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Source contributions to $PM_{2.5}$ and PM_{10} at an urban background and a street location

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HIGHLIGHTS

- Urban PM emissions contribute less than 15% to the urban background.
- Factor 2–3 higher EC, heavy metals and re-suspension concentrations in street canyons.
- ^{14}C analysis indicates increasing contribution of biomass and biofuel to EC.

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ABSTRACT

The contribution of regional, urban and traffic sources to $PM_{2.5}$ and PM_{10} in an urban area was investigated in this study. The chemical composition of $PM_{2.5}$ and PM_{10} was measured over a year at a street location and up- and down-wind of the city of Rotterdam, the Netherlands. The ^{14}C content in EC and OC concentrations was also determined, to distinguish the contribution from "modern" carbon (e.g., biogenic emissions, biomass burning and wildfires) and fossil fuel combustion. It was concluded that the urban background of $PM_{2.5}$ and PM_{10} is dominated by the regional background, and that primary and secondary PM emission by urban sources contribute less than 15%. The ^{14}C analysis revealed that 70% of OC originates from modern carbon and 30% from fossil fuel combustion. The corresponding percentages for EC are, respectively 17% and 83%. It is concluded that in particular the urban population living in street canyons with intense road traffic has potential health risks. This is due to exposure to elevated concentrations of a factor two for EC from exhaust emissions in $PM_{2.5}$ and a factor 2–3 for heavy metals from brake and tyre wear, and re-suspended road dust in PM_{10}. It follows that local air quality management may focus on local measures to street canyons with intense road traffic.

1. Introduction

Exposure to elevated levels of particulate matter (PM) is associated with cardiopulmonary and respiratory diseases and lower life expectancy (e.g. Dockery et al., 1993). The revised EU air quality directive (EC, 2008) includes, alongside PM_{10} limit values, new provisions to reduce the exposure to $PM_{2.5}$ with special reference to the urban background. The $PM_{2.5}$ fraction may be more responsive to such measures, as natural sources such as sea salt and windblown soil mainly contribute to the coarse fraction of PM_{10}.

PM emissions in urban areas come from road traffic, household activities, energy production, building work, (inland) shipping and (small-scale) industry. The urban population is particularly exposed to traffic emissions as these are relatively close to the ground and in the near vicinity of housing (Künzli et al., 2000). Traffic emissions involve both *primary* and *secondary* particles. The former comprise carbonaceous particles – i.e. elemental carbon (EC) and organic compounds (OC) – from exhaust emissions (Maricq, 2007), heavy metals from brake and tyre wear (Denier van der Gon et al., 2007; Thorpe and Harrison, 2008; Gietl et al., 2010) and re-suspension of road dust (Amato et al., 2011). Road traffic emissions of NO_x contribute to secondary inorganic aerosol (SIA) and to secondary organic aerosol (SOA) by condensation of semi-volatile compounds from exhaust emissions (Kumar et al., 2008). Inner-urban roads with buildings on both sides at a distance from the road axis less

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than 1.5 times the height of the building are referred to as "street canyons" (Johnson and Hunter, 1999). Traffic emissions in such roads are diluted and dispersed mainly by vertical mixing into the urban background at building height. As a result, the urban population living in street canyons with intense road traffic is exposed to elevated levels of traffic emissions. A distinction in populations' exposure is important, as traffic emissions are particularly associated with health risks (Cahill et al., 2011; Atkinson et al., 2010; Janssen et al., 2011; Keuken et al., 2011). However, the contribution of traffic emissions to $PM_{2.5}$ and PM_{10} even at locations near intense traffic is relatively small with a maximum around 10% (EEA, 2011). This leads to a dilemma for local air quality management: measures are required to reduce traffic emissions in order to limit health risks, but these measures hardly contribute to compliance with PM-related air quality standards. The following research questions have been addressed in this study which may provide guidance for local air quality management:

- How much do urban sources contribute to $PM_{2.5}$ and PM_{10} at urban background locations and in street canyons?
- What is the specific contribution of primary and secondary PM emissions by road traffic in these urban areas?

2. Methodology

The study was performed in Rotterdam, a city with one of the largest ports in the world and a population of around 570 000 people. We studied the contribution of primary PM emission from urban sources to $PM_{2.5}$ and PM_{10}, in the urban background and in a street canyon with intense road traffic. The urban background was studied by wind- and time-controlled sampling and chemical analysis of $PM_{2.5}$ and PM_{10} during a year at two locations up- and down-wind of the city of Rotterdam. In addition, $PM_{2.5}$ and PM_{10} samples were collected in a street canyon near the centre of Rotterdam. Taking the wind direction into account, this sampling strategy provides information on the regional background levels of $PM_{2.5}$ and PM_{10} and the contribution from urban sources, especially from road traffic. The contribution of secondary PM emissions from urban sources to SIA was also investigated by hourly on-line measurements for a period of four weeks at the two locations up- and down-wind from Rotterdam. Finally, the contribution of the above-mentioned sources to EC and OC concentrations was investigated. The sources of OC are not well known, but in Rotterdam EC is considered to be derived almost exclusively from fossil fuel combustion as contribution from other sources such as biomass or wood burning (Larsen et al., 2012) are negligible. Radiocarbon (^{14}C) measurements make it possible to distinguish between carbon from fossil fuel combustion and "modern" carbon from biogenic emissions, biomass burning and wildfires (Szidat et al., 2004). Wind-controlled PM samples have been collected up- and down-wind of Rotterdam and analysed for the ^{14}C content of EC and OC.

Our study comprised three sampling campaigns: the first for primary PM emissions, the second for secondary PM emissions and the third for ^{14}C in EC and OC. These will be discussed in turn below.

2.1. Sampling campaign for primary PM

PM samples were collected from 1 November 2010 to 31 October 2011 at two locations at the edge of the residential area north and south of Rotterdam (referred to as "R′dam$_N$" and "R′dam$_S$" respectively) and on a street in the centre of the city ("R′dam$_{street}$"). The sampling locations are shown in Fig. 1.

Fig. 1 shows that R′dam$_N$ is downwind of urban emission sources when the wind is from the south, while R′dam$_S$ is downwind of urban emission sources when the wind is from the north. When the wind direction is reversed, regional background emissions are sampled at R′dam$_N$ and R′dam$_S$. The locations are more than 2 km down-wind of the motorway ring around Rotterdam which ensures that motorway emissions are well mixed into the urban background (Keuken et al., 2012). Harbour activities in Rotterdam are concentrated 20–25 km to the west of the residential area and the sampling locations as well as the north and south wind sectors have been selected not to include these harbour emissions. The location R′dam$_{street}$ is at the pavement in a street canyon with 32 000 vehicles per working day, 6% of which are trucks and buses. This is a typical traffic volume for a Dutch inner-urban road with intense traffic. The selected traffic location is not in line with the regional locations, which may eventually result in different urban contributions, such as emissions from the harbour area south-west of the traffic station. From another study (Keuken et al., 2012), it is concluded that the contribution by this source is negligible at a distance of more than 3 km from the harbour area. Hence, the locations of the stations are likely to be adequate for the study.

Sampling at the three locations was performed with the following sampling criteria: wind coming either from a northerly sector (300° to 45°) or a southerly sector (150° to 230°), wind speed greater than 2 m s^{-1} and sampling time on working days between 7 AM and 8 PM. The sampling equipment is shown in Fig. 2.

Samples were collected both on pre-fired quartz filters (QMA, Pallflex) and on PTFE filters (Pall Corporation) with a flow rate of 16.7 l min^{-1} and size-selective $PM_{2.5}$ and PM_{10} sampling inlets. The PTFE filters were analysed for elemental composition by XRF analysis (ThermoNoran QuanX, Cooper Environmental Services, USA) and the quartz filters for EC and OC by thermal analysis using the EUSAAR2 protocol (Cavalli and Putaud, 2007). Two sets of quartz filters were used in parallel: one set with a size-selective $PM_{2.5}$ inlet and an active-carbon denuder (Sunset Labs Inc., USA) in the sampling line, and the other with a size-selective PM_{10} inlet and no denuder. The denuder removes gaseous organic compounds, which may be present in ambient air and may be absorbed by particulate matter on the filter (Snyder and Schauer, 2007).

The sampling flow for both the quartz and the PTFE filter was controlled by critical orifices and checked before and after the sampling period. $PM_{2.5}$ and PM_{10} samples were collected simultaneously at each of the suburban sites when winds came from a northerly sector and when winds came from a southerly sector, but were only taken at the street location when winds came from the south. Due to lack of space, only one set of $PM_{2.5}$ and PM_{10} samplers could be installed at the street location. The southerly wind sector was selected to control sampling at the street location, as the distance over the urban background in the south direction is almost 2/3 of the distance between the locations in the south and the north. The sampling regime at all three locations was controlled by measurements at R′dam$_S$ of wind speed and direction during the selected sampling period. The sampling equipment at the other two sites was controlled from R′dam$_S$ by remote communication. The sampling time and duration were logged and stored at all locations. The overall sampling time per month was 48 h at each location.

2.2. Sampling campaign for secondary PM

Concentrations of SIA (ammonium nitrate and ammonium sulphate) were measured hourly on-line with the Marga (Monitoring instrument for AeRosols and GAses). This instrument, developed by ECN, consists of two boxes: a sampling unit and an analytical unit. A mass-flow-controlled air pump draws 1 m^3 of ambient air per hour through the sampling box, which is placed in series with a wet rotating denuder for gas sampling and a steam jet aerosol collector

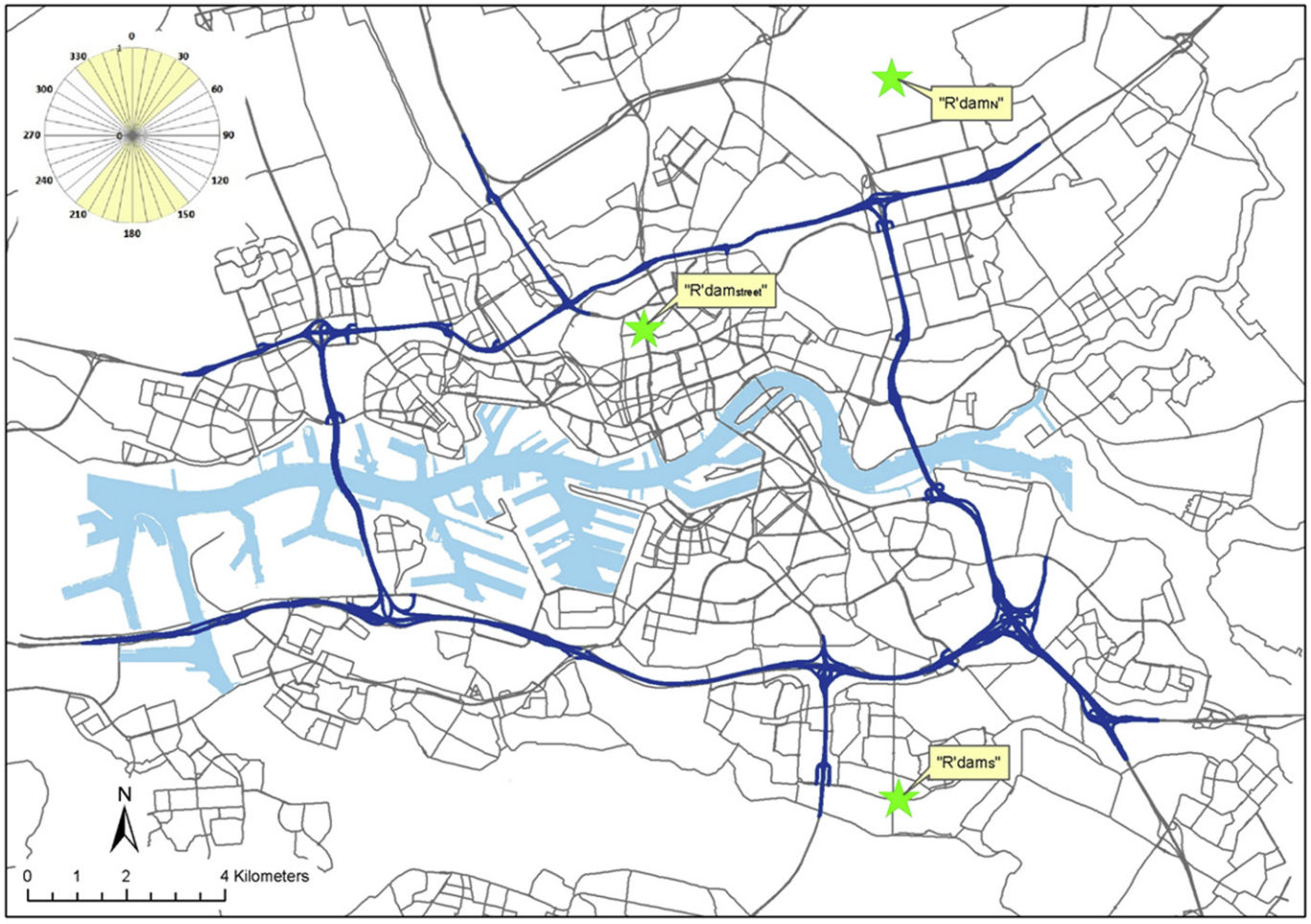

Fig. 1. The sampling locations north ("R′dam$_N$") and south ("R′dam$_S$") of Rotterdam and in the street ("R′dam$_{street}$") in the centre of Rotterdam; also the wind sectors "north" and "south" are indicated as "yellow" in the wind rose.

for aerosol sampling. The air, from which water-soluble gases have been stripped by the wet rotating denuder, is drawn successively through a glass mixing chamber and a 2-micron cut-off glass cyclone. Steam injection in the mixing chamber of the steam jet

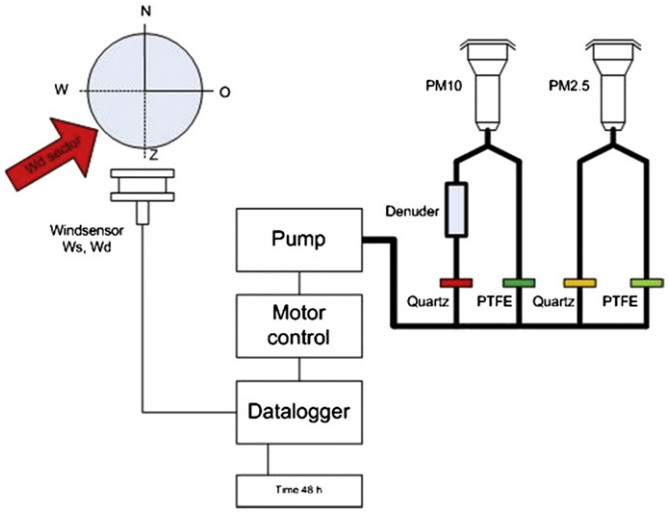

Fig. 2. Wind- and time-controlled sampling of $PM_{2.5}$ and PM_{10} on quartz and PTFE filters.

aerosol collector creates a water supersaturated condition leading to water vapour condensation. The condensate formed causes the water-soluble aerosols to be quantitatively separated in the cyclone; the ammonium, chloride, nitrate and sulphate in the aqueous solution can then be detected on-line (Mikuska et al., 1997). The Marga was fitted with a PM_{10} size-selective inlet during this campaign. Two Marga units were deployed simultaneously from 30 April to 28 May 2011, one at R′dam$_N$ and the other at R′dam$_S$.

2.3. Sampling of EC and OC for ^{14}C analysis

PM samples for ^{14}C analysis were collected by high-volume samplers with pre-fired quartz filters at a sampling flow of 1 m^3 min^{-1} in the period from 27 April to 14 June 2011. The sampling period was one week per sample. As in the case of the monthly sampling campaign, two samplers were located at R′dam$_N$ and two samplers at R′dam$_S$. The samplers at both locations were controlled by the wind direction: one for the northerly wind sector (270°–90°) and one for the southerly sector (90°–270°). No further sampling criteria such as time of day, day of the week or wind speed were applied. The filters used for EC and OC analysis were water extracted and heated to 360 °C for 15 min and to 450 °C for 2 min prior to burning of EC at 650 °C in a pure oxygen flow (Szidat et al., 2004). The procedure is in line with thermal analysis of OC and EC described by Chow et al. (2004). The CO_2 produced by combusting

of OC and EC is trapped by cooling with liquid nitrogen and analysed for ^{12}C, ^{13}C and ^{14}C by an accelerator mass spectrometer (AMS) at the Centre for Isotope Research at the University of Groningen (The Netherlands). The value of f_m (the fraction modern carbon content) in EC and OC was determined from the isotope ratios and by comparison with standards (Szidat et al., 2004).

2.4. Overview sampling strategy

In Table 1 an overview of the sampling programme as described in Sections 2.1–2.3 is presented.

3. Results

3.1. Data analysis of primary PM emissions

A total of twenty-four average monthly samples were collected both at $R'dam_N$ and at $R'dam_S$ in the period from November 2010 to November 2011. Twelve of the samples were collected with the wind in the northerly sector and twelve with the wind in the southerly sector at each location. In addition, twelve samples were collected at $R'dam_{street}$, all with the wind coming from the south.

The samples collected at $R'dam_N$ with a northerly wind and at $R'dam_S$ with a southerly wind provide the average *regional* background levels of $PM_{2.5}$ and PM_{10}. The concentration difference between the upwind location ($R'dam_N$) and the downwind location ($R'dam_S$) with a northerly wind and the similar upwind/downwind concentration difference with a southerly wind yield the average *urban–regional* increment (or "delta") in Rotterdam, which we denote "$\Delta_{urban-regional}$". The concentration difference between $R'dam_{street}$ and $R'dam_S$ with a southerly wind yields the average *street–regional* increment in Rotterdam or "$\Delta_{street-regional}$". From the differences between the "$\Delta_{street-regional}$" and "$\Delta_{urban-regional}$" the "$\Delta_{street-urban}$" has been derived. These relationships may be summarized in equation form as follows:

$$\text{Regional background} = \text{Average}\left[(R'dam_N)_{\text{North wind}}; (R'dam_S)_{\text{South wind}}\right] \quad (1)$$

$$\Delta_{urban-regional} = \text{Average}\left[(R'dam_N - R'dam_S)_{\text{South wind}}; (R'dam_S - R'dam_N)_{\text{North wind}}\right] \quad (2)$$

$$\text{Urban background} = (1) + (2)$$

$$\text{Street} = R'dam_{street}$$

$$\Delta_{street-regional} = (R'dam_{street} - R'dam_S)_{\text{South wind}} \quad (3)$$

$$\Delta_{street-urban} = (3) - 2/3^{*}(R'dam_N - R'dam_S)_{\text{South wind}}$$

It should be noted that the results are not presented as "annual" average due to the sampling strategy: only working days and working hours were sampled with 1152 h for the urban–regional deltas (12 months*48 h per month*2 wind sectors) and 576 h for the street–regional and street–urban deltas (12 months*48 h per month*1 wind sector).

The average regional background and monthly variability in $\mu g\ m^{-3}$ at $R'dam_N$ during northerly wind directions was 18 ± 11 ($PM_{2.5}$) and 24 ± 13 (PM_{10}) and at $R'dam_S$ during southerly wind directions was 18 ± 11 ($PM_{2.5}$) and 21 ± 10 (PM_{10}). It is concluded that the regional background as measured at $R'dam_N$ and $R'dam_S$ are in good agreement. Therefore, the average regional background at these two locations has been used in the data analysis (Equation (1)).

The street–urban deltas have been calculated from the differences between Equation (3) (street–regional deltas) and 2/3 times the differences between $R'dam_N$ and $R'dam_S$ during southerly wind directions. The reason for the factor 2/3 is that the street location is located at about 2/3 of the distance between the locations $R'dam_N$ and $R'dam_S$ (see: Fig. 1) and samples at the street location have been collected only during southerly wind directions.

3.2. Measurement uncertainty

The uncertainty in the measurement of a component, as a result of sampling and chemical analysis, may be assessed by calculating the coefficient of variation (CV) from duplicates (n pairs) and their corresponding samples (S_i and D_i) using Equation (4) (Hoek et al., 2002).

$$CV(\text{component}) = \sqrt{\sum_{i=1}^{n}\frac{(Si-Di)^2}{2^{*}n}} \Big/ \sum_{i=1}^{n}\frac{(Si+Di)}{2^{*}n}{}^{*}100\% \quad (4)$$

No specific duplicate samples have been collected in our study. However, the regional background at $R'dam_N$ during southerly winds and at $R'dam_S$ during northerly are in good agreement (see: Section 3.1). We have used the twelve monthly samples collected at both locations as estimates for duplicates in Equation (4). In this way, the CVs for the components in our study have been derived and presented in Table 2.

The uncertainties in the average urban–regional and street–urban deltas have been estimated from the uncertainty in a monthly delta (e.g. the square root from twice the CV to the power two for a specific component in Table 2) divided by the total number of monthly deltas (n) using Equation (5).

Table 1
Sampling programme in the Rotterdam study.

	PM
$R'dam_N$	48-h (south & north sector); 01/11/2010–01/11/2011; 24 samples
$R'dam_S$	48-h (south & north sector); 01/11/2010–01/11/2011; 24 samples
$R'dam_{street}$	48-h (south sector); 01/11/2010–01/11/2011; 12 samples
	SIA
$R'dam_N$	1-h; 30/04/2011–28/05/2011; 400 on-line measurements
$R'dam_S$	1-h; 30/04/2011–28/05/2011; 400 on-line measurements
	^{14}C
$R'dam_N$	weekly (south & north sector); 27/04/2011–14/06/2011; 6 samples
$R'dam_S$	weekly (south & north sector); 27/04/2011–14/06/2011; 6 samples

Table 2
The uncertainty in the measurements estimated from the coefficient of variation (%).

$PM_{2.5}$ samples:	mass 5%	Al/Si 6%	Cu 7%	Fe_2O_3 5%	Zn 6%
PM_{10} samples:	mass 5%	Al/Si 4%	Cu 5%	Fe_2O_3 4%	Zn 5%
PM_{10} samples:	EC 3%	OC 4%			

$$\mathrm{CV(average\ delta)} = \sqrt{2{*}CV_i^2}\Big/\sqrt{n} \quad (5)$$

The uncertainty in the average deltas for all components is in the range of 1–3%. Per component, a Student's one-tailed, paired *t*-test at 95% confidence was applied to determine whether the urban–regional and street–urban deltas are significant (Microsoft Excel function: TTEST).

3.3. Results for primary PM emissions

The data were analysed as described in Section 3.1 for source-related indicator elements. It is explicitly noted that in our study indicator elements are used as an exploratory technique to identify the contribution from various sources, but *not* to quantify these contributions to PM. The latter requires source apportionment techniques such as principal component analysis and multiple linear regression analysis (Thorpe and Harrison, 2008). As discussed in their review, quantification of source contribution remains problematic, in particular for non-exhaust PM, due to lack of specific tracer elements or to distinguish directly emitted particles (e.g. brake, tyre and road wear) from re-suspension of deposited wear particles or wind-blown soil particles (Thorpe and Harrison, 2008). Therefore, our study is limited to assess the urban–regional and the street–urban deltas of a number of indicator elements (Weijers et al., 2011): EC and OC (carbonaceous PM from exhaust); aluminium (Al) and silicon (Si) (mineral PM from road wear and road dust); iron (Fe) (from vehicle, brake and road wear, and road dust); zinc (Zn) (from tyre wear, exhaust, road furniture and road dust) and copper (Cu) (from brake wear and road dust). The results are presented in Figs. 3–8. These relate to $PM_{2.5}$ and PM_{10} (Fig. 3), EC and OC (Fig. 4), Al plus Si (Fig. 5), Fe (Fig. 6), Zn (Fig. 7) and Cu (Fig. 8). Apart from regional, urban and street concentrations, these figures also show $\Delta_{urban-regional}$ and $\Delta_{street-urban}$.

The regional concentrations in Rotterdam is 18 μg m^{-3} $PM_{2.5}$ and 22 μg m^{-3} PM_{10}. The *urban–regional* delta is 3 μg m^{-3} $PM_{2.5}$ and 3 μg m^{-3} PM_{10}, while the *street–urban* delta is 3 μg m^{-3} $PM_{2.5}$ and 13 μg m^{-3} PM_{10}. A *t*-test (see: Section 3.2) showed that all deltas are significant with the exception of the street–urban delta for $PM_{2.5}$.

The regional concentration in Rotterdam is 1.5 μg m^{-3} EC and 4 μg m^{-3} OC. The *urban–regional* delta is 0.3 μg m^{-3} EC and 0.1 μg m^{-3} OC, while the *street–urban* delta is 1.8 μg m^{-3} EC and 1.1 μg m^{-3} OC. These differences are significant with the exception of the urban–regional delta for OC. The reason for the latter is the relatively high regional background of OC when compared with the contribution from urban emission sources. The deltas for EC indicate that exhaust emissions from road traffic result especially at the street location in elevated EC levels while the urban background is only limited elevated against the regional background.

Aluminium and silicon are elemental indicators for mineral dust (MD) from wind-blown soil and construction activities, wear of road pavement and re-suspended road dust (Thorpe and Harrison, 2008). In the present study, the MD fraction was estimated from the oxides of aluminium and silicon (Al_2O_3 and SiO_2) in $PM_{2.5}$ and PM_{10}. The regional concentrations in Rotterdam were 0.5 μg m^{-3} MD in $PM_{2.5}$ and 1.6 μg m^{-3} MD in PM_{10}. This shows that the contribution of mineral dust to PM is relatively small and mainly in the coarse fraction ($PM_{2.5-10}$). The *urban–regional* delta in Rotterdam is 0.0 μg m^{-3} MD in $PM_{2.5}$ and 1.1 μg m^{-3} MD in PM_{10}, while the *street–urban* delta is 0.0 μg m^{-3} MD in $PM_{2.5}$ and 2.8 μg m^{-3} MD in PM_{10}. MD is significantly increased only in the coarse fraction of PM_{10} both at the urban background and in the street canyon, likely as a result of re-suspended road dust.

Iron oxide in PM samples may originate from a number of sources such as vehicle and brake wear, and re-suspension of road dust (Thorpe and Harrison, 2008; Gietl et al., 2010). In our study, it was not included in the mineral fraction of re-suspended road dust, but treated as an indicator for vehicle wear in general and in particular for brake wear, in addition to copper (see: Fig. 8). The regional concentration in Rotterdam is 0.2 μg m^{-3} Fe_2O_3 in $PM_{2.5}$ and 0.3 μg m^{-3} Fe_2O_3 in PM_{10}. This shows that Fe_2O_3 levels at the regional background are relatively low. The *urban–regional* delta in Rotterdam is 0.1 μg m^{-3} Fe_2O_3 in $PM_{2.5}$ and 0.3 μg m^{-3} Fe_2O_3 in PM_{10}. The *street–urban* delta is 0.0 μg m^{-3} Fe_2O_3 in $PM_{2.5}$ and 1.6 μg m^{-3} Fe_2O_3 in PM_{10}. All deltas for iron oxide are significant with the exception in the fine fraction of the street–urban delta. It is concluded that iron oxide in PM (similar to aluminium and

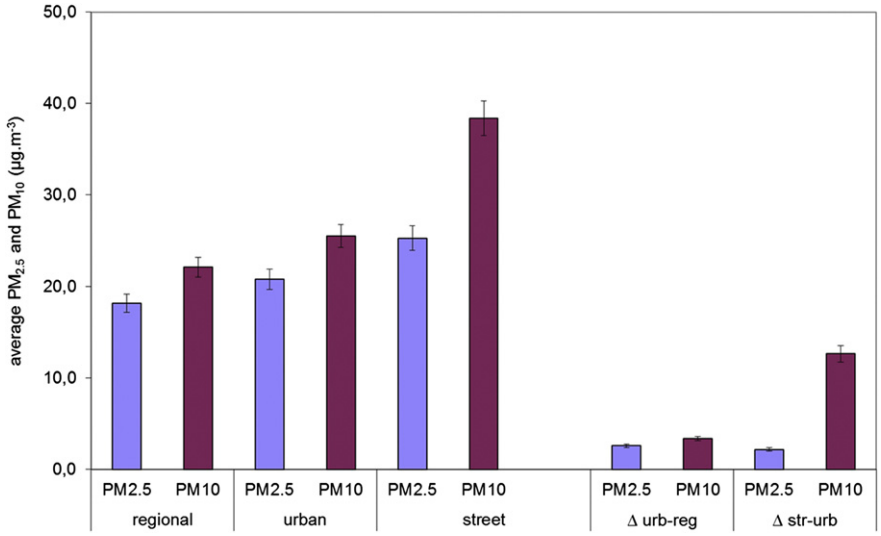

Fig. 3. The average concentrations and uncertainty of $PM_{2.5}$ and PM_{10} at regional, urban and street locations in μg m^{-3}. Also shown are the average deltas and uncertainty for the urban–regional concentrations ($\Delta_{urban-regional}$) and for the street–urban concentrations ($\Delta_{street-urban}$).

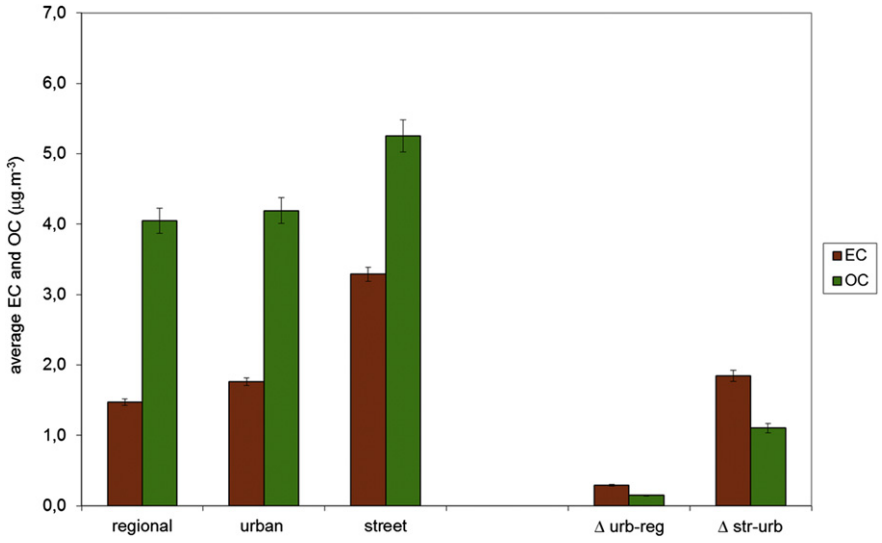

Fig. 4. As Fig. 3, but for EC and OC.

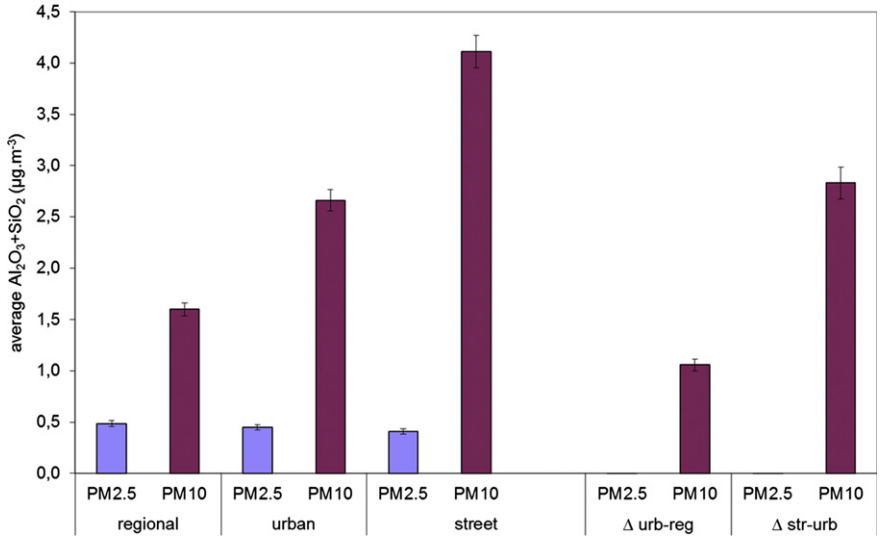

Fig. 5. As Fig. 3, but for aluminium and silicon oxides.

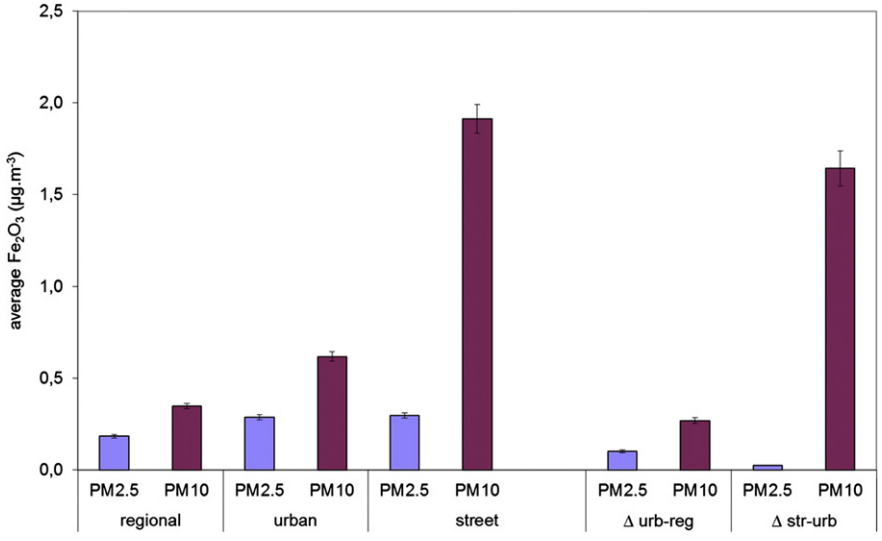

Fig. 6. As Fig. 3, but for iron oxide.

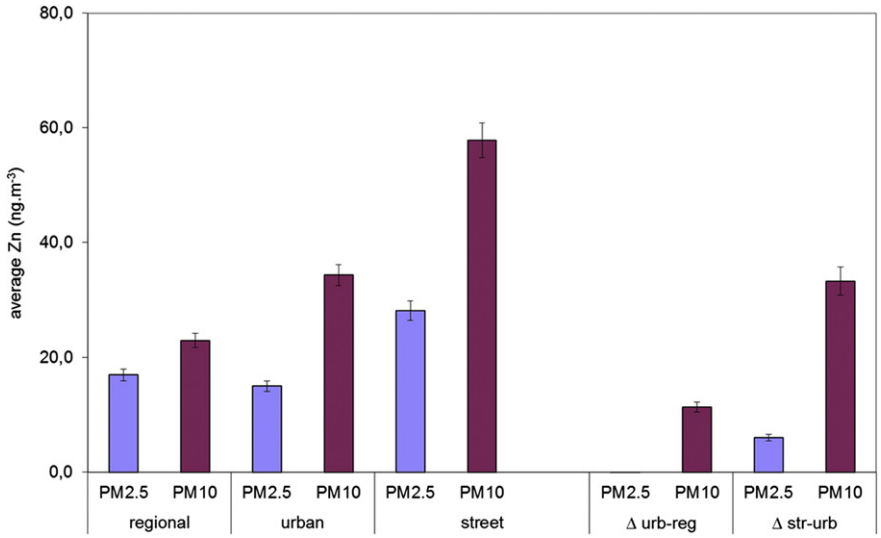

Fig. 7. As Fig. 3, but for zinc in ng m^{-3}.

silicon) is especially elevated at the street location mainly in the coarse fraction probable as a result from re-suspended road dust and direct wear emissions.

The concentration of zinc is a factor 1000 lower than the elemental indicators presented in Figs. 3–6. Near road traffic, zinc may be used as an indicator element for tyre wear, exhaust emissions and re-suspended road dust containing wear of crash barriers and road furniture, in general (Councell et al., 2004; Thorpe and Harrison, 2008). Zinc is not a specific indicator for traffic-related PM emissions as zinc is also emitted by metallurgy industries in general. The regional concentration in Rotterdam is 17 ng m^{-3} Zn in $PM_{2.5}$ and 23 ng m^{-3} Zn in PM_{10}. The *urban–regional* delta in Rotterdam is 0 ng m^{-3} Zn in $PM_{2.5}$ and 11 ng m^{-3} Zn in PM_{10}. The *street–urban* delta is 6 ng m^{-3} Zn in $PM_{2.5}$ and 33 ng m^{-3} Zn in PM_{10}. All deltas for zinc are significant with the exception of the urban–regional delta in the fine fraction. It is concluded that zinc is in particularly elevated at the street location in the coarse fraction (e.g. re-suspended road dust and tyre wear).

Copper concentrations are of the same order of magnitude as zinc. Copper is an indicator of brake wear both from direct emissions and from re-suspended road dust with brake wear particles (Denier van der Gon et al., 2007; Thorpe and Harrison, 2008; Gietl et al., 2010). The regional concentration in Rotterdam is 4 ng m^{-3} Cu in $PM_{2.5}$ and 8 ng m^{-3} Cu in PM_{10}. This shows that copper is equally present in the fine and coarse fractions of regional background PM. The *urban–regional* delta in Rotterdam is 3 ng m^{-3} Cu in $PM_{2.5}$ and 6 ng m^{-3} Cu in PM_{10} while the *street–urban* delta is 5 ng m^{-3} Cu in $PM_{2.5}$ and 46 ng m^{-3} Cu in PM_{10}. All deltas for copper are significant with the exception of the street–urban delta in the fine fraction. It is concluded that copper is in particular elevated at the street location mainly in the coarse fraction (e.g. brake wear and re-suspended road dust).

3.4. Data analysis and results for SIA

SIA concentrations were measured simultaneously at $R'dam_N$ and $R'dam_S$ for 400 h in the period from 30 April to 28 May 2012.

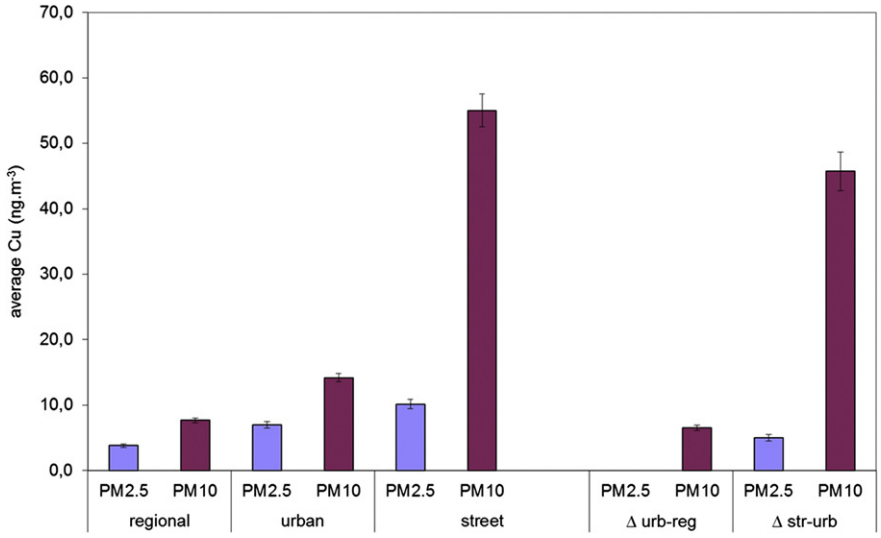

Fig. 8. As Fig. 3, but for copper in ng m^{-3}.

The distribution of the wind directions during these measurements was 17% North, 16% East, 49% West and 18% South. The hourly concentrations of nitrate, sulphate and ammonium at R′dam$_N$ and R′dam$_S$ with the wind coming from various directions are presented in Fig. 9.

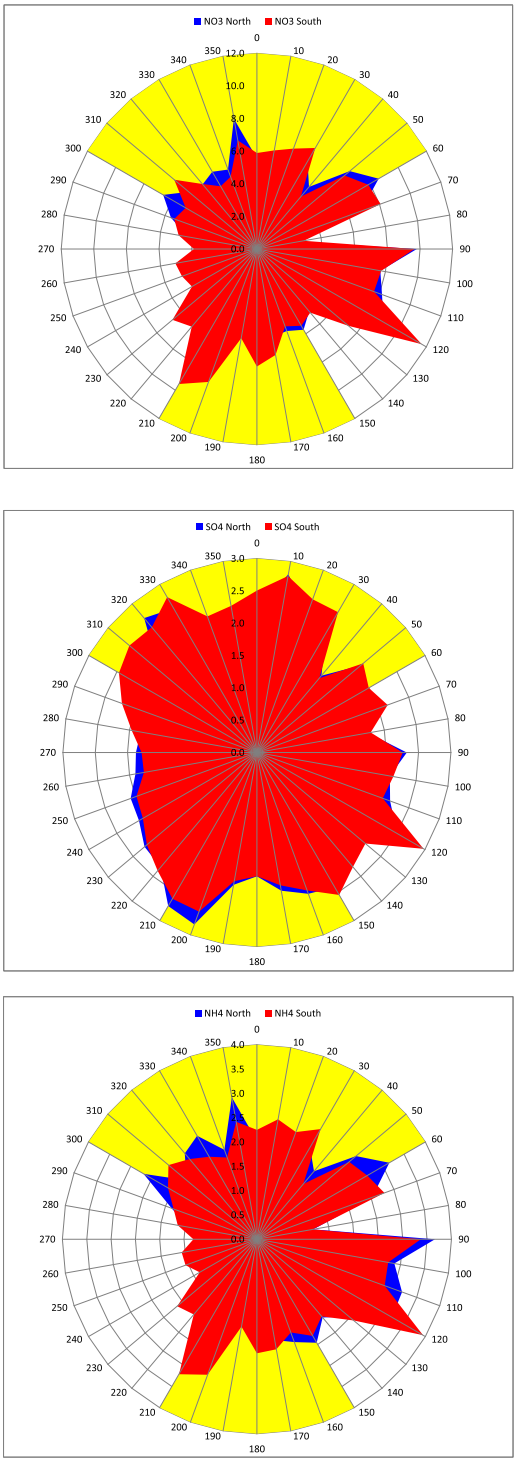

Fig. 9. The hourly concentrations of nitrate, sulphate and ammonium (μg m^{-3}) at R′dam$_N$ (blue) and R′dam$_S$ (orange) as a function of wind direction during sampling in the period 28 April to 30 May 2011. The northerly and southerly wind sectors which have been used to analyse the contribution to nitrate, sulphate and ammonium emissions from urban sources are shown in yellow.

The data presented in Fig. 9 show that the highest nitrate and ammonium concentrations are measured at both locations when the wind comes from the east and the south, and the lowest when the wind comes from the north and the west. This is to be expected, as easterly and southerly winds bring continental air masses with long-range transport of ammonium nitrate from source areas with emissions of gaseous precursors (e.g. NO_x from road traffic and ammonia from extensive husbandry), while northerly and westerly winds bring air masses from the North Sea. Fig. 9 also shows that for ammonium sulphate no specific wind direction is identified with significant higher concentrations. This indicates that harbour activities with potentially relatively high sulphur dioxide, NO_x and PM emissions (Pandolfi et al., 2011) about 20–25 km to the west of Rotterdam do not result in elevated ammonium sulphate concentrations at R′dam$_N$ and R′dam$_S$ during westerly wind directions. From these results, it is concluded that emissions of gaseous precursors of SIA in a city with the size of Rotterdam (8*12 km^2) do not contribute significantly to SIA concentrations at the urban background.

3.5. Data analysis and results for ^{14}C

The results of the ^{14}C analysis in EC and OC for the three sampling periods in April–June 2011 at the sampling locations R′dam$_N$ and R′dam$_S$ are presented in Fig. 10.

Fig. 10 shows that the fraction of modern carbon (f_m) is 72 ± 11% for OC and 27 ± 12% for EC, for both sampling locations and both wind directions. The result for OC agree with other studies in Zürich, Göteborg and Birmingham (Szidat et al., 2009; Heal et al., 2011), which attribute the content of modern carbon in OC to biogenic emissions (60%), combustion of biomass (10%) and combustion of fossil fuel (30%). The results for EC with a f_m of 27% implies that 17% of EC originates from biomass burning, assuming a f_m of 115% for wood burning (this f_m is larger than 100% as a result of the impact of nuclear testing in the 1950s' on ^{14}C in the atmosphere) and a f_m of 5% for fossil fuel for road transport, which contains 5–10% biofuels in The Netherlands. The contribution of biomass burning of 17% to EC is rather high for springtime. This was caused by the relative high f_m of 38% during the first sampling period from 27 April to 4 May 2011 which was likely caused by a strong drought that led to several wildfires in and around the Netherlands. This was exceptional as most wildfires in the Netherlands occur in summer time during dry conditions (www.cbs.nl).

4. Discussion and conclusion

The contribution of urban sources to the urban background levels of $PM_{2.5}$ and PM_{10} was estimated by measuring up- and down-wind concentrations near the built-up area of the city of Rotterdam. The samples were collected only during daytime hours on working days, at times when the wind was coming from specific directions during a monthly sampling period. The sampling procedure explains why the absolute levels found were higher but within the range than those obtained from the 24-h sampling of $PM_{2.5}$ and PM_{10} in routine monitoring networks (Mooibroek et al., 2011). It was found that the urban background level when compared to the regional background is elevated by 17% for $PM_{2.5}$ and by 18% for PM_{10} at working days during daily hours. This implies that the average annual urban background of PM is increased maximum in the order of 10–15%. Consequently, local measures to improve urban background levels of PM may only have a limited effect in Rotterdam.

The measured *urban–regional* deltas led to the conclusion that the relatively small increase in the fine fraction is mainly attributable to EC and OC from combustion emissions (e.g. road traffic and

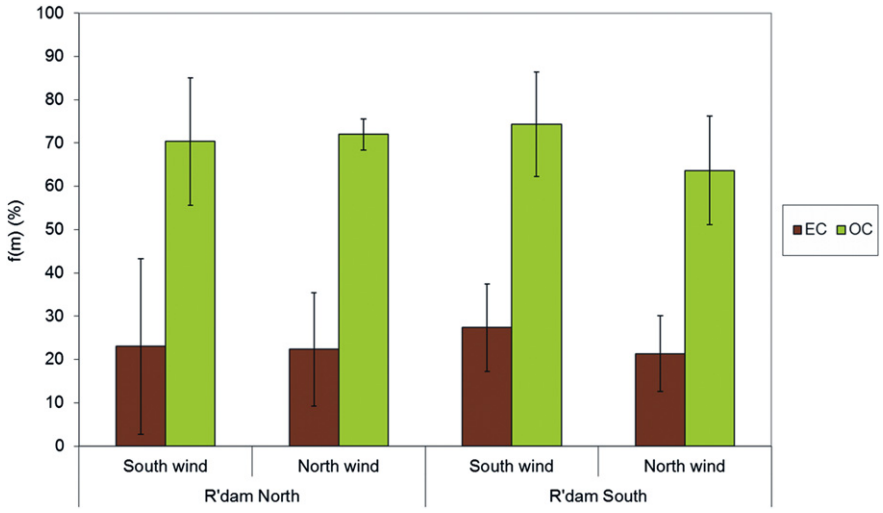

Fig. 10. The average and standard deviation of the fraction modern carbon f(m) in EC and OC at the location $R'dam_N$ and $R'dam_S$ during south wind and north wind in the period 27 April till 14 June 2011 ($N = 3$).

households), and the increase in the coarse fraction to aluminium, iron and silicon oxides probable from non-exhaust emission (e.g. re-suspension of road dust and direct wear emissions) and construction activities (e.g. re-suspension of mineral dust). The investigation of SIA indicated that urban sources, including road traffic, do not contribute significantly to elevated urban background levels of $PM_{2.5}$. This conclusion may change in wintertime with relative more emissions from households by gaseous precursors, such as NO_x. The gap in the mass closure e.g., the difference between the delta in PM and the sum of the deltas of the components, is attributed to the relatively small contributions by urban sources and uncertainties in sampling and analysis.

Both zinc and copper showed a 10% increase in $PM_{2.5}$ and a 100% increase in the $PM_{2.5-10}$ fraction at the urban background as compared to the regional background. Most likely sources in Rotterdam for these trace metals are re-suspension of road dust and direct emissions from tyre wear and exhaust (zinc) and from brake wear (copper). It should be noted, however, that these increases in the levels of trace metals, while relatively important, do not make a significant contribution to $PM_{2.5}$ and PM_{10} in absolute terms.

The urban background level for EC was significant elevated while that for OC was not. Analysis of ^{14}C in EC and OC led to the conclusion that 70% of OC comes from biogenic emissions and 30% from fossil fuel combustion. We found 17% of EC to be derived from modern carbon, while from other studies (Szidat et al., 2009; Heal et al., 2011) a range of 5–15% modern carbon in EC was expected. The higher value in our study may be caused by exceptional wildfires in and around The Netherlands during the first sampling period. It should also be noted that the sampling of ^{14}C was limited to the spring season and therefore cannot be extrapolated to annual averages.

From the measured *street–urban* deltas, it was concluded that $PM_{2.5}$ was not significantly increased in the street canyon, while PM_{10} was increased by 50%. The former is related to the dominant regional background level of $PM_{2.5}$, while the latter is mainly attributed to re-suspension of road dust. Considering the location of the street location relative to the sampling stations in the North and the South of Rotterdam, the urban–regional deltas (at the street location) has been overestimated and consequently, the street–urban deltas have been underestimated. In view of the relatively large street–urban deltas compared to urban–regional deltas, this overestimation is limited. Forty per cent of the increase in PM_{10} is explained by the elemental indicators aluminium, silicon and iron. EC concentrations were elevated by a factor two in the street canyon when compared with the urban background, while OC levels were increased by 25%. These findings show that in particular EC is a better indicator of exhaust emissions than $PM_{2.5}$.

Zinc levels were significantly elevated at the street canyon: by a factor two in both the fine and coarse fraction. Copper concentrations in the street canyon were a factor three higher in the coarse fraction. These elevated levels of zinc and copper (and probable other heavy metals) in the street canyon may be associated with potential health risks (Cahill et al., 2011). The investigation of the street–urban increment showed that in particular people living in street canyons with intense traffic – who make up about 5% of the population of Rotterdam – are exposed to elevated levels of EC and OC from exhaust emissions, heavy metals from brake and tyre wear, and mineral particles from re-suspension of road dust. Consequently, it is recommended to focus local air quality management towards control of traffic emissions in street canyons, as local measures are hardly effective to reduce the urban background of PM.

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