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Spatial variation of ultrafine particles and black carbon in two cities: Results from a short-term measurement campaign

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HIGHLIGHTS

- A short-term monitoring campaign was performed in Amsterdam and Rotterdam.
- 30 minute BC and UFP measurements were made at 161 sites and repeated in 3 seasons.
- For UFP and BC the within to between site variance ratios were 2.17 and 2.44.
- Variance ratios were much higher than in campaigns with longer sampling times.
- Busy street to urban background ratios were 1.6 and 1.5 for UFP and BC.

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ABSTRACT

Recently, short-term monitoring campaigns have been carried out to investigate the spatial variation of air pollutants within cities. Typically, such campaigns are based on short-term measurements at relatively large numbers of locations. It is largely unknown how well these studies capture the spatial variation of long term average concentrations. The aim of this study was to evaluate the within-site temporal and between-site spatial variation of the concentration of ultrafine particles (UFPs) and black carbon (BC) in a short-term monitoring campaign.

In Amsterdam and Rotterdam (the Netherlands) measurements of number counts of particles larger than 10 nm as a surrogate for UFP and BC were performed at 80 sites per city. Each site was measured in three different seasons of 2013 (winter, spring, summer). Sites were selected from busy urban streets, urban background, regional background and near highways, waterways and green areas, to obtain sufficient spatial contrast. Continuous measurements were performed for 30 min per site between 9 and 16 h to avoid traffic spikes of the rush hour. Concentrations were simultaneously measured at a reference site to correct for temporal variation. We calculated within- and between-site variance components reflecting temporal and spatial variations. Variance ratios were compared with previous campaigns with longer sampling durations per sample (24 h to 14 days).

The within-site variance was 2.17 and 2.44 times higher than the between-site variance for UFP and BC, respectively. In two previous studies based upon longer sampling duration much smaller variance ratios were found (0.31 and 0.09 for UFP and BC). Correction for temporal variation from a reference site was less effective for the short-term monitoring campaign compared to the campaigns with longer duration. Concentrations of BC and UFP were on average 1.6 and 1.5 times higher at urban street compared to urban background sites. No significant differences between the other site types and urban background were found.

The high within to between-site concentration variances may result in the loss of precision and low explained variance when average concentrations from short-term campaigns are used to develop land use regression models.

1. Introduction

Risk assessment of morbidity and mortality associated with traffic-related air pollution exposure is a difficult challenge (Hoek et al., 2010). Monitoring networks of air quality can provide appropriate information on temporal variability of pollutant concentrations, however small-scale spatial variation is typically not well-characterized by these

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networks (Larson et al., 2009). Ultrafine particles are airborne nanoparticles with a diameter less than 100 nm. They typically account for approximately 80% of the total particle number concentration but contribute little to ambient particle mass (HEI review panel, 2013). Ultrafine particles have high spatial and temporal variability within a city (HEI Review Panel, 2013). Close to highways the concentration of ultrafine particles can be up to 25 times higher than at background sites (Zhu et al., 2002). Ultrafine particle (UFP) concentrations can drop to background levels in open terrain approximately 300 m from a source. Because of especially dispersion processes, the total particle number concentration decreases rapidly with an increasing distance from the source. UFP has a higher spatial variation than for example $PM_{2.5}$ which is characterized by a high regional background (HEI, 2013; Zhu et al., 2002; Morawska et al., 2008). Because of the shorter atmospheric lifetime of ultrafine particles (related to processes including coagulation, volatilization and deposition) the regional background is less important than for fine particles.

Thus far, there are very few epidemiology studies on health effects of long-term UFP exposure, partly due to the lack of spatially resolved exposure data (Hoek et al., 2010). UFP is typically not measured in routine monitoring networks. The instruments available to measure ultrafine particle or total particle number concentrations are either too expensive or require too much operator interference to be used in the monitoring campaigns designed to build land use regression models (Hoek et al., 2002). These campaigns typically involve selection of 40–80 sampling sites in a study area and monitoring of 1 to 2 weeks per site with instruments left unattended (Hoek et al., 2002; Eeftens et al., 2012). As an alternative, in the last few years several short-term or mobile measuring campaigns have been carried out with constant technician supervision to measure the spatial variation of UFP and other pollutants in cities (Abernethy et al., 2013; Larson et al., 2009; Merbitz et al., 2012; Padró-Martínez et al., 2012; Rivera et al., 2012; Peters et al., 2013; Li et al., 2013; Kozawa et al., 2012). The campaigns were often designed to develop land use regression models and typically have short sampling periods per location (15–60 min) and a small number of repeats at each site. On-road mobile monitoring has also been used with typically even shorter sampling periods in a specific street but more repeats (Larson et al., 2009; Merbitz et al., 2012; Padró-Martínez et al., 2012; Peters et al., 2013; Li et al., 2013; Kozawa et al., 2012). The strength of the design is the large number of sites that can be measured e.g. over 600 sites in the Girona study (Rivera et al., 2012). Because of the short sampling period temporal fluctuations have more impact on results of measurements than in studies using longer sampling times. Therefore, these short-term sampling campaigns might be less precise in determining spatial variation of long-term average concentrations, which could affect the development of robust land use regression models based upon the monitored average concentrations. Short-term campaigns are characterized by monitoring at different sites and different times. A major challenge of short-term campaigns is therefore to separate temporal variation from spatial variation, often achieved by one or a few continuous monitoring sites. Little attention has been paid to methodological issues of short-term campaigns, including the separation of spatial (between-site) and temporal variations (within-site) and the effectiveness of correction for temporal variation to account for non-simultaneous measurements at different sites.

The Measurements of Ultrafine particles and Soot in Cities (MUSiC) study focused on the improvement of exposure assessment of ultrafine particles (UFPs) and black carbon (BC) using a short-term monitoring campaign. Ambient concentrations of UFP and BC were measured at 161 locations for 30 min, three times at each site, in different seasons. The aim of this paper is to evaluate the between and within-site variances of the short-term air pollution measurements reflecting spatial and temporal variability. The estimated between and within-site variance components were compared with previous monitoring campaigns with longer term measurements of BC and UFP. The effectiveness of correcting for temporal variation using a single continuous reference site was explored.

2. Materials & methods

2.1. Study design

We selected 80 sites in Rotterdam and 81 in Amsterdam. Six different types of sites were defined: street, urban background, urban green, waterway, highway and regional background sites. For site selection, the ESCAPE protocol was followed (Eeftens et al., 2012). Street sites were located in major roads defined as a traffic intensity of more than 10,000 vehicles per day. Urban background sites were sites with no major road within a distance of 100 m. Urban green sites were background sites at the edge of a park. Waterway sites were sites selected on the edge of a water body with potentially significant shipping emissions. Highway sites were sites within 100 m of a road classified as a highway. Regional background sites were background sites selected typically about 10 km outside the city. All sites were selected to minimize influences of other local sources (e.g. gas stations) and were situated close to building facades, except for the water body sites. In both cities approximately 30 street sites and 30 urban background sites were selected. Street sites were overrepresented to increase the contrast in concentrations. Furthermore four regional background sites, roughly at every cardinal direction outside the city, were chosen. Further details about the sites can be found in the Supplemental information (SI, Table S1 and S2). The average traffic intensity was about 13,000 vehicles per day for the street sites, 155,000 for the highway sites and less than 1000 for the other sites (Table S1). The fraction of heavy duty vehicles (using diesel) was 8% for the highway sites and 4% for the street sites. For the other sites counts were between 2 and 6% but these fractions are less reliable because of low counts. The distribution of sites in the two cities is shown in Fig. 1. Examples of two sites are given in Fig. S1. Highway sites were located between 22 and 79 m from the edge of the highway, with vegetation, earth wall or noise barriers in between (Table S2).

The ambient concentrations of ultrafine particles and black carbon were measured in real-time for 30 min at each site. An electric car (REVA, Mahindra Reva Electric Vehicles Pvt. Ltd., Bangalore, India) was used to transport the equipment to the sites and as equipment support. The instruments were installed in the back of the car. Because of seasonal variations in air pollutant concentrations, measurements were conducted in winter (January–March), spring (April–May) and summer (June–July) 2013. In total 483 measurements at 161 sites were conducted, spread over six measurement campaigns (three seasons, two cities).

2.2. Equipment

A CPC 3007 (TSI Inc. Tennessee, USA) was installed in the back of the car to measure UFP. The CPC 3007 measures particles above 10 nm and includes particles larger than 1000 nm. Total particle number counts are typically dominated by ultrafine particles, defined as particles <100 nm (HEI review panel, 2013; de Hartog, 2005). This instrument had 1 second intervals between measurements. A Micro Aethalometer (Aethlabs, CA, USA) was used to measure BC continuously, with 1 minute intervals. The BC monitoring interval was set at 1 min because of insufficient precision at shorter time intervals. The rear window of the car was replaced by PET (Polyethylene terephthalate) glass. Conductive silicone tubes (TSI Inc. Tennessee, USA) connected the instrument inlets to copper pipes, which were placed through holes in the PET glass out of the car, to sample the ambient air. Sharp bends were avoided and the total length of tubing was around 0.5 m per instrument. Flow rates for the CPC and Aethalometer were set at 100 cm^3/min and 150 cm^3/min, respectively. Furthermore, the PET glass and the top of the car were covered with conductive foil to counteract the electrostatic capture of

Fig. 1. Study areas, Amsterdam (left) and Rotterdam (right).

particles. Two car batteries were placed in the back of the car as power supply for the instruments. Standard operating procedures were used according to the manufacturer's specifications.

Quality control included zero checks and regular co-located measurements with all instruments in an indoor facility in the lab in Utrecht. Co-located measurements were performed for 2–3 days before and after all six measurement campaigns for about 6 h per day. All instruments were positioned next to each other. The inlets of all devices were attached to a tube that was connected to a box with a small fan to mix the air.

2.3. Monitoring campaign

Measurements were taken between 9:00–16:00 (avoiding the rush hour) to obtain comparable concentrations between sites. At sampling days measurements were done at eight pre-selected sites, consequently requiring 10 measurement days per city per season to visit all 80 (81) sites. The sequence of sites visited in a day was arranged such that different site types were measured at different times of the day. Moreover, routes were spread across the cities to restrict the impact of temporal variation on the concentrations measured in a certain neighborhood. Because the study will be used for human exposure assessment, measurements were conducted close to the facade of homes. The instruments in the back of the car measured continuously during the whole day. Before and after the 30-minute sampling period, a high efficiency particulate air (HEPA) filter was attached to the CPC for a zero measurement to define the start and end of the site measurement.

2.4. Reference site

To be able to correct for temporal variation, a reference site was set up just outside the University campus of Utrecht, located in the outskirts of the city. One reference site was selected in the center of the country to be able to combine measurements from Amsterdam and Rotterdam using a single source for temporal correction. The specific site was chosen close to our laboratory. The reference site was situated about 39 km away from the center of Amsterdam and 50 km from the center of Rotterdam. To minimize the influence of traffic, the site was located in a rural area, in the garden of a house. Previously this site was used as a reference site for the ESCAPE and VE^{3}SPA projects (Eeftens et al., 2012; Montagne et al., 2013). Concentrations at this site were monitored during all sampling days, using the same devices and methods as for the short-term measurements. The instruments were installed in a bike trailer with the same tube length and sample height as at the short-term monitoring sites. The trailer was brought to the reference site every measurement day and retrieved at the end of the day.

Data for the weather conditions were retrieved from the Royal Dutch Meteorological Institute (KNMI, the Netherlands) from nearby stations Schiphol (for Amsterdam) and Rotterdam. A summary can be found in the Supplemental information (SI Table S3).

3. Data analysis

3.1. Data cleaning

We evaluated the basic 1-sec (UFP) and 1-minute (BC) data. If the ratio of the UFP concentration and the UFP concentration measured at the next second was above 10 or below 0.10 the measurement was considered unreliable and deleted, following previous studies (Strak et al., 2011; Boogaard et al., 2010). Application of the criterion was needed in less than 0.01% of the observations. Additionally, if the ultrafine particle concentration was below 500 particles per cm^3 the data was removed, since this is very likely an artifact. Less than 1% of the reference UFP measurement and 0.05% of the UFP measurements at the short-term sites was deleted because of UFP concentrations below 500 particles/cm^3. These observations occurred connected to CPC readings of zero related to low alcohol in the CPC.

No data cleaning was performed for BC. We did not use a recently developed noise reduction method (Hagler et al., 2011), as we use 30-minute concentrations in further calculations. For all 30-minute periods, the change in attenuation was substantially larger than 0.05, the value used in the Hagler-method to redefine the time base. As the Hagler method averages the uncorrected BC concentrations for the new time base, application of this method would not have any effect on our 30-

minute data. We further note that there was little noise in the 1-minute data, and less than 5% of the 1-minute values were negative. Small negative values (<1 μg/m^3) were retained.

BC concentrations may be underestimated with increasing attenuation (Virkkula et al., 2007). We did not apply correction procedures reported previously (Virkkula et al., 2007; Apte et al., 2011), because the correction factors differed almost two-fold between studies and between seasons in the Virrkula study. Attenuation factors in our study never exceeded 100, the set maximum of the instrument, and 91% of the data had attenuation factors below 75 used by Dons et al. (2012) to delete observations. The consequence may be some additional error in the data, but as the various site types were visited on each sampling day and in random order, no bias in comparison between site types occurred. The additional error affects within- and between-site variations similarly, as the same site may be measured with low and high attenuation in the three seasons.

All further calculations were performed with the 30-minute average at each site. We used the 30-minute mean instead of the 30-minute median to better reflect the impact of relatively infrequent sources, e.g. ships and road traffic for background locations.

3.2. Missing data

Missing data at the reference site due to equipment failure occurred for 6% (UFP) and 20% (BC) of the observations. As this implied that we could not correct the monitoring site measurements for temporal variation, we evaluated whether we could impute reference site missing values, exploiting the often high temporal correlation at nearby sites. As UFP and BC concentrations were not measured in the National Air Quality monitoring network, we evaluated the correlation of BC/UFP at the reference sites with NO_2, NO_x and PM_{10} measurements. BC was imputed using PM_{10} at the nearby regional background site Cabauw: BC (ng/m^3) = −173.8 + 46.2 ∗ PM_{10} (μg/m^3) (adjusted R^2 = 0.62). Ultrafine particles had a very low correlation with all PM_{10}, NO_2 and NO_x measurements (adjusted R^2 below 0.05). Consequently, no missing data were imputed for ultrafine particles.

Equipment failure was responsible for some missing data at the short-term monitoring sites, a few sites therefore have 2 measurements instead of 3 and 1 site in Rotterdam had only 1 BC sample. For 88% (BC) and 89% (UFP) of the sites three measurements were available. Missing measurements at the short-term monitoring sites were not imputed.

3.3. Co-located measurements

The median ratios of co-located instrument readings were determined per co-location day. To correct for differences between instruments, the median ratios of the 2 to 3 co-located measurements prior to and immediately after a field campaign were multiplied with the reference site concentrations for that campaign. For BC the corrections were done per instrument number, because four different Aethalometers were used during the study. The ratios and correlations can be found in SI Tables S4 and S5.

3.4. Correction for temporal variation

To estimate the average concentration per site, the three 30-minute mean concentrations were averaged, after correcting for temporal variation using measurements from the reference site. To evaluate how well the temporal variation at the short-term monitoring sites was reflected by the reference site for these short-term samples, the correlation between the measurements at the sites and the corresponding 30-minute reference site measurement was calculated per site. The correlation coefficient for an individual site is not robust, as it is based upon three samples. However, the median of the individual correlations is more robust and was used for interpretation.

We used the difference method for correction (Eeftens et al., 2012; Hoek et al., 2002). In this method, the overall mean concentration at the reference site ($C_{ref,\ avg}$) was determined and then the 30 minute measurement at time t at the reference site ($C_{ref,\ t}$) was subtracted to calculate the difference ($C_{diff\ ref,\ t} = C_{ref,\ avg} - C_{ref,\ t}$). Next, this difference was added to the 30-minute mean concentration at short-term monitoring sites to obtain the corrected concentration at time t ($C_{x,t,\ corr} = C_{x,t} + C_{diff,\ ref,t}$). A comparison with the ratio correction method used by some other researchers (Abernethy et al., 2013) is provided in SI Table S6.

3.5. Evaluation of within and between-site variances of concentrations

Analysis of variance was used to obtain the estimated within- and between-site components of variance. The variance ratio was calculated by dividing the estimated within-site by the between-site variance for all sites with three valid measurements. For comparison, the same analysis of variance was performed with data from the ESCAPE, RUPIOH and VE^{3}SPA studies (Eeftens et al., 2012; Hoek et al., 2011; Montagne et al., 2013). These studies involved much longer sampling times at each site (14 days for ESCAPE, 24 h for RUPIOH and 96 h for VE^{3}SPA) and were thus expected to have smaller within-site/between-site variance ratios. For RUPIOH, sampling was continuous for one week. To avoid autocorrelation, we included 24-hour average UFP concentrations measured at the 1st, 4th and 7th days for the variance component analyses for the RUPIOH data. The analysis of variance was performed with uncorrected and corrected concentrations to evaluate the effectiveness of the correction procedure.

Using the variance components, we calculated the repeatability of the spatial contrast between sites expressed as the intra-class correlation coefficient (ICC) (Armstrong et al., 1992). We calculated the ICC for single measurements as the ratio of between-site variance and the sum of between and within-site variances: var(site) / (var(site) + var(error)). We further calculated the ICC for the average of the three repeats because the average is used in further modeling, using the formula $ICC_{avg,\ k=3}$ = var(site) / (var(site) + var(error)/k). To investigate how many repeats are needed to achieve similar repeatability of the average of the campaigns with longer duration, we also calculated the ICC for 5 and 10 repeats.

3.6. Concentration variability

The concentration variability between different site types was investigated by a general linear model of the natural logarithms of the mean site concentrations with site type as the independent variable. The urban background sites were used as the reference category. The exponent of the slopes in the model can be interpreted as concentration ratios and represents the contrast between site types.

4. Results

Fig. 2 illustrates the large temporal variability of the individual 30-minute average concentrations at the reference site, both between and within days. The temporal variation at the reference site was highly correlated with the corresponding 30-minute BC concentrations at the short-term monitoring sites (Table 1). The temporal correlation for UFP was lower than for BC, suggesting that correction may be less effective for UFP than for BC. The correlation was highest for the background sites, suggesting that correction is more effective for these sites than for the traffic sites.

4.1. Within and between-site variances of concentration and correction for temporal variation

The estimated within and between-site variance components are shown in Table 2. For BC, the within-site variance component, corrected

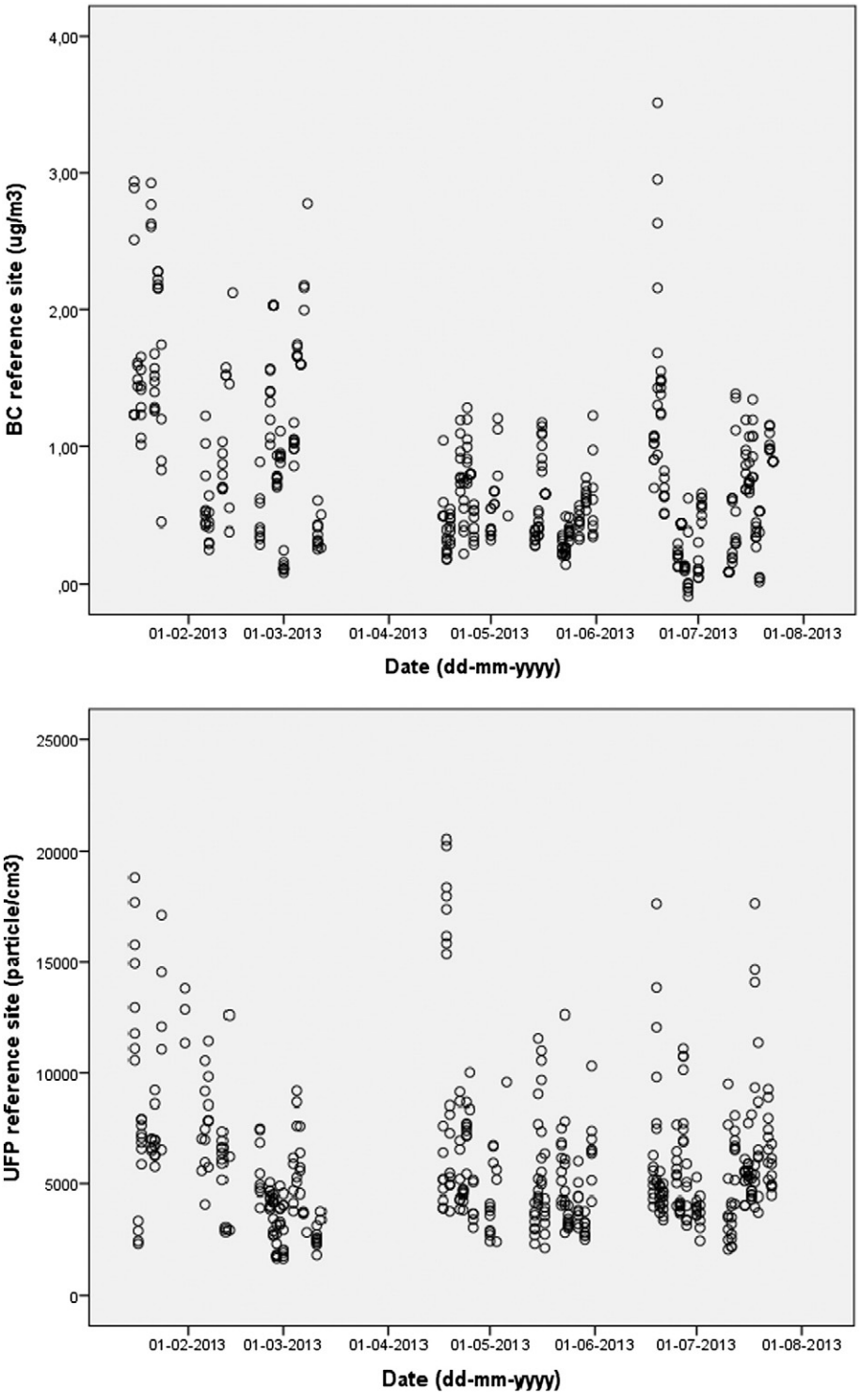

Fig. 2. Temporal variability of 30-minute average BC ($\mu g/m^3$) and UFP (cm^{-3}) at the reference site.

for temporal variation, was 2.44 times larger than the between-site variance component. For UFP, the within-site variance component was 2.17 times larger than the between-site variance component. The variance ratio decreased after adjusting for temporal variation for BC but not for UFP. In comparison, the within-site components of variance in the ESCAPE and VE^{3}SPA study for Black Carbon and in the RUPIOH study for UFP were much lower than the between-site components of variance, whereas the between-site components of variance were more comparable between studies. The pattern of variance ratios followed the sampling duration, with progressively higher within-site variances with shorter sampling times (Table 2).

Furthermore the decrease in variance ratio in the RUPIOH, VE^{3}SPA and ESCAPE studies after correction for temporal variation was larger than in the current short-term monitoring campaign, indicating that the correction was more effective in the studies with longer sampling periods.

Intraclass correlation (ICC) calculated from the variance components for single observations was low for the short-term monitoring

Table 1
The median temporal Pearson R between individual 30-minute mean concentrations at the short-term monitoring sites and the reference site.

Component	Pooled		Amsterdam		Rotterdam	
	Median	N	Median	N	Median	N
All sites						
UFP	0.50	113	0.43	67	0.67	46
BC	0.85	141	0.76	80	0.89	61
Without traffic sites						
UFP	0.74	63	0.56	38	0.80	25
BC	0.91	82	0.92	45	0.90	37

Only sites with 3 measurements included (N = number of sites).

campaign (Table 2), indicating that a single measurement does not represent the spatial contrast well. The ICC of the average of three repeats was moderate for the short-term campaigns and high to very high for the longer duration campaigns. More than 10 repeats are needed to achieve similar ICC values for the average as obtained in longer duration campaigns.

Within-site variance was much larger for street sites than for urban background sites: 1.28 vs 0.39 μg/m^3 for BC and $38 * 10^6$ vs $20 * 10^6$ cm^3 for UFP. Between-site variance was much larger for street sites for BC (0.41 vs 0.03) and UFP ($11 * 10^6$ vs $5 * 10^6$). The variance ratio for street sites was lower for BC (3.1 vs 14.7) and similar for UFP (3.4 vs 3.6). The lower within-site variance for background sites suggests that fewer repetitions could be considered for these sites in future campaigns.

4.2. Spatial contrast across site types

Table 3 shows that the mean UFP and BC concentrations were higher at the street sites in both cities. Increases compared to urban background sites were similar for BC and UFP. UFP but not BC concentrations were increased at highway sites. The mean concentrations of UFP and BC measured were lowest at the regional sites. Furthermore, the contrast between the different site types, with the urban background sites as reference is shown. The overall mean concentration of UFP at the reference site was 5825 particles/cm^3 and 0.80 μg/m^3 for BC. This was 1.43 and 1.22 times lower than the pooled concentrations at regional sites for UFP and BC, respectively.

The spatial variation of the UFP and BC concentrations is the highest between different street sites (Figs. 3 and 4). The highest individual mean concentration was measured at site A17 for both components. This site was located in the center of Amsterdam, close to a traffic light (29 m) with stop and go traffic.

5. Discussion

Ambient UFP and BC concentrations were measured for 30 min in three different seasons at 161 locations to assess spatial variation in two cities. Within to between-site variance ratios were larger than unity. Variance ratios were much larger than calculated for previous campaigns with sampling periods of 24 h to 14 days. Correction for temporal variation was less effective than for the studies with longer sampling periods. The BC and UFP concentrations at street locations were on average 1.60 and 1.49 times higher, respectively, than at urban background sites.

5.1. Temporal variation correction

Measurements were not taken simultaneously but sequentially in the field, because only one mobile platform was available. Therefore, temporal variation in concentrations needed to be accounted for. Previous studies had documented substantial temporal variation of UFP both between and within sampling days (Rivera et al., 2012; Peters et al., 2013; Abernethy at al., 2013). To restrict the impact of temporal variation, continuous BC and UFP measurements were done at a reference site. The within to between-site variance ratios were substantially decreased for BC, but much less so for UFP. This is consistent with the lower temporal correlation between reference site and short-term sampling sites (Table 1), indicating that the reference site was less representative for temporal variations of UFP. A possible explanation might be that UFPs are more reactive than BC, therefore local circumstances have more influence on UFP than on BC concentrations. Another explanation is that UFP may be more dominated by local sources. A potential problem might be that the reference site may have been less representative for temporal variation in the study areas, because it was situated in Utrecht, located 35–50 km away from the two monitoring cities. However, the pattern of lower correlations between reference and field measurements for UFP than for BC was also observed in a study of four cities where the reference site was located within the city, suggesting that local variation plays a more important role than the location of the reference site (Puustinen et al., 2007). The temporal correlation between a central site and residential outdoor sites 24-hour average concentrations in Amsterdam was 0.76 for UFP and 0.94 for $PM_{2.5}$ absorbance measured as an integrated 24-hour sample in that study (Puustinen et al., 2007). The correlation for hourly UFP concentrations was lower than for 24-hour averages (0.66 in Amsterdam), supporting

Table 2
Within and between-site outdoor concentration variances for BC and UFP in relation to sample duration.

Project	Duration	Repeats	Components	Var(Error)[a]	Var(site)[b]	Variance ratio[c]	ICC single	ICC Average, k = 3	ICC Average, k = 5	ICC Average, k = 10
MUSiC	30 min	3	Corr BC	0.76	0.31	2.44	0.29	0.55	0.67	0.80
			BC	1.12	0.35	3.25	0.24	0.48	0.61	0.75
			Corr UFP	26.E6	12.E6	2.17	0.31	0.58	0.70	0.82
			UFP	31.E6	14.E6	2.21	0.32	0.58	0.70	0.82
ESCAPE	14 days	3	Corr $PM_{2.5}$ abs	0.03	0.29	0.09	0.92	0.97	0.98	0.99
			$PM_{2.5}$ abs	0.11	0.27	0.39	0.72	0.88	0.93	0.96
RUPIOH	24 h	3	Corr UFP	89.E6	285.E6	0.31	0.76	0.91	0.94	0.97
			UFP	123.E6	244.E6	0.50	0.67	0.86	0.91	0.95
VE^{3}SPA	96 h	6	Corr $PM_{2.5}$ abs	0.08	0.11	0.69	0.59	0.81	0.88	0.94
			$PM_{2.5}$ abs	0.23	0.09	2.55	0.28	0.54	0.66	0.80

BC in μg/m^3, UFP in (particles/cm^3). $PM_{2.5}$ abs (10^{-5} m^{-1}) is a surrogate for BC (μg/m^3).
ICC = intra class correlation coefficient for single measurements and average of k observations (calculated for 3, 5 and 10 repeats). ICC calculated as var(site) / (var(site) + var(error)) for single observations and var(site) / (var(site) + var(error) / k) for average.
Sample duration is for individual samples. Corr is corrected for temporal variation using the difference method. BC and UFP are uncorrected. In ESCAPE Netherlands, 37 sites had 3 samples. In VE^{3}SPA, 13 out of 15 sites had 6 samples.
[a] Within-site concentration variance.
[b] Between-site variance.
[c] Within/between-site variance.

Table 3
Distribution of average concentrations of ultrafine particles and black carbon per site type.

		UFP (particles/cm^3)				BC (μg/m^3)			
Site type	N	Mean	(Min–Max)	SD	Ratio	Mean	(Min–Max)	SD	Ratio
Amsterdam									
Green	9	11,606	(6611–20,806)	4273	1.19	1.07	(0.89–1.47)	0.21	1.02
Highway	3	14,095	(10,726–18,118)	3739	1.50′	1.12	(0.93–1.39)	0.24	1.07
Region	4	7860	(6890–9039)	910	0.85	0.80	(0.45–1.59)	0.54	0.67*
Street	32	17,051	(6636–57,897)	9698	1.66*	1.93	(0.88–5.67)	1.00	1.69*
Urban	28	9587	(5282–16,082)	2826	1.00	1.09	(0.62–2.33)	0.39	1.00
Water	5	8583	(5346–11,126)	2245	0.91	0.92	(0.46–1.15)	0.27	0.85
Rotterdam									
Green	5	8827	(6039–14,080)	3269	0.89	0.95	(0.80–1.09)	0.12	0.90
Highway	2	14,827	(11,879–17,776)	4170	1.53	1.02	(0.66–1.39)	0.51	0.92
Region	4	8910	(4902–11,886)	3087	0.89	1.37	(0.81–2.01)	0.55	1.24
Street	29	13,713	(5034–23,414)	5176	1.33*	1.73	(0.59–3.68)	0.78	1.50*
Urban	32	10,104	(4910–17,144)	3565	1.00	1.10	(0.40–2.21)	0.36	1.00
Water	8	10,993	(6180–15,241)	2887	1.12	1.36	(0.70–0.00)	0.58	1.21
Pooled									
Green	14	10,614	(6039–20,806)	4054	1.07	1.03	(0.80–1.47)	0.19	0.98
Highway	5	14,388	(10,726–18,118)	3391	1.50	1.08	(0.66–1.39)	0.31	1.01
Region	8	8385	(4902–11,886)	2180	0.87	1.09	(0.45–2.01)	0.59	0.91
Street	61	15,464	(5034–57,897)	7995	1.49*	1.83	(0.59–5.67)	0.90	1.60*
Urban	60	9863	(4910–17,144)	3225	1.00	1.09	(0.40–2.33)	0.37	1.00
Water	13	10,066	(5346–15,241)	2834	1.03	1.19	(0.46–2.28)	0.52	1.06

Concentrations are the averages of the three 30-minute samples corrected for temporal variation using the difference method.
SD is the standard deviation. Ratio is the ratio with the urban background sites as the reference sites, calculated as the exponential Beta of the lnUFP/lnBC general linear model.
* Significant at the $p < 0.05$ level.
′ Significant at the $p < 0.10$ level.

the hypothesis that temporal correction will be less effective for shorter sampling times (Puustinen et al., 2007). Our correlation is similar to the correlation observed in Amsterdam and the other three cities for hourly observations. The lower correlation for 30-minute averages compared to 24-hour averages is likely explained by a larger impact of short-duration local sources (e.g. higher than usual traffic intensity) or weather conditions (e.g. wind direction). With short-duration sampling, the air parcels affecting different sites are furthermore different. In a study in the Boston area, the temporal correlation of UFP measurements at 18 homes with three central monitors was between 0.45 and 0.73 (Fuller et al., 2012). The location of the reference site in a nearby suburban area in our study likely does not fully explain the lower correlation for UFP compared to BC in our study.

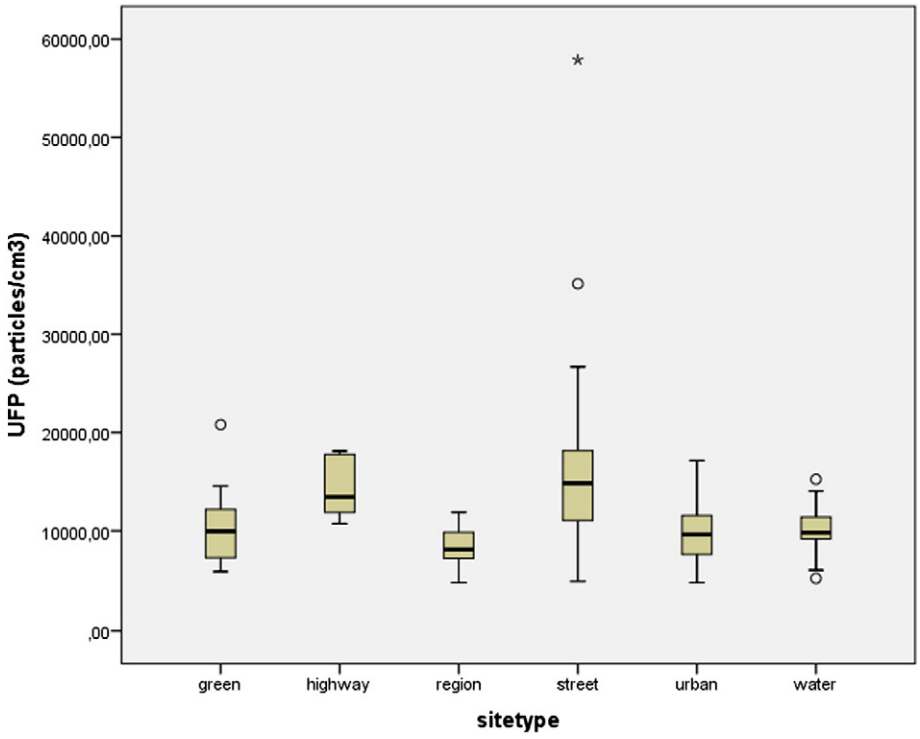

Fig. 3. The distribution of corrected UFP site mean concentrations (counts/cm^3) per site type. Box indicates 25th and 75th percentiles, and horizontal line in box is the median. Individual observations shown if more than 1.5 (○) or 3 (*) times the interquartile range away from the box. Site mean is an average of up to three 30-minute mean concentrations.

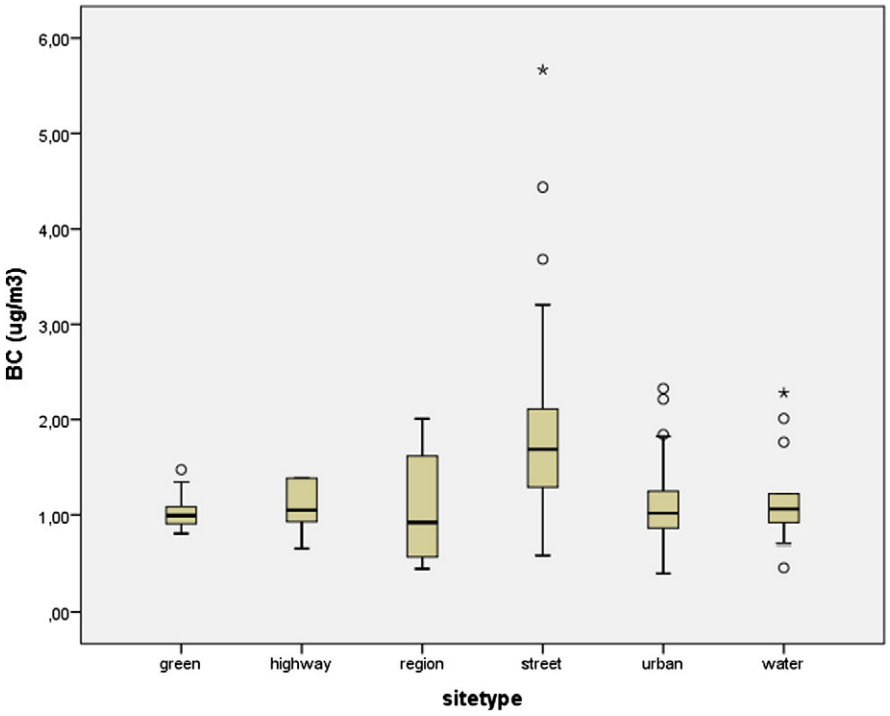

Fig. 4. The distribution of BC site mean concentrations (μg/m^3) per site type. Box indicates 25th and 75th percentiles, and horizontal line in box is the median. Individual observations shown if they are more than 1.5 (○) or 3 (*) times the interquartile range away from the box. Site mean is an average of up to three 30-minute mean concentrations.

5.2. Within to between-site variance ratios

The variance ratios for BC and UFP were larger than two, reflecting a higher within-site variation than between-site variation. In RUPIOH and ESCAPE, studies with longer sampling times, the variance ratios were lower than one. In ESCAPE, samples were taken during 2 weeks in 3 seasons at 40 sites in the Netherlands and Belgium (Eeftens et al., 2012). For RUPIOH 3 samples of each 24 h in one week at 50 sites in Amsterdam were used for our comparison (Hoek et al., 2011). For MUSiC, the UFP ratio was 4.2 times larger compared to RUPIOH and the BC ratio was 8.3 times larger than $PM_{2.5}$ absorbance in ESCAPE. The short sampling times of the mobile campaign made it possible to sample more sites than in previous campaigns. However, the shorter sampling duration resulted in a very substantial increase of within-site variation when compared to previous campaigns. With the same number of repeats, the precision of the site-specific mean will thus be substantially lower than in previous campaigns. To improve precision, future mobile campaigns could increase the number of repeats and/or increase the sampling duration per individual sample. Based upon the calculation of the intra-class correlation coefficient for the average of k repeats, more than 10 repeats are needed to approach the repeatability of the campaigns with longer duration. This number of repeats is difficult to achieve.

The ratio of variance components for UFP may be affected by the size fraction measured by the CPC 3007: particles larger than 10 nm. With the CPC 3007 particles of 10 nm are detected with 50% efficiency and particles of 18 nm with 100% efficiency (Mordas et al., 2008). Particles of 10 nm and smaller likely have higher spatial and possibly temporal variations as their fraction in fresh (traffic) emissions may be higher and the distance decay faster (Zhu et al., 2002; Kozawa et al., 2012).

5.3. Implications for land use regression models

When these site-specific mean concentrations are used to develop land use regression models, the larger number of monitoring sites to develop models may partly outweigh the loss in precision in establishing mean concentrations. In land use regression models, the site-specific mean is used as the dependent variable with traffic and land use predictors as the independent variables. Traffic and land use variables are typically fixed, that is they differ spatially between sites but not temporally. Insufficient correction of temporal variation from the average concentration data can be viewed as a measurement error. Measurement error in a continuous dependent variable does not result in biased regression coefficients but it does result in a loss in precision and power (Armstrong, 1998). Hence, in a study with a limited sample size, the influence of important predictors on concentrations may not be detected as statistically significant. Furthermore, even when the identified model may be correct, the explained variance of the model will be lower if more measurement error is present in the dependent variable. This is likely one explanation for the fairly low explained variances of land use regression models reported in the literature that are based upon mobile or short-term monitoring campaigns (Abernethy et al., 2013; Larson et al., 2009; Rivera et al., 2012).

5.4. Spatial variation

The average ratio between street and urban background sites was 1.49 and 1.60 for UFP and BC concentrations, respectively. The street to urban background concentration ratio in the Dutch ESCAPE campaign was 1.52 for $PM_{2.5}$ absorbance (Eeftens et al., 2012). In a Dutch study conducted between June 2008 and January 2009, UFP was measured at 2 street sites and 2 corresponding background sites and $PM_{2.5}$ absorbance at 8 street sites and corresponding background sites (Boogaard et al., 2011). The average street/urban background concentration ratio for $PM_{2.5}$ absorbance was 1.9 with a range of 1.5 to 2.2, with the higher ratio found for street canyons and streets with buildings on one side of the street. UFP street/background ratios were 1.3 and 2.4 with the highest ratio for the one-sided built street. The UFP ratios were almost the same as the ratios for $PM_{2.5}$ absorbance in the same streets, similar to our observations. Average UFP concentrations in the two streets (16,191 and 10,443 particles per cm^3) also agreed well with our measurements. In a study conducted for one month in the fall of 2008, mean UFP and $PM_{2.5}$ absorbance concentrations at the street site in

Utrecht were 3 times higher than at the urban background location (Boogaard et al., 2010). In that study, the mean UFP concentration at the street site was 38,635 particles/cm^3 and at city background sites 14,094 particles/cm^3. The overall higher concentrations found in the 2008 study could be due to the configuration of the street site (homes on one side of the street only), different weather conditions in the relatively short autumn campaign and the different sampling periods from noon to 6 pm including the evening rush hour. In Amsterdam in the RUPIOH study, 24-hour average PNC and $PM_{2.5}$ absorbance concentrations at 22 traffic sites were on average 1.9 and 1.4 times higher than at the central urban background site. Average PNC concentrations were much higher in RUPIOH (18,090 particles/cm^3 for the central urban background and >30,000 particles/cm^3 for the street sites), possibly related to different equipment (CPC3022 vs CPC 3007 in the current study) and trends in time. Our average concentration at urban background agrees well with the overall average of 24 previous urban monitoring studies of 10,800 p/cm^3 (Morawska et al., 2008). The review documents a large variability of UFP concentrations within major roads, often at substantially higher levels than measured in our study (Morawska et al., 2008).

For our five highway sites, we found (non-significantly) increased UFP and no increased BC concentrations relative to the urban background sites. The low contrast compared to previous studies near highways (HEI Review panel, 2013; Padró-Martínez et al., 2012) is probably due to the siting of the highway sites with (noise) barriers between site and highway and the low fraction of wind from the highway to the site (Table S2). Short-term campaigns with short sampling duration and a small number of repeats are probably not effective for highway sites because of the strong dependence on wind direction during sampling. In contrast, measurements in urban streets in the compact Dutch urban areas are less dependent on wind direction. For near-highway communities, on-road mobile monitoring with a significant number of repeats has been successful to characterize spatial variation (Padró-Martínez et al., 2012; Kozawa et al., 2012).

We developed a short-term campaign to assess spatial variation for UFP. We added BC to be able to assess the specificity of the UFP spatial contrasts. We found a squared correlation of 0.62 between the average UFP and BC concentrations which suggests that the established UFP spatial pattern does not fully mirror a BC pattern in the cities. The correlation is higher than the correlation reported for 2-minute average concentrations in a study in a near-freeway neighborhood near Boston (Spearman $R^2 = 0.39$), but lower than reported for the RUPIOH study in Amsterdam based on fixed sampling with longer duration ($R = 0.85$) (Padró-Martínez et al., 2012; Hoek et al., 2011). The difference likely reflects the impact of temporal variation on the compared concentrations, as temporal correlations between UFP and BC may be low. In our study the temporal correlation between UFP and BC at the reference site was 0.10.

6. Conclusion

Within to between-site concentration variance ratios for BC and UFP were larger than two. These variance ratios were much larger than for previous campaigns with sampling periods of 24 h to 14 days (variance ratios of 0.09 to 0.77). Correction for temporal variation was less effective than for the studies with longer sampling periods. The implication for the use of the site-specific mean concentration as dependent variable in land use regression studies is loss in precision and low explained variance of the models. To achieve the same repeatability of the average as for the campaigns with 24 hour to 14 day sampling times, more than 10 repeats are needed. An alternative is to increase the sampling duration. The BC and UFP concentrations at street locations were on average 1.60 and 1.49 times higher than at urban background sites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.11.088.

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