the combustion of light fuel oil [%]

Source	PM_1	Remarks
APEG, 1999	18	% of PM_{10}, public power generation
	17	% of PM_{10}, industrial combustion
	85	% of PM_{10}, small combustion
US EPA, 1998	8	Industrial boilers
	37	Commercial boilers

Based on the shares and absolute numbers in Table 4.48 and Table 4.49 (mainly from US EPA 1998), the PM_1 share in TSP emissions is estimated at 10 percent for power plants and industry and at approximately 40 percent for the domestic sector. To derive the BC and OC shares for power plants and industry, results of Hildemann *et al.* (1991) were used. Results from Hangebrauck *et al.* (1964) were not included, since their reported emission factors for TSP are very high, which is probably influenced by the different quality of fuel oil in the US 40 years ago and the very different combustion technologies. The numbers from Hildemann *et*

al. (1991) (see Table 4.50) were converted to refer to TSP using the current RAINS $PM_{2.5}$ shares. With this, the estimated shares are five percent for BC and 0.8 percent for OC in TSP. For the domestic sector, the BC and OC shares were derived assuming that 40 percent of total particles is carbonaceous (TC). A BC to OC ratio of approximately four, as reported by Ålander (2000), was applied to the TC share, which results in 32.4 percent of BC and 8.1 percent of OC for burning of light fuel oil in domestic sector.

Table 4.50: Summary of the BC and OC shares in total particulate matter for the combustion of light fuel oil [%]

Source	BC	OC	Remarks	Method
Hangebrauck *et al.,* 1964		9.4-60	Small units	SE
		1 & 2.7	Large units	
Hildemann *et al.,* 1991	28.9	4.80	% of PM_2, industrial scale boiler	TO
Sabbioni & Zappia, 1992		2.36	TC of TSP. Large boiler used, e.g., in shopping centers.	T
		2.18	A single house boiler	
Wolff *et al.,* 1981	16		Utility and industrial boilers (based on Watson 1979)	Unknown
Ålander, 2000	85-70	15-30	% of TC, small domestic boilers	TO

4.2.2.3 Natural Gas

Over 85 percent of natural gas is methane, with small amounts of other gaseous substances (US EPA, 1998). Because it is a gaseous fuel without solid ash, particulate emissions are typically very low. Emissions are influenced by the quality of combustion and consist mainly of unburned organic carbon, practically totally found in the submicron mode (Hangebrauck *et al.,* 1964; Hildemann *et al.,* 1991; US EPA, 1998; APEG, 1999).

Table 4.51: Summary of the PM_1, BC and OC emission factors for combustion of natural gas [mg/MJ].

Source	BC	OC	PM_1	Remarks	Method
Bond, 2000 [a]			0.067	Small plant (2MW), residential	
Hangebrauck *et al.,* 1964		0.99		Process heating (firetube boiler)	SE
		1.12		Hospital heating (scotch-marine boiler)	
		0.69-2.11		Home heating (hot air furnace, double shell boiler & wall space heater)	
Hildemann *et al.,* 1991	0.0031	0.0389		PM_2, residential heater	TO
Muhlbaier & Williams, 1982	0.0072	0.036		Residential heater, methane gas (normal and fuel rich conditions)	T (mod.)
	1.242	0.891			
	0.0224	0.112		Residential heater, propane gas (normal, fuel rich)	
	4.232	3.036			
US EPA, 1998			0.82	Filterable PM, boilers and furnaces	-

[a] original value 0.003 g/kg

Table 4.52: Summary of the shares of PM_1, BC and OC in fine particulate matter for the combustion of natural gas [%].

Source	BC	OC	PM_1	Remarks	Method
APEG, 1999			100	Industrial combustion, power generation and small combustion	
US EPA, 1998			100		
Hangebrauck *et al.,* 1964		11		Process heating (firetube boiler)	SE
		8		Hospital heating (scotch-marine boiler)	
		19-33		Home heating	
Hildemann *et al.,* 1991	6.7	84.9		% of PM_2, residential heater	TO
Muhlbaier & Williams, 1982	4	8		Laboratory (10 tests)	T (mod.)
				Residential heater, methane gas, normal operating conditions.	
	8	40		Residential chimney (1 test)	
				methane gas	
	89	5		Laboratory (6 tests)	
				Residential heater, propane gas, fuel rich operating conditions	
	46	33		Residential chimney (1 test)	
				methane gas	

Based mainly on the information from US EPA (1998) it was assumed that all PM is emitted as PM_1. For the domestic sector, the BC and OC numbers for RAINS were derived from the study by Hildemann *et al.* (1991), who also measured fine particle emissions in the range currently in RAINS. The reported shares of BC and OC were 6.7 percent and 84.9 percent, respectively. The OC share, however, is very uncertain. Hildemann *et al.* (1991) estimated that up to 61.7 percent may result from gas-phase adsorption. We relied on the BC share reported by Hildemann *et al.* (1991), but scaled down the OC share to 75 percent so that the BC+OM adds up to about 97 percent. Applying these shares results in emission factors of about 7 and 75 µg/MJ for BC and OC, respectively.

Table 4.53: Shares and ranges of BC, OC and PM_1 emission factors for liquid and gaseous fuels as used in the RAINS model

	Share in TSP [%]			Emission factors [mg/MJ]		
	BC	OC	PM_1	BC	OC	PM_1
Heavy fuel oil						
Power plants	0.2-10 (4.3)	0-2 (1.9)	40	0.74-0.84	0.33-0.37	6.9-7.8
Industry	0.2-10 (4.3)	0-2 (1.9)	30	0.67	0.29	4.7
Residential	3	1	15	1.3	0.38	5.7
Light fuel oil						
Power plants	5	0.8	10	0.11-0.18	0.018-0.029	0.22-0.36
Industry	5	0.8	10	0.11	0.018	0.22
Residential	32.4	8.1	40	0.53	0.13	0.66
Natural gas	7	75	100	0.007	0.075	0.1

4.3 Industrial Processes

Many industrial processes emit particulate matter into the atmosphere. Emissions vary between countries and processes because of varying process designs and different levels of abatement. The origin of these emissions is more complex than that of stationary combustion sources, especially since there are many sub-processes and open, re-emitting sources that contribute to the emission load (Berdowski *et al.,* 1997; Klimont *et al.,* 2002).

The emission characteristics are highly dependent on the activity. Some may be high emitters of coarse and large particles, while the emissions in the fine size range are negligible. The lack of detailed studies limits, however, the possibility to establish robust emission estimates, especially when the focus is on the submicron particles or on chemical speciation of PM emissions.

Industrial processes are estimated to be an important contributor to the total European emissions in the fine and submicron size fractions (Berdowski *et al.,* 1997; APEG, 1999; Klimont *et al.,* 2002) with a contribution from around 15 to 30 percent (APEG, 1999; Klimont *et al.,* 2002). The available studies indicate that most of the particulate emissions from stationary non-combustion processes originate from metallurgical industry with cement industry and petroleum refining as the second largest emitters. According to calculations by Berdowski *et al.* (1997), these industries contributed over 95 percent of the European PM_{10} emissions from industrial non-combustion processes in the beginning of 1990's. For smaller size fractions ($PM_{2.5}$ and $PM_{0.1}$), they estimated the emissions from cement industry to be negligible, but metallurgical industry and petroleum refining still contributed 95 percent of the total emissions (Berdowski *et al.,* 1997).

Measurements of carbonaceous emissions are scarce and were only found for few processes. However, based on the knowledge about different stages of the process and the raw materials used, an attempt was made to estimate their share in emitted particles. In general it can be expected that industrial processes are not a major source of BC and OC, but they may be relatively important for the submicron size range.

The choice of sectors is based on the RAINS PM module (Klimont *et al.,* 2002). The approach to calculate the emission factors is basically the same. Some sectors that are included in the RAINS structure are not dealt in this section, since their contribution to submicron and/or carbonaceous emissions is negligible.

4.3.1 Iron and Steel Industry

Iron and steel industry includes several distinct production processes/stages. Emissions from coke production, sintering, blast furnace, basic oxygen furnace, electric arc furnace, open-hearth furnace and iron and steel foundries are discussed separately.

4.3.1.1 Coke Production

Coke is produced through pyrolysis of coal and there are several stages in the process, which release particulate matter. These include mechanical operations, e.g., crushing and blending of the raw coal and coke as well as the actual coking phase, where the volatile species are

removed from the coal (US EPA, 1998, Passant *et al.,* 2000). Mechanically produced particles are in general coarse in size, whereas the volatilized vapors, e.g., from the coal preheating and coking, may form smaller particles (US EPA, 1998). Due to the chemical properties of the raw material (coal) and the end product (coke), most of the particles generated during coke production are probably also carbonaceous.

Emission factors and shares of PM_1 in TSP are shown in Table 4.54. The only reported numbers for uncontrolled carbonaceous emissions from coking were found in the SPECIATE 3.2 database (US EPA, 2002), where BC and OC for a coke cooler are reported (profile 26208). The emissions were mainly BC, constituting 90 percent of PM_{10} and 74 percent of fine particles. OC shares were 3.3 percent and 1.9 percent, respectively. Bond *et al.* (2004) assumed that 95 percent of the emissions is carbonaceous, half of which is BC and the other half OM. The emission factors for RAINS were derived following the same logic as in Bond *et al.* (2004). However, relying on the SPECIATE numbers that apply only to the cooling phase might lead to an underestimation of OC in emissions. Using a conversion factor of 1.3 to 1.4 for calculating OC and relating emissions to submicron particles, emission factors of 0.75 kg/ton for BC and 0.54 kg/ton for OC were estimated.

Table 4.54: Shares and emission factors for coke production [kg/ton coke], PM_1 –shares based on US EPA (1998 and 2002), underlined TSP emission factors from Klimont *et al.* (2002).

	BC	OC	PM_1 [kg/ton]	PM_1 in TSP	TSP [kg/ton]
AP-42					
Coal pre-heater	-	-	1.36	48.5 %	2.8
Oven charging	-	-	0.10	25.2 %	0.38
Oven door leaks	-	-	---	---	0.43
Oven pushing	-	-	0.07	7.7 %	0.93
Quenching (dirty water)	-	-	0.36	13.8 %	2.62
Quenching (clean water)	-	-	0.02	4.0 %	0.57
Quenching with baffles (dirty water)	-	-	0.06	8.5 %	0.65
Quenching with baffles (clean water)	-	-	0.005	1.2 %	0.43
SPECIATE v 3.2					
Coke cooler	90 %	3.3 %	-	-	-
	74 %	1.9 %	-	-	-

Table 4.55: Emission factor and the share of PM_1 in fine particles proposed for the RAINS model for coke production [kt/ton coke].

Sector	RAINS code	BC	OC	PM_1 [a]	% of TSP	TSP
Coke Production	IN_PR_COKE	0.75	0.54	1.535	30.8 %	4.976

[a] PM_1 value based on the sum of the underlined EFs, see Klimont *et al.,* 2002

4.3.1.2 Sinter Plants

Sinter plants convert raw materials like iron ore and limestone into an agglomerated form to be used in further processes. This is done through heating the crushed and mixed raw materials, i.e., iron ore, coke and limestone, so that the surface melts and agglomerate is formed. The mixture is placed on a traveling grate and the coke is ignited with a burner. The primary source of particulate emissions is the windbox exhaust, which draws the combusted air from the material bed into a common duct. Particles in the exhaust including submicron particles are entrained from the bed material or combustion products. They consist mainly of oxides of iron and sulfur, but also carbonaceous particles are formed. The process continues with a phase where the formed agglomerate (the sinter product) is crushed and screened in the discharge end. This is another source of particles, consisting mainly of iron and calcium oxides. In addition to these processes, fugitive emissions may also emerge, e.g., during handling and transportation of the raw materials. The shares reported by US EPA (1998) and Engelbrecht *et al.* (2002) (Table 4.56) were used to derive the emission factors for sinter processes (Table 4.).

Table 4.56: Shares of PM_1, BC and OC for sinter processes [a] [kg/ton finished sinter]

Source	BC	OC	PM_1	Remarks	Method
US EPA, 1998; AWMA, 2000 (Windbox)			4	Of TSP	-
Engelbrecht *et al.,* 2002	0.4	2		Of PM_{10} (bag filter dust)	TO

[a] the size distribution reported for windbox (US EPA, 1998; AWMA, 2000) is assumed to be representative for all uncontrolled emissions from sinter plant, see Klimont *et al.* (2002).

Table 4.57: Emission factors of PM_1, BC and OC in TSP proposed for the RAINS model for sinter processes [kg/ton finished sinter].

Sector	RAINS code	BC	OC	PM_1	PM_{10} [a]	TSP [a]
Sinter processes	IN_PR_SINT	0.005	0.026	0.34	1.285	8.563
Sinter fugitive	IN_PR_SINT_F	-	-	0.06	0.24	1.6
Pellet Plant	PR_PELL	-	-	0.03	0.03	0.03

[a] PM_{10} and TSP, see Klimont *et al.* (2002)

4.3.1.3 Pig Iron Production (Blast Furnace)

Blast furnaces reduce iron bearing materials with hot gas to produce pig iron, which then later acts as "raw material" for the steel making process. The furnace is charged form the top with iron and with flux material such as limestone. Also coke is added as a fuel (other fuels can be used as well, e.g., oil, gas or coal). The charge reacts with air blown from below to form molten iron and slag. Sometimes cavities may be formed in the charge, which later collapse. The resulting pressure increases are released from the furnace through a valve. In these "slips", large quantities of dust may be released from the charge into the atmosphere. This dust is usually coarse in size (US EPA 1998). Its composition resembles that of the charge

and thus may contain also carbonaceous particles. The by-product gas contains particles as well, but it is recovered to be used as a fuel.

Molten iron and slag are moved from the bottom of the furnace in operations called casting and tapping. Particles are released when the molten iron and slag get in contact with air. Drilling and plugging of the tap hole is also a source of PM. Sometimes a clogged hole is opened with an oxygen lance, which results in large emissions of particles. The primary particles emitted from these operations can be oxides of iron, magnesium or calcium, but carbonaceous particles can be emitted as well (US EPA, 1998; Passant *et al.,* 2000). Before the molten iron is used for steel making it is desulphurised. PM emissions from that phase contain only little submicron particles and are mainly oxides of iron and calcium (US EPA, 1998, Passant *et al.,* 2000).

US EPA (1998) reports size profiles for some of the operations in pig iron production. However, there was no quantitative data available for carbonaceous emissions. Bond *et al.* (2004) estimated that BC comprises 30 percent of the submicron emissions and that the rest consists of trace metal oxides. They assumed OC to be zero, because of the reducing atmosphere of the furnace. In the absence of specific studies these values are also used in RAINS. Emission data for pig iron production are reported in Table 4.58 and Table 4.59. To derive the RAINS emission factors for PM_1 (Table 4.60), the size fractions reported by US EPA (1998) for "furnace with local evacuation' and 'hot metal desulphurization' were used for non-fugitive and fugitive emissions, respectively.

Table 4.58: Emission factors reported in US EPA (1998) for major sources in pig iron production in blast furnaces [kg/ton pig iron].

Process	PM_1	TSP
Slip	ND	39.5 [a)]
Casthouse (older type)	0.05	0.3
Furnace with local evacuation	0.06	0.65
Taphole and trough only	ND	0.15
Hot metal desulphurization	0.01	0.55

[a)] The value is given in kg/t slip. According to Passant *et al.* (2000) the overall contribution to emissions is small, with an estimated total particulate emission factor of 0.002 kg/t pig iron.

Table 4.59: Shares reported in US EPA (1998) for major sources in pig iron production in blast furnaces [kg/ton pig iron].

Process	PM_1	Remarks
Casthouse (older type)	15 %	of TSP
Furnace with local evacuation	9 %	of TSP
Hot metal desulphurization	2 %	of TSP

Table 4.60: Emission factors used in RAINS model for pig iron production [kg/ton pig iron].

Sector	RAINS code	BC	OC	PM_1	TSP
Pig iron production	PR_PIGI	0.018	0	0.04	1.48
Pig iron production (fugitive)	PR_PIGI_F	0	0	0.05	2.5

4.3.1.4 Open-Hearth Furnace

In open-hearth furnaces molten iron from a blast furnace and iron scrap are refined into steel by melting them. Refining is accomplished by the oxidation of carbon (into carbon monoxide) in the metal and the formation of slag to remove impurities. In most furnaces an oxygen lance may be operated to enhance the process. Particles are produced in different stages of the process and there are also fugitive emissions from, e.g., charging and transfer activities. The emissions consist mainly of iron oxides (US EPA, 1998). No specific emission estimates for carbonaceous particles from open hearth furnaces were found, but probably only small amounts are released or formed as indicated by measurements from other iron and steel production processes (see Engelbrecht *et al.,* 2002). Currently, no carbonaceous emissions were assumed for open-hearth furnaces.

Table 4.61: Emission factors reported in the literature for open-hearth furnace [kg/ton steel].

Literature source	Abatement	PM_1	% of TSP	TSP
US EPA, 1998	Uncontrolled	2.22	21 %	10.55

Table 4.62: Emission factors used in the RAINS model for open hearth furnace [kg/ton steel].

Sector	RAINS code	BC	OC	PM_1	TSP
Open-hearth furnace	PR_HEARTH	0	0	2.22	10.55

4.3.1.5 Basic Oxygen Furnace

In basic oxygen furnaces molten iron and iron scrap are refined into steel by lancing oxygen into the furnace. The oxygen reacts with carbon and other impurities to remove them. The most significant particulate emissions happen during the oxygen blow period. The oxygen can be blown through the top of the furnace or through tuyeres in the bottom of the furnace. The PM contains also smaller size fractions and is composed mainly of iron oxides with possibly some heavy metals and fluorides (US EPA 1998, Passant *et al.,* 2000). The SPECIATE3.2 database (US EPA 2002) provides two source profiles for basic oxygen furnaces (profiles 28303 and 28307) that include also OC. In the first profile (28303), OC in total PM is 20 percent, while in the second profile (28307) OC was not detected. BC is not reported in these profiles.

Table 4.63: Emission factors and shares of PM_1, BC and OC reported by US EPA (1998, 2002) for basic oxygen furnace [kg/ton of steel]

Process / Abatement	BC [%]	OC [%]	PM_1 [kg/ton]	% of TSP	TSP
AP-42 (unabated)					
Top blown (melting and refining)	-	-	n.a.	n.a.	14.25
Charging (at source) [a]	-	-	0.05	12 %	0.43
Tapping (at source)	-	-	0.05	11 %	0.46
Hot metal transfer [a]	-	-	n.a.	n.a.	0.14
SPECIATE v3.2					
Profile 28303 (ESP)	-	0	-	-	-
Profile 28307 (unabated)	-	20	-	-	-

[a] US EPA (1998) reported in kg/ton of pig iron; here it is converted to kg/t steel assuming 0.7 t pig iron/t steel.

Based on the average values from the SPECIATE 3.2 database, a share of 10 percent of OC was derived for RAINS resulting in an emission factor of 2.09 kg/ton. SPECIATE 3.2 does not report any BC and consequently no such emissions are assumed in RAINS. No conclusive data about submicron emission was available either. The emission factor for PM_1 was derived assuming that submicron particles comprise approximately 30 percent of fine particles. This resulted in an emission factor of about 3 kg/ton.

Table 4.64: Emission factors [kg/ton] used in the RAINS model for basic oxygen furnace [kg/ton steel], for TSP estimate see Klimont *et al.* (2002).

Sector	RAINS code	BC	OC	PM_1	TSP
Basic oxygen furnace	PR_BAOX	0	2.09	3	20.9

4.3.1.6 Electric Arc Furnace

Electric arc furnaces are used to produce carbon and alloy steels. Particulates are formed during charging, melting and casting and are mainly iron and calcium oxides. The emissions from these operations also include submicron particle, but very little carbonaceous PM is emitted (US EPA, 1998; Engelbrecht *et al.,* 2002).

Table 4.65: Emission factors reported in the literature for electric arc furnace [kg/ton steel].

Literature source	Process / abatement	PM_1	% of TSP	TSP
US EPA, 1998	Uncontrolled			
Melting and refining – carbon steel		4.37	23 %	19.0

Since a typical plant is assumed to include moderate control of fugitive emissions, the primary sources of PM are melting and refining operations. Thus the US EPA (1998) size distribution (uncontrolled profile) was used to derive PM_1 factors for RAINS (Table 4.67). For BC and OC the only study found (Engelbrecht *et al.,* 2002), was used by taking the average of the reported shares and using the RAINS PM_{10} emissions factor (10.18 kg/ton) from Klimont *et al.* (2002) to derive the emission factors.

Table 4.66: Share of PM_1, BC and OC reported in the literature for electric arc furnace.

Source	Abatement	BC	OC	PM_1	Remarks	Method
US EPA, 1998						
Melting and refining – C steel (uncontrolled)		-	-	23	of TSP	-
Melting, refining, charging, tapping, slagging – C steel (controlled)		-	-	74	of TSP	-
Engelbrecht *et al.,* 2002	Duct measurement	0	2	-	of PM_{10}	TO
	Bag filter dust	0	1.5	-	of PM_{10}	TO

Table 4.67: Unabated emission factors used in RAINS for electric arc furnace [kg/ton steel].

Sector	RAINS code	BC	OC	PM_1	TSP
Electric arc furnace	PR_EARC	0	0.18	4.04	17.55

4.3.1.7 Iron and Steel Foundries

Iron foundries produce high-strength castings, e.g., for industrial and heavy transport applications. Raw materials like pig iron, iron/steel scrap and foundry returns are commonly processed in cupola, electric arc and electric induction furnaces. Fluxes and fuels used are similar as in pig iron production. Particulate emissions are released during conveying, loading and handling of materials as well as from the metal melting process in the furnace. Emissions contain submicron particles. In electric arc and induction furnaces, particles are mainly iron or metallic oxides vaporized from the charge, but in cupolas emissions comprise also material from the burned coke (or other fuel) and thus some carbonaceous particles may therefore be released.

Table 4.68: Emission factors reported in the literature for iron foundries [kg/ton iron].

Literature source	Process / abatement	BC	OC	PM_1	% of TSP	TSP	Method
Ehrlich *et al.,* 2001	Cupola furnace, PM_1 (fabric filter)	-	-	-	19.8%	-	-
	Cupola furnace, PM_1 (cyclone, scrubber)	-	-	-	72.4%	-	-
	Induction furnace, PM_1 (fabric filter)	-	-	-	18.1%	-	-
	Cast iron processing (fabric filter)	-	-	-	9.5%	-	-
US EPA, 1998 (unabated)	Cupola furnace	-	-	4.8	69.1 %	6.9	-
	Electric arc furnace	-	-	0.8	13 %	6.4	-
	Pouring, cooling	-	-	0.4	19 %	2.1	-
	Shakeout	-	-	0.59	37 %	1.6	-
Engelbrecht *et al.,* 2002	Iron & steel plant (electric arc), % of PM_{10}	0 % 0 %	1.5 % 2.0 %	-	-	-	TO
US EPA, 2002	Steel foundry (profile 90011)	-	3.0 %				

The average of the emission factors for cupola and electric arc furnaces from US EPA (1998) were used to derive the RAINS non-fugitive emission factors for PM_1, while the emission factors from pouring and cooling were used for fugitive sources. Shares of BC and OC reported by Engelbrecht *et al.* (2002) and in the SPECIATE 3.2-database (US EPA 2002) for an electric arc furnace in an iron and steel plants were used for carbonaceous emissions.

Table 4.69: Unabated emission factors used in RAINS for iron foundries [kg/ton iron].

Sector	RAINS code	BC	OC	PM_1	PM_1 % of TSP	PM_{10}	TSP
Iron foundries	PR_CAST	0	0.27	2.8	19 %	13.55	15.05
Iron foundries (fugitive)	PR_CAST_F	0	0	0.4	7 %	2.82	5.75

4.3.2 Non-ferrous Metal Industry

4.3.2.1 Primary Aluminum Production

Primary aluminum refers to aluminum that is produced directly from mined ore. The process is based on electrolytic reduction where aluminum is produced from alumina (US EPA, 1998; Passant *et al.,* 2000). To lower the melting point of alumina, fluorides are added. There are two types of electrolytic cells used, the Soderberg self-baking anodes and the pre-baked anodes. Soderberg anodes use the heat of the molten alumina to acquire a carbon paste from a mixture of pitch and coke. Pre-baked anodes are baked separately and thus have to be replaced once they are consumed. In the reduction cells aluminum deposits on the cathode and oxygen on the anode. The aluminum is periodically tapped from the cathode and further cast into slabs, billets and other products.

Particles are produced during the baking of the anodes (pre-baked anodes), the operation of the reduction cells, tapping and casting. They include fluorides of, e.g., aluminum and calcium but also carbonaceous particles may be emitted in several stages of the process (US EPA, 1998). In this study only emission factors and shares of PM_1 were estimated. This data was taken from (US EPA, 1998) and is presented in Table 4.70.

Table 4.70: Shares and emission factors for aluminum production [kg/ton aluminum produced], PM_1 –data based on US EPA (1998), other fractions from Klimont *et al.* (2002).

Source	PM_1	% of TSP	TSP
Prebake cells	8.46	18 %	47
Prebake cells, fugitive only	0.92	18 %	2.5
Horizontal stud Soderberg	15.7	32 %	49
Horizontal stud Soderberg, fugitive only	1.3	13 %	5.0

Emission factors introduced into RAINS are listed in Table 4.71. The emission factor for PM_1 is based on US EPA (1998) for prebake cells (see Klimont *et al.,* 2002). No studies reporting data on carbonaceous PM was found. For the time being no emissions were assumed for BC and OC.

Table 4.71: Emission factor and the share of PM_1 in fine particles proposed for the RAINS model for aluminum production [kg/ton aluminum produced].

Sector	RAINS code	BC	OC	PM_1	PM_1 % of TSP	TSP
Aluminum production	IN_PR_ALPRIM	0	0	8.46	18 %	47.00

4.3.2.2 Secondary Aluminum Production

In this process aluminum is produced from recycled aluminum scrap. No studies reporting submicron emissions were found, but the relatively high share of $PM_{2.5}$ in emissions measured by Olmez *et al.* (1988) and US EPA (1998) suggests that also PM_1 emissions might be significant.

Olmez *et al.* (1988) measured with thermal methods the shares of OC and EC in emissions of a secondary aluminum smelter. The smelter processed aluminum by smelting and recasting the metal and dross in batches with a rotary aluminum dross furnace. The samples were collected from a breach after the baghouse. Most of the measured PM was found in the fine fraction comprising 81 percent of PM_{10}. The derived shares of carbonaceous particles were 0.18 percent of EC and 1.6 percent of OC in fine particles and four percent of EC and 43 percent of OC in the coarse mode.

Table 4.72: Shares of BC and OC in PM_{10} for secondary aluminum [%].

Source	Process / abatement	BC	OC	PM_1	Method
Ehrlich *et al.,* 2001	Aluminum-remelt (fabric filter)	-	-	35.8	-
	Aluminum chippings drying (fabric filter)	-	-	20.3	-
	Aluminum chippings drying (fabric filter)	-	-	32.8	-
Olmez *et al.,* 1988	Smelting (baghouse)	0.4	4.4	-	T

Assuming that approximately 50-60 percent of the emissions are PM_{10} as reported by US EPA (1998) and applying these to the BC and OC shares given by Olmez *et al.* (1988) results in 0.01 percent of BC and 0.11 percent of OC. Applying these shares to the current RAINS TSP emission factor results in 0.0012 and 0.013 kg/ton for BC and OC, respectively. Only one study (Ehrlich *et al.,* 2001) reported shares of PM_1 in abated PM_{10} emissions. Based on this study a share of 20 percent in PM_{10} (which gives 12 percent in TSP using the current RAINS numbers) was assumed for submicron particles. The lowest share from Ehrlich *et al.* (2001) was used, since the reported size profiles relate to abated emissions and the efficiency is typically lower for particles in the submicron size range.

Table 4.73: Emission factor and share of PM_1 in fine particles used in the RAINS model for secondary aluminum production [kg/ton aluminum produced].

Sector	RAINS code	BC	OC	PM_1	PM_1 % of TSP	TSP
Aluminum production	IN_PR_ALSEC	0.0012	0.013	1.428	12 %	11.9

4.3.2.3 Other Non-ferrous Metals Production

This sector includes production of primary and secondary copper, lead, zinc, and primary production of nickel. Details of the production processes can be found in, e.g., AWMA, 2000; US EPA, 1998; EEA, 1999; TA Luft, 1986; and Passant *et al.,* 2000.

The generalized particle size distributions from US EPA (1998) were used to derive the PM_1 emission factor for non-ferrous metals production. The share reported in Table 4.74 does not include materials handling and transfer activities, which usually have very low emission shares in the submicron size range (US EPA, 1998). Consequently, the share of PM_1 was scaled down to 24 percent in TSP. It has to be noted that this number is subject to major uncertainties. Only one study was found reporting BC and OC emissions from non-ferrous processes (aluminum excluded). Olmez *et al.* (1988) reported results for Antimony ore roasting. The measurements were made after a bag house during a period when oxide ores were roasted. The fine fraction of the particles was 81 percent with 0.099 percent of EC and

0.94 percent of OC. The shares for the coarse fraction were 0.2 percent of EC, while OC was not detected. These results do not represent all diverse processes of different metals, but they indicate that carbonaceous particulate emissions from most of the processes probably are small and therefore zero emissions are assumed for the time being.

Table 4.74: PM_1 size fraction reported by EPA for non-ferrous metals production [% TSP].

Source	Process	PM_1	TSP
US EPA, 1998	Smelting, refining of metals [a]	72 %	100 %

[a] Generalized particle size distribution, excluding aluminum

Table 4.75: Emission factors used in the RAINS model for other non-ferrous metals production [kg/ton metal].

Sector	RAINS code	BC	OC	PM_1	TSP
Other Non-ferrous metals	PR_OT_NFME	0	0	3.6	15.0

4.3.3 Other Industrial Processes

4.3.3.1 Coal Briquettes Production

Although included in the RAINS structure and being also a possible source of submicron and carbonaceous particles, there were no studies available providing emissions from coal briquettes production. However, the contribution of this sector to total European emissions of fine particles is almost negligible. Therefore, it is reasonable to assume that no major bias will be introduced to the emission estimates of submicron and carbonaceous particles if these emissions are ignored.

4.3.3.2 Cement Production

Cement production (mainly Portland cement) includes several stages that emit PM. These include dry raw material storage, pretreatment of raw materials, clinker production in the rotary kiln, clinker cooling and its grinding and blending as well as storage and loading of the final product. The primary sources of particles are the kiln and clinker cooling exhaust stacks (e.g., Passant *et al.,* 2000).

US EPA (1998) reported for unabated process that seven percent (for the wet process) and 18 percent (for the dry process) was $PM_{2.5}$. However, the study did not report the fraction of submicron particles. Kakareka *et al.* (1999) have shown relatively high shares of submicron particles in cement production from studies made in the former Soviet Union countries, ranging from 6 to 36 percent depending on the process. Ehrlich *et al.* (2001) reported PM_1 shares up to 53 percent in TSP for abated emissions. On the other hand, Berdowski *et al.* (1997) quotes zero emissions for particles smaller than $PM_{2.5}$. These examples illustrate the large discrepancies between studies, possibly caused by different operating practices, levels of abatement, plant sizes, etc. No reliable data for unabated submicron emissions was found for this study.

A similar problem occurs for carbonaceous emissions. For example, Kakareka *et al.* (1999) stated that dust from cement production contains organic substances in significant amounts. On the other hand, US EPA (1998) reports no data on carbonaceous PM, but state that small amounts of VOC may be released, which could indicate some emissions of organics as particulates as well. This is confirmed by the profiles given in the SPECIATE 3.2 database (US EPA, 2002), which show negligible amounts of BC and up to five percent of OC in the emission profiles for cement kilns.

Table 4.76: PM_1 size fractions reported in the literature for cement production [% of TSP].

Source	Process / abatement	BC	OC	PM_1
Ehrlich *et al.,* 2001	Rotary kiln (ESP)			52.6
	Rotary kiln (ESP)			39
	Grate cooler (fabric filter)			1.2
	Grate cooler (fabric filter)			0.6
	Heat exchanger (ESP)			42.9
	Heat exchanger (ESP)			25
	Lepol-kiln (ESP)			39.2
	Lepol-kiln (ESP, multi-cyclone)			23.2
US EPA, 2002 (SPECIATE v3.2)	Cement kiln, gas-fired (baghouse), in PM_{10} (profile 27201)		1.2 %	
	Cement kiln, coal-fired (ESP), in PM_{10} (profile 27203)	0.2 %	5.4 %	

There were no studies found that report unabated submicron emission factors for cement production. The main sources of PM are the kiln and the clinker cooler. The results from Ehrlich *et al.* (2001) indicate that the submicron emissions from coolers are very small (Table 4.76). Also the unabated PM_1 shares shown by US EPA (1998) for lime kilns in paper industry (Table 4.84) suggest a low share also from cement kilns. For RAINS a share of five percent of PM_1 in TSP is assumed. The values for BC and OC were developed based the emission characteristics from different fuel fired kilns and combining them with country specific fuel use currently in RAINS for the year 2000. For gas- and coal-fired cement kilns, the data from SPECIATE (US EPA, 2002) was used assuming that the abatement does not significantly affect the profile of carbonaceous emissions.

Since there were no studies reporting emission characteristics from heavy fuel fired cement kilns, BC and OC data of large scale combustion of heavy fuel was used. However, emissions can be expected to be fairly similar to gas- and coal-fired cement kilns, so that the measurements by Olmez *et al.* (1988) from a cyclone controlled power plant and the SPECIATE-profile 11509 were taken as starting points. Taking the numbers referring to PM_{10}, as is the case with gas- and coal-fired kilns, results in average shares of 0.25 percent for BC and 1.4 percent for OC. These shares were used to derive the emission factors for heavy fuel oil fired cement kiln.

Table 4.77: Emission factors used in the RAINS model for cement production [kg/t cement].

Sector	RAINS code	BC [a]	OC [a]	PM_1	PM_{10}	TSP
Cement production	PR_CEM	0-0.14	0.66-2.95	6.5	54.6	130

[a] Country specific

4.3.3.3 Lime Production

In the lime making process limestone (calcium carbonate) is heated to drive off carbon dioxide and leave lime (CaO). The limestone is crushed and inserted in a kiln, e.g., rotary, vertical shaft or moving grate kilns, where the heating takes place. The most important source of particles is the kiln; also fugitive emissions can be released from several stages of the process.

There were no studies reporting PM_1 emissions from lime production. US EPA (1998) gives a share of 1.4 percent of $PM_{2.5}$ in TSP for uncontrolled emissions from a rotary kiln. It was decided that for the time being only a small share, about 0.5 percent, is assumed for submicron emissions. Engelbrecht *et al.* (2002) measured BC and OC in PM_{10} and $PM_{2.5}$ (TO-method) from a lime kiln with relatively small shares of around two percent for BC and seven percent for OC. Also the SPECIATE3.2 database (US EPA 2002) reports shares below one percent for BC and nine percent for OC. The BC shares from the SPECIATE-database and the shares in PM_{10} from Engelbrecht *et al.* (2002) (Table 4.78) were used to derive the RAINS emission factors for lime production (Table 4.79). With the current shares some carbonaceous emissions are estimated to be larger that PM_1.

Table 4.78: BC and OC fractions reported in the literature for lime production [%].

Source	Abatement / process	BC	OC	Method
Engelbrecht *et al.,* 2002	Lime kiln (unabated), % in PM_{10}	1.8	11.5	TO
	Lime kiln (unabated), % in $PM_{2.5}$	2.1	6.1	
US EPA, 2002	Lime kiln (wet scrubber) (profile 23202)	0.5	9.3	

Table 4.79: Emission factors used in the RAINS model for lime production [kg/t lime].

Sector	RAINS code	BC	OC	PM_1	PM_{10}	TSP
Lime production	PR_LIME	0.2	1.4	0.46	12	100

4.3.3.4 Petroleum Refining

Primary particulate emissions from petroleum refining originate from conversion processes like cracking and coking and process heating (US EPA, 1998). Fuel oil and natural gas are used for process heating in the refining process. The emissions from these combustion processes are dealt in Section 4.2.2. Due to the nature of the processes it can be expected that carbonaceous particles are emitted at some stages. The only study reporting carbonaceous emissions concentrated on a catalytic cracker (Olmez *et al.,* 1988).

Berdowski *et al.* (1997) provide information about the PM size distribution. They reported that 80 percent of PM_{10}-particles were below $PM_{2.5}$ and 21 percent below $PM_{0.1}$. Although no specific studies reporting submicron emissions from petroleum refining were found, it is possible that a large share of particles is submicron. The PM size distribution reported by Berdowski *et al.* (1997) was used to estimate the PM_1 fraction, resulting in 43 percent of submicron particles in PM_{10}. The TSP and PM_{10} emission factors were taken from Klimont *et al.* (2002).

Olmez *et al.* (1988) reported shares of EC and OC measured with thermal methods for an oil refinery catalytic cracker, after ESP. The mass fraction in fine ($PM_{2.5}$) particles was 97 percent with the rest in coarse mode. The share of EC in the fine fraction was 0.16 percent, while OC was not detected. Carbonaceous particles were not detected in the coarse mode.

Table 4.80: Emission factor and share of PM_1 in TSP used in the RAINS model for petroleum refining processes [kg/ton crude oil throughput].

Sector	RAINS code	BC	OC	PM_1	PM_1 % of PM_{10}	PM_{10}	TSP
Petroleum refining	IN_PR_REF	0 [a)]	0	0.05	43%	0.120	0.122

[a)] BC emission factor: 0.00015 kg/ton

4.3.3.5 Fertilizer Production

No detailed and conclusive data on submicron and carbonaceous emissions from fertilizer production was found. Berdowski *et al.* (1997) reported a relatively high $PM_{2.5}$-fraction (70 %) in PM_{10}, but zero emissions for $PM_{0.1}$. They indicate that there might be some emissions in the submicron range, yet this share could not be estimated. The only source reporting carbonaceous emissions from fertilizer plants is the SPECIATE 3.2-database: a source profile for phosphate fertilizer calciner (profile 25418) with carbonaceous species. The shares of BC and OC are very small, 1.1 percent and three percent in fine particles, respectively. No emissions of BC and OC are assumed in the RAINS model.

4.3.3.6 Carbon Black

Carbon black are submicron soot or black carbon particles, which are used as reinforcing agents in rubber, e.g., tires, and as pigments in inks and paints. It is produced from hydrocarbon fuels such as oil or gas through combustion under conditions with limited air supply. After these small (10 to 500 nm) particles are produced they are collected from the gas stream with a fabric filter.

Although one would expect this process to be a source of submicron and carbonaceous particles the atmosphere, no studies were found reporting size or chemical profiles of emissions from the production of carbon black. It was assumed that the submicron particles comprise a large portion, approximately 60 percent, of the $PM_{2.5}$ mass. Further, based on the nature of the process, it was assumed that the submicron fraction is composed totally of BC. These shares were applied to TSP emission factors used currently in RAINS, resulting in 1.1 kg/ton for both PM_1 and BC.

Table 4.81: Emission factor for carbon black production [kg/ton carbon black].

Sector	RAINS code	BC	OC	PM_1
Carbon black production	PR_CBLACK	1.1	0	1.1

4.3.3.7 Glass Production

There are several materials that cover a wide range of compositions that can be called glass. A large proportion of glass products are, however soda-lime glasses, which are produced by melting oxides of silicon, sodium and calcium together with small amounts of additives. Main raw materials are sand, soda ash and limestone. In general, glass making is not a major emitter of fine particles in Europe, and this probably applies to submicron particles as well. Ehrlich *et al.* (2001) reported an average submicron fraction of about 22 percent in abated emissions. The RAINS PM_1 emission factor is estimated using this share to be 0.715 kg/ton.

Based on the raw materials and the process of glass production, the carbonaceous particulate emissions can be expected to be small. This is confirmed by the SPECIATE 3.2-database (US EPA, 2002), where a share of 0.06 percent of BC and 0.7 percent of OC in fine particle emissions from a glass furnace are shown (profile 27102). Applying these shares to RAINS emission factor for TSP results in 0.00195 kg/ton and 0.02 kg/ton for BC and OC, respectively.

Table 4.82: PM_1, BC and OC shares in TSP reported in the literature for glass production [%].

Source	Process / abatement	BC	OC	PM_1
Ehrlich *et al.,* 2001	Batch glass (lime-sorption, ESP)	-	-	21.2
	Flat glass (desulphurization – lime, ESP)	-	-	23.7
US EPA, 2002	Glass furnace (unabated) (profile 27102)	0.06	0.7	

Table 4.83: Emission factors for carbon black production [kg/ton carbon black].

Sector	RAINS code	BC	OC	PM_1
Glass production	PR_GLASS	0.00195	0.02	0.715

4.3.3.8 Pulp Production

The pulp industry includes chemical and mechanical pulp making. Chemical pulp making uses a combination of chemicals and heat to dissolve lignin from the wood fibers. In mechanical processes, the fibers are separated by abrasion. In chemical pulp making, the sulphate and the sulphite method have been used. Nowadays, the sulphate method is getting more common. In this section only the emissions from sulphate method pulping (kraft pulping) are estimated, based on US EPA data (1998). A description of the process can be found in US EPA (1998). Particulate emissions from the kraft process occur largely from the recovery furnace, the lime kiln and the smelt dissolving tank. Particles are mainly sodium and calcium salts (US EPA, 1998).

Table 4.84: PM$_1$ emission factors and shares from kraft pulping (the sulphate method) [kg/Mg of air-dried pulp]

Source	Process / abatement	PM$_1$	% of TSP	TSP
US EPA, 1998 (unabated)	A recovery boiler, with a direct-contact evaporator	41	45.3 %	90
	without a direct contact evaporator	35	30 %	115
	Lime kiln	2.0	7.1 %	28
	Smelt dissolving tank	1.4	40 %	3.5
	SUM,	41.4	30.9 %	134 [a]

[a] The average of the values reported for recovery boilers with or without a direct-contact evaporator was used in calculations.

Table 4.85: BC and OC shares in TSP from kraft pulping (the sulphate method) [%]

Source	Process / abatement	BC	OC	Method
Engelbrecht *et al.,* 2002	Lime kiln (% of PM$_{10}$)	1.8	11.5	TO
US EPA, 2002 SPECIATE v3.2	Pulp and paper industry (profile 90015)	2	25	
	Kraft recovery furnace (ESP, wet scrubber) (profile 23103)	0.04	1.95	
	Kraft recovery furnace (unabated) (profile 23104)	1.5	5.2	

Table 4.86: Emission factor and share of PM$_1$ in fine particles proposed for the RAINS model for pulp production [kg/Mg of air dried pulp].

Sector	RAINS code	BC	OC	PM$_1$	PM$_{10}$	TSP
Pulp production	IN_PR_PULP	2	10	41.4	103.6	134

4.4 Mining

This sector includes mining of coal (brown coal and hard coal) and metallic and non-metallic ores (zinc, iron, copper, manganese, bauxite, etc.). Information on emissions from operations associated with mining is scarce. APEG (1999) reports eight percent of PM$_1$ in PM$_{10}$, but no data about BC and OC emissions.

Table 4.87: Emission factors used in the RAINS model for mining of coal and ores [kg/ton].

Sector	RAINS code	BC	OC	PM$_1$	PM$_{10}$	TSP
Brown coal mining	MINE_BC	0	0	0.004	0.05	0.1017
Hard coal mining	MINE_HC	0	0	0.004	0.05	0.1017
Other mining	MINE_OTH	0	0	0.004	0.05	0.1017

4.5 Agriculture

Particulate emissions from livestock farming include mainly feed and faecal material and possibly bedding. Lower contributions originate from skin, hair, mould, pollen grains and insect parts (Lükewille *et al.,* 2001). According to Louhelainen *et al.* (1987) and Berdowski *et*

al. (1997), the emissions are over 1 μm in diameter and mainly organic in composition. Louhelainen *et al.* (1987) measured the share of organic dust to be 92 percent of the total mass in sow buildings and 88 percent in pig fattening buildings. For arable farming, the current RAINS version (Klimont *et al.,* 2002) assumes no emissions of $PM_{2.5}$ and consequently the same assumption applies to carbonaceous fractions.

4.6 Waste

This sector includes flaring in the oil and gas industry and open burning of agricultural and residential waste. The information on emissions from these sources is scarce and they are very often not included in the particulate inventories. An attempt was made to derive emission factors for this sector.

According to US EPA (1998), emissions from gas flaring may include soot and organic particles depending on fuel characteristics and the distribution of oxygen in the combustion. US EPA (1998) estimated soot emissions resulting in concentration in a range of 0-274 μg/l.

Two studies (Andrae & Merlet, 2001 and Turn *et al.,* 1997) reported BC and OC in emissions for open burning of agricultural residues and herbaceous fuels. These studies were used to estimate the emissions of BC and OC for open burning of agricultural waste for RAINS. From the study by Turn *et al.* (1997) both shares and emission factors for wheat, barley and corn in fine particles were used since rice straws and sugar cane were assumed to be irrelevant for the European case. Using the BC and OC shares reported by Turn *et al.* (1997) and combining them with the current $PM_{2.5}$ emission factor in RAINS (6.3 g/kg) results in 0.9 g/kg for BC and 2.3 g/kg for OC. The average emission factors in Andrae & Merlet (2001) are 0.7 and 3.3 g/kg, and in Turn *et al.* (1997), 0.9 and 2.3 g/kg, respectively. Calculating an average of these numbers to derive the RAINS emission factors results in 0.8g/kg for BC and 2.6 g/kg for OC.

The emission factor for PM_1 was derived based on the same studies as for BC and OC (Turn *et al.,* 1997; Andrae & Merlet, 2001). It was assumed that most of the submicron fraction is carbonaceous with BC and OM and that there is an additional five percent to include other inorganic material. The OM content was derived by multiplying OC with a factor of 1.7 to take into account the mass of other elements than carbon. The conversion factor is based on the study by Hegg *et al.* (1997) and is assumed to represent biomass burning.

Table 4.88: Summary of the emission factors of PM_1, BC and OC in fine particulate matter for open burning of biomasses [g/kg].

Source	BC	OC	Remarks	Method
Andrae & Merlet, 2001	0.69	3.3	Agricultural residues	Unknown
Turn *et al.*, 1997	1.4	2.2	Wind tunnel measurements simulating open burning emissions from *wood fuels*, Walnut Prunings (PM_{10}, $PM_{2.5}$)	TO
	1.2	2.3		
	1.0	2.1	Almond Prunings (PM_{10}, $PM_{2.5}$)	
	1.2	2.1		
	1.6	3.1	Ponderosa Pine Slash (PM_{10}, $PM_{2.5}$)	
	1.5	2.5		
	2.6	9.9	Douglas Fir Slash (PM_{10}, $PM_{2.5}$)	
	2.0	10.0		
	1.7	4.3	Averages of the *wood fuel* measurements (PM_{10}, $PM_{2.5}$)	
	1.4	4.2		
Turn *et al.*, 1997	0.5	0.94	Wind tunnel measurements simulating open burning emissions from *herbaceous fuels*, Rice straw (PM_{10}, $PM_{2.5}$)	TO
	0.46	0.9		
	0.8	3.0	Wheat straw (PM_{10}, $PM_{2.5}$)	
	0.79	2.2		
	1.2	3.2	Barley straw (PM_{10}, $PM_{2.5}$)	
	1.2	3.0		
	0.75	1.8	Corn stover (PM_{10}, $PM_{2.5}$)	
	0.67	1.7		
	0.61	1.5	Sugar Cane (PM_{10}, $PM_{2.5}$)	
	0.59	1.5		
	0.78	1.9	Averages of the *herbaceous fuel* measurements (PM_{10}, $PM_{2.5}$)	
	0.75	1.8		

Table 4.89: Summary of the shares of PM_1, BC and OC in fine particulate matter for open burning of biomasses [%].

Source	BC	OC	Remarks	Method
Turn *et al.,* 1997	29	47	Wind tunnel measurements simulating open burning emissions from *wood fuels*,	TO
	23	39	Walnut Prunings (PM_{10}, $PM_{2.5}$)	
	25	43	Almond Prunings (PM_{10}, $PM_{2.5}$)	
	22	46		
	26	52	Ponderosa Pine Slash (PM_{10}, $PM_{2.5}$)	
	28	48		
	15	58	Douglas Fir Slash (PM_{10}, $PM_{2.5}$)	
	12	60		
	25	49	Averages of the *wood fuel* measurements (PM_{10}, $PM_{2.5}$)	
	22	46		
Turn *et al.,* 1997	18	20	Wind tunnel measurements simulating open burning emissions from *herbaceous fuels,* Rice straw (PM_{10}, $PM_{2.5}$)	TO
	23	22		
	14	38	Wheat straw (PM_{10}, $PM_{2.5}$)	
	14	37		
	16	40	Barley straw (PM_{10}, $PM_{2.5}$)	
	16	38		
	15	35	Corn stover (PM_{10}, $PM_{2.5}$)	
	14	33		
	15	37	Sugar Cane (PM_{10}, $PM_{2.5}$)	
	15	37		
	16	31	Averages of the *herbaceous fuel* measurements (PM_{10}, $PM_{2.5}$)	
	18	31		

Table 4.90: Emission factors used in the RAINS model for flaring [kt/PJ] and open burning of waste [kg/t].

Sector	RAINS code	BC	OC	PM_1	$PM_{2.5}$	PM_{10}	TSP
Gas flaring	WASTE_FLR	0.05	0.01	0.06	0.064	0.064	0.064
Open burning of waste, agriculture	WASTE_AGR	0.83	2.62	5.6	6.3	7.1	8.5
Open burning of waste, residential	WASTE_RES	1.48	1.48	4.0	6.0	8.0	10.0

4.7 Other Sources

This sector includes several miscellaneous sources, such as construction, barbeques, cigarette smoking, fireworks. Information on emissions from several of these categories is scarce and the available estimates of emission factors should be used with great care. This also applies to submicron and carbonaceous emissions. Emission profiles were found only for cigarette smoking, barbeques and meat frying. In general particles emitted from other activities, such as construction, are mechanically formed and thus mainly coarse in size. Since no combustion is involved it can be expected that they are not a source of BC and OC either. However, some

carbonate particles may be emitted if they are present in the raw materials. However, taking into account their size profile they have only short residence times in the atmosphere.

Only few studies (Hildemann *et al.,* 1991 and Schauer *et al.,* 1999) reported BC and OC emissions from cigarette smoking and meat charbroiling and frying operations. Negligible emissions of BC were detected, while for OC the range of emissions varied from 34 to 60 percent in fine particles. Based on these studies, an average OC share of 46 percent was derived for meat frying and charbroiling. Emissions from cigarette smoking were based on Hildemann *et al.* (1991), who measured an OC share of 60 percent. These studies were used for deriving the emission factors in Table 4.93. No studies reporting submicron emissions were found, so it was decided to use the same emission factors as for $PM_{2.5}$ in current RAINS (see Klimont *et al.,* 2002).

Table 4.91: Shares of BC and OC reported in the literature for other sources

Source	Emission source	BC	OC
Hildemann *et al.,* 1991	Cigarette smoking (% in PM_2)	0.49	59.5
	Meat charbroiling	0	58.8
	Meat frying	0	34.8-57.4
Schauer *et al.,* 1999	Meat charbroiling (% in $PM_{1.8}$)	0	33.8

Table 4.92: Uncontrolled emission factors reported in the literature for other sources

Source	Emission source [unit]	BC	OC
Hildemann *et al.,* 1991	Cigarette smoking [kg/t tobacco], in PM_2	0.1	12.1
	Meat charbroiling [kg/t meat]	0	23.4
	Meat frying [kg/t meat]	0	0.45-0.74
Schauer *et al.,* 1999	Meat charbroiling [kg/t meat], in $PM_{1.8}$	0	6.35

Table 4.93: Emission factors used in the RAINS model for other sources [kg/capita].

Sector	RAINS code	BC	OC	PM_1	TSP
Cigarette smoking	RES_CIGAR	0.00008	0.0099	0.0165	0.0165
Barbeques, etc.	RES_BBQ	0.01	0.035	0.075	0.075
Fireworks	RES_FIREW	n.a.	n.a.	0.035	0.035
Other	OTHER	n.a.	n.a.	n.a.	n.a.

5 Results

Based on the methodology and data introduced above, an estimate of the emissions of PM_1, BC and OC in Europe was derived. No detailed European or national studies are available, so the emission estimates are still highly uncertain and more work is needed to narrow down this uncertainty. Thus, all numbers presented in this chapter should be considered as preliminary and subject to future revision.

5.1 European Emissions of PM_1, BC and OC

Table 5.1 lists the total European emissions of PM_1, BC and OC for the years 2000 and 2010 as calculated with the data discussed in the preceding sections. The projections for the year 2010 assume full implementation of the current emission control legislation (CLE), e.g., the EURO-IV emission standards for cars and trucks, or stricter emission limit values for large combustion plants resulting from the recent revision of the Large Combustion Plant Directive.

In 2000, roughly half of the European emissions of submicron particles originated from non-EU countries, and the other half from sources in the EU-25. The overall emissions decline until 2010 mainly due to EU legislation for transport sources but also owing to the continuing structural changes in the non-EU countries that will lead to reduced consumption of solid fuels, especially in the residential sector. However, the relative importance of the emissions from non-EU countries rises and in 2010 60 percent of the PM_1 is estimated to be emitted outside the EU.

European emissions of BC and OC in 2000 are dominated by the EU-25. Until 2010 the situation is projected to change with most of the emissions coming from non-EU countries. The overall European emissions of BC and OC decline mainly due to measures taken in the EU-25, while in the non-EU countries the emissions decrease only slightly. The observed trend in the EU-25 is a result of switching to cleaner fuels and implementation of better control equipment on exhaust emissions from transport sector. The development of emissions outside the EU-25 is a result of increasing emissions from the domestic sector and an increase in the traffic volume growth, which compensate the improvements from stricter emission control measures.

Table 5.1: European[a] emissions of submicron and carbonaceous particles; current legislation scenario [kt].

	PM_1		BC		OC	
	2000	2010	2000	2010	2000	2010
EU-15	1022	718	322	211	372	260
New EU member states	287	201	66	43	103	76
Rest of Europe	1462	1314	284	273	513	471
Total Europe	2771	2233	672	527	988	807

[a] Excludes Atlantic Ocean, North Sea, Baltic Sea, and Mediterranean Sea.

The sectoral emissions of PM_1, BC and OC emissions in Europe (by SNAP code) are presented in Table 5.2, Table 5.3 and Table 5.4. In 2000, the major source of BC and OC in the EU-15 was the transport sector (road- and off-road vehicles) with 67 percent and 36 percent respectively. Transport was followed by non-industrial (domestic) combustion contributing 25 percent of BC and 54 percent of OC. In 2010 the contribution of the transport sector is calculated to decrease to 57 percent for BC and 33 percent for OC due to implementation of the EURO-standards. The relative contribution of non-industrial combustion increases to 33 percent for BC and to 54 percent for OC.

The relative importance of individual sectors and the development of emissions are slightly different for submicron particles (PM_1) than for BC and OC. The main contributors are, however, the same, transport and non-industrial combustion with approximately equal shares (39 and 38 percent) in 2000. Stricter controls on exhaust emissions from transport (first of all from road transport and to a lesser extent from the off-road sector) result in a lower share of mobile sources in the total PM_1 emissions in 2010 representing 31 percent of the total. The relative contributions of all other sectors either remain the same or increase compared to 2000, and in 2010 non-industrial combustion will become the biggest source with a 41 percent of the total PM_1.

Table 5.2. PM emissions in the EU-15 countries by SNAP 1 sectors.

SNAP 1 sector	PM_1		BC		OC	
	2000	2010	2000	2010	2000	2010
1: Combustion in energy industries	38	27	2	2	2	2
2: Non-industrial combustion plants	403	293	82	70	200	139
3: Combustion in manufacturing industry	44	29	2	1	3	2
4: Production processes	38	35	4	3	1	1
5: Extraction and distribution	0	0	0	0	0	0
7: Road transport	256	121	158	75	86	49
8: Other mobile sources and machinery	136	102	59	45	50	36
9: Waste treatment	14	13	8	7	4	4
10: Agriculture	45	47	3	3	9	9
12: Other (not included in CORINAIR)	48	49	4	4	17	17
TOTAL	1022	718	322	211	372	259

For the countries that joined the EU in May 2004 the emissions in 2000 are dominated by non-industrial combustion with 52 percent for BC and 64 percent for OC. Transport is the second important sector with a share of 34 percent for BC and 12 percent for OC. Although the fuel consumption in the transport sector increases during the period from 2000 to 2010, emissions decline due to introduction of abatement. By 2010, the emissions of BC and OC are expected to decline in most of the sectors. The shares of individual sectors remain fairly constant.

For PM_1 non-industrial combustion is the largest source of emissions representing 49 percent of the total in 2000. The other sectors, i.e., road transport, other mobile sources and machinery, combustion in energy industries and agriculture, have fairly similar relative contributions to overall emissions with 7 to 11 percent shares each. By 2010, emissions are projected to decline in most of the sectors and the relative contributions remain in general the

same. In relation to year 2000, emissions decrease for the most in production processes with emissions in 2010 being only 1/3 of the 2000 level.

Table 5.3: PM emissions in the new EU member countries by SNAP 1 sectors [kt]

SNAP 1 sector	PM_1		BC		OC	
	2000	2010	2000	2010	2000	2010
1: Combustion in energy industries	30	20	0	0	1	1
2: Non-industrial combustion plants	139	100	34	23	66	47
3: Combustion in manufacturing industry	11	6	0	0	1	0
4: Production processes	15	4	3	1	2	0
5: Extraction and distribution	1	0	0	0	0	0
7: Road transport	26	12	14	7	9	5
8: Other mobile sources and machinery	20	13	9	6	7	4
9: Waste treatment	3	3	1	1	1	1
10: Agriculture	33	33	4	4	13	13
12: Other (not included in CORINAIR)	9	9	1	1	3	3
TOTAL	287	201	66	43	103	76

In the non-EU countries the overall emissions of BC and OC are calculated to slightly increase between the years 2000 and 2010. For BC the main contributor is non-industrial combustion with 46 percent in 2000 and 52 percent in 2010. It is followed by transport representing about 30 percent in both 2000 and 2010. Waste treatment and industrial production processes have a larger relative importance in the non-EU countries than in the EU-25. Non-industrial combustion is the biggest source of OC. The sector accounts for about 60 percent of the emissions in both 2000 and 2010. The second largest emitter of OC is agriculture with 15 percent shares in 2000 and 2010. Transport is almost as important with 15 percent in both 2000 and 2010.

Table 5.4: PM emissions in the non-EU countries by SNAP 1 sectors [kt]

SNAP 1 sector	PM_1		BC		OC	
	2000	2010	2000	2010	2000	2010
1: Combustion in energy industries	96	94	1	1	4	4
2: Non-industrial combustion plants	613	565	131	132	305	275
3: Combustion in manufacturing industry	65	63	2	2	7	7
4: Production processes	251	172	27	22	20	16
5: Extraction and distribution	1	1	0	0	0	0
7: Road transport	98	76	41	35	52	44
8: Other mobile sources and machinery	93	96	41	42	27	28
9: Waste treatment	18	18	11	11	5	5
10: Agriculture	185	188	25	25	78	78
12: Other (not included in CORINAIR)	40	39	3	3	14	14
TOTAL	1462	1314	284	273	513	471

Similarly as for carbonaceous emissions, non-industrial combustion is the most important sector for PM_1, with a contribution of 42 percent of the total in 2000, followed by production processes and agriculture with 17 and 13 percent shares, respectively. In 2000, combustion in energy and manufacturing industries and transport sector (both on- and off-road) have relatively similar contribution to the total emissions, around five percent each. The emissions decrease slightly until 2010 mainly due to measures for on-road transport, production

processes and non-industrial combustion plants. In other sectors the absolute levels stay the same or a small increase is estimated.

In Table 5.5, Table 5.6 and Table 5.7 emissions are grouped according to fuel use. In the EU-15 countries, the majority of BC emissions originate from the use of liquid fuels, especially diesel oil. Emissions from the use of diesel, mainly in transport sector, constitute 63 percent of the total emissions in 2000. The agreed implementation of strict controls on exhaust emissions for diesel vehicles will significantly lower the total emissions of BC. Another important source of BC in the EU-15 is the use of biomass fuel, mainly wood. In 2000, this source made up 22 percent of the emissions and by 2010 its relative importance is projected to rise to 31 percent. For OC the fuel based source profile is slightly different. Most emissions of OC in the EU-15 countries come from burning of biomass, with 51 percent of emissions in 2000 and 46 percent in 2010. It is followed by emissions from the use of liquid fuels, mainly in the transport sector. Diesel combustion is the biggest source of OC from liquid fuels, but the relative importance of gasoline is higher than for BC.

For submicron emissions the sector profile is different from that of carbonaceous particles, with emissions coming mainly from combustion of biomass, diesel oil and from non-combustion sources in industry, included in 'Other' in Table 5.5. In 2000, each of these sectors contributed between 19 and 42 percent to the total emission of PM_1. In 2010 the main sources will remain. However, the effect of the control measures in traffic can be seen in the declined relative contribution of diesel fuel to 29 percent.

Table 5.5:Emissions by fuel in EU-15 countries [kt]

Fuel	PM_1		BC		OC	
	2000	2010	2000	2010	2000	2010
Coal	50	25	7	2	9	2
Biomass	383	289	73	67	191	136
Liquid and gas	409	236	221	123	138	88
Diesel	352	195	206	109	98	61
Gasoline	36	24	8	8	34	22
Other liquid and gas	22	17	7	6	5	5
Other	181	168	20	18	34	32
TOTAL	1022	718	327	216	372	295

The main sources of BC and OC in the new EU member countries are in general the same as for EU-15, but the use of coal plays a bigger role in the emissions. In 2000, the share of BC and OC in emissions from coal burning is estimated at 26 percent and 22 percent, respectively. Up to 2010, the relative importance of this source is expected to decrease to 20 percent of BC emissions and 15 percent of the OC emissions. Combustion of coal and biomass are the main PM_1 emitting activities in 2000, but non-combustion sources have almost equally important contributions to total emissions. Together they explain approximately 84 percent of the emissions in 2000. The emissions will decline until 2010 in all of the sectors, though slowest for biomass burning, which is projected to be the most important sector in 2010.

Table 5.6: Emissions by fuel in new EU member countries [kt]

Fuel	PM$_1$		BC		OC	
	2000	2010	2000	2010	2000	2010
Coal	86	47	18	9	24	12
Biomass	86	74	16	14	43	36
Liquid and gas	48	26	23	13	16	9
Diesel	41	22	22	12	12	7
Gasoline	5	3	1	1	4	2
Other liquid and gas	2	2	0	0	0	0
Other	68	54	9	7	20	18
TOTAL	287	201	66	43	103	76

The situation is fairly similar for the non-EU countries as for the new EU member states. The main sources of BC and OC are the use of liquid fuels in transport as well as biomass and coal burning in domestic sector. However, the development of the emissions in the future will be different. Emissions of BC and OC from the use of these fuels are estimated to increase, while the relative importance is estimated to stay fairly constant.

The major part of the PM$_1$ emissions in 2000, 38 percent, comes from non-combustion sources, i.e., industrial processes, mining and agriculture. Biomass and coal are the biggest fuel sources having emission shares of 30 and 18 percent respectively. A slight decline is estimated for 2010, though with a similar sectoral distribution as in 2000.

Table 5.7: Emissions by fuel in non EU countries [kt]

Fuel	PM$_1$		BC		OC	
	2000	2010	2000	2010	2000	2010
Coal	264	255	52	56	92	86
Biomass	443	399	79	75	216	192
Liquid and gas	204	187	85	80	81	74
Diesel	160	152	79	74	51	49
Gasoline	31	20	4	4	28	23
Other liquid and gas	13	14	3	3	2	2
Other	550	472	68	62	124	120
TOTAL	1462	1314	283	273	513	471

Table 5.8 shows European emissions of PM$_1$, BC an OC by country for the years 2000 and 2010, assuming full implementation of current legislation (CLE). Reductions are expected for the majority of countries. As discussed before, the reductions are largest in the EU member states.

Table 5.8: Estimates of PM emissions by country for the years 2000 and 2010 assuming full implementation of current legislation [kt].

Country	PM$_1$		BC		OC	
	2000	2010	2000	2010	2000	2010
Albania	8	7	2	1	4	3
Austria	36	27	11	8	14	10
Belarus	36	35	7	8	13	13
Belgium	27	16	10	5	7	4
Bosnia-Herzegovina	12	10	1	1	2	2
Bulgaria	39	32	5	4	9	7
Croatia	16	14	3	3	6	5
Czech Republic	36	24	9	5	12	8
Denmark	22	17	6	5	8	6
Estonia	15	10	2	1	4	3
Finland	31	26	9	7	14	11
France	242	160	75	48	96	61
Germany	148	116	47	32	52	42
Greece	39	38	9	8	14	14
Hungary	41	24	7	5	12	9
Ireland	10	8	4	3	3	3
Italy	156	95	45	29	59	34
Latvia	6	5	1	1	2	2
Lithuania	16	13	3	3	7	6
Luxembourg	2	2	1	0	1	0
Netherlands	30	23	11	7	10	7
Norway	23	16	8	5	9	5
Poland	148	106	38	24	57	41
Portugal	37	32	10	8	15	13
R. of Moldova	16	15	4	4	7	6
Romania	110	88	18	15	38	31
Russia[a]	635	622	133	139	231	241
Slovakia	12	11	2	2	3	3
Slovenia	12	7	2	2	4	3
Spain	125	84	38	26	40	28
Sweden	25	16	7	4	10	6
Switzerland	10	6	3	2	4	2
FYR Macedonia	6	5	1	1	1	1
Ukraine	213	195	44	47	66	65
United Kingdom	93	57	37	21	28	18
Yugoslavia	29	27	4	4	8	7
Cyprus	2	1	0	0	0	0
Malta	0	0	0	0	0	0
Turkey	308	241	51	40	116	82
Total	2772	2233	672	527	988	807

[a] only European part

5.2   Comparisons with Other Studies

There are only a handful of studies that present emission estimates of submicron or carbonaceous particles in Europe or some European countries. However, one has to be careful in comparing the results since the individual studies use different activity data sets base years, geographical coverage and sources coverage. .

5.2.1 Comparison of PM$_1$ Emissions in the UK

An emission inventory for submicron particulates in the United Kingdom was compiled by the Aerosol Expert Group in the UK (APEG, 1999), largely based on US EPA (1998) emission factors. A comparison with the RAINS results from this study shows similar total emissions and main emitting sectors. In both studies, transport is the most important source of PM$_1$, while estimates for other sectors differ to some extent. RAINS estimates higher emissions from residential combustion, whereas APEG from industrial processes. Both results show declining emissions between 1990 and 1995. RAINS suggests a continuing decrease at least up to 2010 (see Table 5.8).

Table 5.9: Submicron emissions in the UK as estimated by APEG (1999) and RAINS [kt]

	1990		1995	
Sector	APEG	RAINS	APEG	RAINS
Residential combustion	19	28	13	22
Power plants and industrial combustion	25	17	16	13
Transport	53	61	44	61
Industrial processes	30	8	30	7
Waste treatment	28	26	5	4
Other	2	10	3	10
TOTAL	157	150	111	118

5.2.2 Comparison with Other Studies Reporting Carbonaceous Emissions

Global inventories for BC (some of them include also OC) done by Penner *et al.* (1993), Cooke & Wilson (1996), Cooke *et al.* (1999) Bond (2000), and Bond *et al.* (2004) report also total European emissions. Some regional scale inventories for emissions of BC and OC have been reported in the scientific literature for, e.g., India (Reddy & Venkataraman, 2002a & 2002b) and China (Streets *et al.,* 2001; Streets *et al.,* 2003), but none were found for Europe. An estimate of BC emissions from Western European sources was done by Derwent *et al.* (2001) using dispersion modeling to back calculate the source strength required to explain the ambient concentrations observed in 1995-1998 at Mace Head (west coast of Ireland). The estimates for emissions of BC and OC in Europe found from different studies are shown in Table 5.10.

The estimates of the total emissions of BC and OC in Europe vary widely, i.e., between 0.5 Tg/year (Bond *et al.,* 2004) up to over 2.5 Tg/year (Cooke & Wilson, 1996) for BC. Part of the variation can be explained by the different base years and different geographical coverage. However, the main factor for the differences is that the earlier estimates used higher emission factors. Bond *et al.* (2004) state that they often found no evidence from measurement data to support such high emission factors as used by Cooke *et al.* (1999). The difference is clearly seen in a comparison made by Bond *et al.* (2004), where they applied Cooke *et al.* (1999) emission factors to their own activity data (1996 fuel use) and arrived at almost three times higher emissions of BC than in their own calculation. As striking the difference is, one has to note the large uncertainties linked to the BC emission estimates, estimated by Bond *et al.* (2004) to be in the order of factor two, largely due to uncertainties in

emission factors. European BC (excluding the Former Soviet Union) estimated in this study for 1995 is about 10 percent higher than the estimate by Bond *et al.* (2004) (see Table 5.10).

Table 5.10: Various estimates of European emissions of BC and OC (excluding the Former Soviet Union), [Tg C/year].

Study	BC	OC	Base year	Remarks
Penner *et al.,* 1993	1.97		1980	Diesel fuel and domestic & commercial coal
	2.14			Additionally wood & bagasse burning
Cooke & Wilson, 1996	2.65		1984	Fossil fuel and some biomass sources
Cooke *et al.,* 1999	1.74	1.64	1984	Fossil fuel emissions in total PM
	1.26	1.36		Fossil fuel emissions in submicron PM
	0.55	0.68		EU15, in total PM
	0.47	0.51		EU15, in submicron PM
Bond, 2000	0.69	0.76	1994	BC in submicron size range
Bond *et al.,* 2004	0.47	0.57	1996	Excluding open burning sources
	0.53	1.26	1996	Including open burning
	1.22	3.00	1996	Bond *et al.,* using Cooke *et al.* 1999 emission factors
Derwent *et al.* 2001	0.48-0.51		1995-1998	Western Europe

Table 5.11: European emissions of BC and OC as calculated in this study [Tg C/year].

BC	OC	Base year	Remarks
0.50	0.69	1990	Europe, excluding FSU, Turkey and wildfires
0.51	0.60	1995	
0.47	0.57	2000	
0.33	0.42	2010	
0.33	0.47	1990	EU-15, excluding wildfires
0.35	0.40	1995	
0.32	0.37	2000	
0.21	0.26	2010	
0.86	1.40	1990	Total Europe, excluding wildfires
0.70	1.03	1995	
0.67	0.99	2000	
0.53	0.81	2010	

In general, the current global emission models under-predict the optical depth on a global scale when compared to aerosol absorption measurements from satellites and of the AERONET network (Kinne *et al.,* 2003; Sato *et al.,* 2003). This trend is, however, not observed over Europe where there is a rather opposite trend (Kinne *et al.,* 2003; Bond *et al.,* 2004). The cause for this has been suspected to be old emission estimates that over-predict the European emission strength in 2001 (Kinne *et al.,* 2003; Bond *et al.,* 2004). RAINS estimate is in the lower range, closer to Bond *et al.* (2004), and its accuracy/verification should be made against measurement data in a separate study.

Comparisons of the BC estimates made in the last decade for different years reveal a declining trend (Figure 5.1). Novakov *et al.* (2003) have made an estimate of the large historical changes in the emissions of fossil fuel BC. For some regions of Europe (FSU, United Kingdom, Germany) the emissions started to decline from approximately 1980's onward. A decreasing trend has also been observed in the concentration measurements done in the UK (Novakov & Hansen, 2004). Sharma *et al.* (2004) observed a decreasing trend of BC concentrations in the Canadian Arctic and hypothesized that the declined emissions in the former Soviet Union would be mostly responsible for it.

Figure 5.1 Comparison of black carbon emission inventories for Europe

5.2.3 Future Work

This paper describes an assessment of European emissions of primary submicron particles, black carbon (BC) and organic carbon (OC), applying an extended PM module of the RAINS model. The estimate includes all European countries covering the period from 1990 to 2010. As shown by Bond *et al.* (2004) such an effort is subject to significant uncertainties. Consequently, one of the main tasks in the future will be to reduce these uncertainties. This can be achieved, i.e., by keeping up-to-date with the work done to reduce the gaps in knowledge about emission characteristics from several sectors discussed in this paper. Also it is important to use the results of this work for comparing the implications of the emission strengths with atmospheric measurements. Shorter term tasks include extending the time span of emission estimates as well as making the calculation available in the Internet using the RAINS PM Web Module.

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ANNEX 1 Mobile Sources

Table A 1 Emission factors of PM_1 for light duty diesel vehicles.

Source	Unit	PM_1	Remarks
Norbeck *et al.,* 1998a ; Durbin *et al.,* 1999	g/km	0.324 [a]	US, models mainly from the 1980s
CONCAWE, 1998	g/km	0.0868	ECE+EUDC cycles
		0.2113	DI, without catalyst
Kerminen *et al.* 1997	g/km	0.0562	No catalyst, FTP-cycle
		0.0522	catalyst, FTP-cycle
Williams *et al.,* 1989b	g/kg	3.30	Australia, models 1978-1986

[a] Calculated using the shares/values/figures in the report/article

Table A 2 Emission factors of BC and OC for light duty diesel vehicles.

Source	Unit	BC	OC	Remarks	Method
Norbeck *et al.* 1998a & Durbin *et al.* 1999	g/km	0.159	0.154	US, models mainly from the 1980s	TO
Israel *et al.,* 1996	g/km	0.0108	0.0096	Tunnel measurements	T
Williams *et al.,* 1989b	g/kg	2.18 [a]	0.891 [a]	Australia, models 1978-1986	TO

[a] Calculated using the shares/values/figures in the report/article

Table A 3 Emission factors for PM_1 for diesel heavy duty vehicles.

Source	Unit	PM_1	Remarks
Hildemann *et al.,* 1991	g/km	0.408	PM_2, US models 1987
Lowenthal *et al.,* 1994	g/km	0.625	$PM_{2.5}$, US (without particulate trap)
		0.125	$PM_{2.5}$, US (with particulate trap)
Schauer *et al.* 1999	g/km	0.185	$PM_{1.8}$, medium duty, 1995 models
Norbeck *et al.,* 1998b	g/km	0.153	US 1982-1996 medium- and light heavy duty
		0.229	Pre-1992 models, without oxidation catalyst
		0.047	Models 1994-1996, with oxidation catalyst
Williams *et al.,* 1989b	g/km	1.71	TSP, Australia, 1978-1986 models, averages
		1.34	with and without the high emitter
Shi *et al.* 2000	g/kWh	0.11	Mainly submicron, US 1995 certified test engine
Ojanen *et al.* 1998	g/kWh	0.101	TSP, European

Table A 4 Emission factors for BC and OC for diesel heavy duty vehicles.

Source	Unit	BC	OC	Remarks	Method
Hildemann *et al.,* 1991	g/km	0.165	0.133	PM2, US models 1987	TO
Israel *et al.* 1996	g/km	0.235	0.136	TSP, Europe tunnel measurements	T
Lowenthal *et al.,* 1994	g/km	0.32 [a]	0.23 [a]	PM2.5, US (without particulate trap)	TO
		0.02 [a]	0.09 [a]	PM2.5, US (with particulate trap)	TO
Schauer *et al.* 1999	g/km	0.056	0.036	PM1.8, medium duty, 1995 models	TO
Norbeck *et al.,* 1998b	g/km	0.105	0.059	TSP US medium- and light heavy duty	TO
		0.128	0.060	Models pre 1992, without oxidation catalyst	
		0.041	0.008	Models 1994-1996, with oxidation catalyst	
Williams *et al.,* 1989b	g/km	0.68 [a] 0.53 [a]	0.95 [a] 0.74 [a]	TSP, Australia models ranging 1974-1985, averages with and without the high emitter	TO
Kirchstetter *et al.,* 1999	g/kg	1.3	0.50	PM$_{2.5}$, US tunnel measurements	TO
Miguel *et al.,* 1998	g/kg	1.44		PM$_{1.3}$, US Tunnel measurements	TO
Shi *et al.* 2000	g/kWh	0.031 0.049	0.039 0.032	TSP, US 1995 certified test engine, 1600 and 2500 rpm	T

[a] Calculated values using shares from the article/report

Table A 5 The emission factors of PM_1 for LD gasoline engines [mg/km].

Source	Unit	PM_1	Remarks
Unleaded fuel			
Cadle *et al.,* 2001	mg/km	3.5	FTP-cycle, US 1990 or later, oxygenated fuel
		6.6	REP05-cycle, 1990 or later, oxygenated fuel
Hildemann *et al.,* 1991	mg/km	11.1	PM2, US (catalyst) unleaded
Norbeck *et al.,* 1998a; Durbin *et al.* 1999	mg/km	19	US, FTP-cycle, pre 1981
		27	1981-85 models
		8	1986-90 models
		1	1991-97 models
Norbeck *et al.,* 1998c	mg/km	12.42	US, Unified cycle, six pre 1987 vehicles
		1.61	Four 1989-1994 models
CONCAWE, 1998		1.56	ECE+EUDC cycles, European
Direct injection engine			
Hall & Dickens, 1999	mg/km	5.24	ECE+EUDC-test, European
Kwon *et al.,* 1999	mg/km	8-14	Total PM, a mix of FTP and EURO III cycles
		13	Average for the EURO III
Lappi *et al.,* 2001b	mg/km	4-14	ECE+EUDC-test
Two-stroke			
Patschull & Roth, 1995	g/kg	6.9-90 [a]	6.3 kW, single cylinder two-stroke
Leaded fuel			
Hildemann *et al.,* 1991	mg/km	59.4	PM2, six US non-catalyst, leaded fuel (0.07-0.09 g Pb/l)
Williams *et al.,* 1989a	g/kg	0.64	Australia, 22 SI-vehicles models 1965-1983 using leaded fuel (0.4 g Pb/l)

[a] Observed mass concentrations: ~0.5-6.5 g/m^3

Table A 6 The emission factors of BC and OC for LD gasoline cars [mg/km].

Source	Unit	BC	OC	Remarks	Method
Unleaded fuel					
Cadle *et al.,* 1999	mg/km	11.9	38.6	FTP-cycle, pre 1981 models, US	TO
		8.3	14.3	1981-85 models, US	
		3.2	7.5	1986-90 models, US	
		3.5	6.8	1991-96 models, US	
		31	190.3	High emitters	
Cadle *et al.,* 2001	mg/km	2.2	1.2	FTP-cycle, 1990 or later models, US, oxygenated fuel	TO
		2.6	2.2	REP05-cycle	
Hildemann *et al.,* 1991	mg/km	2.51	5.56	PM_2, catalyst, unleaded, US	TO
Norbeck *et al.,* 1998a	mg/km	3.3	12.5	FTP-cycle, pre 1981 models, US	TO
		5.5	14.5	1981-85 models, US	
		2.0	5.6	1986-90 models, US	
		0.7	0.3	1991-97 models, US	
Norbeck *et al.,* 1998c	mg/km	1.62	9.9	Unified cycle, 1979-87 models, six vehicles, US	TO
		0.57	0.32	four vehicles 1989-94 models, US	
Sagebiel *et al.,* 1997	mg/km	7.6	23.6	normal emitters 1976-90, US	TO
		22.3	229	High emitters 1976-90, US	
		9.3	31.0	Nine normal emitters 1976-86.US	
		5.2	12.5	Six normal emitters 1986-90 , US	
Schauer *et al.,* 2002	mg/km	0.8	3.3	$PM_{2.5}$, nine catalyst vehicles, 1981-1994 models, US	TO
		8.3	498	$PM_{2.5}$, two non-catalyst, high emitters, models 1969 & 1970,US	TO
Kirchstetter *et al.,* 1999	g/kg	0.035	0.053	$PM_{2.5}$, tunnel measurements, 98% gasoline vehicles, US	TO
Miguel *et al.,* 1998	g/kg	0.030		$PM_{1.3}$, Tunnel measurements, (mean model year 1990, with 1.5% diesel and 0.07% heavy duty vehicles), US	TO
Direct injection engine					
Lappi *et al.,* 2001	mg/km	1.0-6.7	0.6-2.2	$PM_{2.5}$, 50 km/h, Europe	TO
Leaded fuel					
Hildemann *et al.,* 1991	mg/km	4.76	38.9	PM_2, six non-catalyst vehicles, leaded fuel (0.07-0.09 g Pb/l), US	TO
Williams *et al.,* 1989a	g/kg	0.030	0.20	Australia, 22 SI-vehicles models 1965-1983 using leaded fuel (0.4 g Pb/l)	TO

Table A 7 The emission factors of PM_1 for off-road vehicles.

Source	Unit	PM_1	Remarks
Land-based & Marine vessels			
APEG, 1999; Berdowski *et al.,* 1997	g/kg	1.38	APEG: Fuel oil, PM_1 23% of PM_{10}
		1.53	Diesel, PM_1 85%
		0.102	Gasoline, PM_1 85%
			TNO: PM_{10} Fuel oil 6 3.5 g/kg
			Diesel 1.8 1 g/kg
			Gasoline 0.12 0.07

Table A 8 The emission factors of BC and OC for off-road engines.

Source	Unit	BC	OC	Remarks	Method
Land-based					
Mayer *et al.,* 1999	g/kWh	0.07	0.01	g/kWh, Construction site engines	Unknown

ANNEX 2 Wood Combustion and Waste Incineration

Table A 9 Summary of the emission factors of BC and OC in fine particulate matter for wood burning.

Source	Unit	BC	OC	Remarks	Method
Andrae & Merlet, 2001	g/kg	0.59	4.0	Biofuel burning	Unknown
Cooper, 1980	g/kg	0.7	4.2	Wood burning stoves	Unknown
		1.2	4.2	Fireplaces	Unknown
Cooper, 1980	g/MJ	0.0430	0.2494	Wood burning stoves	Unknown
		0.0688	0.2494	Fireplaces	Unknown
Butcher & Sorenson, 1979	g/kg		1.09	Small wood stove burning oak (draft setting/fuel moisture: full/23.8%, 0.5/23.8%, 0.25/8.7%, 0.25/23.8%)	SE
			2.92		
			2.06		
			16.2		
			6.27	Small wood stove burning pine (burning conditions: ¼ draft, 42.4% fuel moisture)	
Fine et al., 2002	g/kg	0.231	5.77	In $PM_{2.5}$, fireplace combustion, hardwoods (yellow poplar, white ash, sweetgum, mockernut hickory)	TO
		0.211	2.53		
		0.095	2.76		
		0.082	5.05		
		0.662		In $PM_{2.5}$, fireplace combustion, softwoods (loblolly pine, slash pine)	
		0.227			
Hildemann et al., 1991	g/kg	0.680	6.292	In PM_2, fireplaces, softwood	TO
		0.276	2.556	hardwood	
		1.500	6.840	synthetic log	
Muhlbaier Dasch, 1982	g/kg	2.97	3.42	Residential fireplaces, softwoods, 12 tests	T (mod.)
		0.8	4.6	hardwoods, 24 tests	
		2.25	7.35	synthetic logs, 3 tests	
Muhlbaier & Williams, 1982	g/kg	1.3	2.8	Residential fire places, softwoods, 4 tests	T (mod.)
		0.39	4.7	hardwoods, 6 tests	
		3.5	1.7	synthetic logs, 3 tests	

Table A 10 Summary of the emission factors of PM_1 in fine particulate matter for wood
        burning.

Source	Unit	PM_1	Remarks
Bond, 2000	g/kg	3.1	g/kg, firewood, residential stove
US EPA, 1998	g/MJ	0.1634	g/MJ, boilers, wood/bark-fired
		0.1161	
		0.0946	
Purvis *et al.,* 2000	g/kg	~6.755	g/kg, fireplaces, wet/seasoned oak/Douglas fir

Table A 11 Summary of the emission factors of PM_1, BC and OC in fine particulate matter for
        waste incineration.

Source	Unit	OC	PM_1	Remarks	Method
Hangebruck *et al.,* 1964	g/kg	0.0261		Large units, incineration	SE
		0.0055			
		0.0242		Small units, incineration	
		0.1317			
US EPA, 1998	g/kg		0.82	Medical waste	
			0.47	Sewage sludge, multiple hearth incinerator	
			0.60	Sewage sludge, electric infrared incinerator	