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Correlations of particle number concentrations and metals with nitrogen oxides and other traffic-related air pollutants in Glasgow and London

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Research Highlights

- Particle number concentration (PNC) and transition metals in particulate matter have been associated with health outcomes.
- PNC and metals are difficult and expensive to measure, so they are not routinely monitored.
- NO_2 and NO_x can be used as surrogates for PNC and water-soluble metal at background sites but not at street canyons.
- Weekly NO_2 measurements derived from passive diffusion tubes could be used as metrics for long-term exposure to PNC.

Abstract

Particle number concentration (PNC) and transition metal content are implicated in the health effects of airborne particulate matter (PM) but they are difficult to measure so consequently their temporal and spatial variations are not well characterized. Daily concentrations of PNC and particle-bound water-soluble metals (V, Cr, Mn, Fe, Ni, Cu, As, Cd and Pb) were measured at background and kerbside sites in Glasgow and London to examine if other metrics of air pollution such as optical darkness (absorbance) of collected filter samples of PM, gravimetric PM, and NO, NO_2 and CO gas concentrations, can be used as surrogates for the temporal and spatial variations of the former. NO_2 and NO_x exhibited a high degree of within-site correlation and with PNC and water-soluble metals (Fe, Cu, As, Cd, Pb) at background sites in both cities. There is therefore potential to use NO_2 and NO_x as surrogates for PNC and water-soluble metal at background sites. However, correlation was weaker in complex street canyon environments where pollutant concentrations are strongly affected by local sources and the small-scale variations in pollutant dispersion induced by the wind regimes within street canyons. The corollary of the high correlation between NO_2 and PNC and water-soluble metals at the background sites is that the latter pollutants may act as confounders for health effects attributed to NO_2 from such sites. Concentrations of CO cannot be used as a surrogate for PNC. Increments in daily NO_x and NO_2 concentrations between trafficked and background sites were shown to be a simple and novel surrogate for daily spatial variation of PNC; for example, increments in NO_x explained 78-79% of the variance in PNC at the paired sites in both Glasgow and London, but relationships were city specific. The increments in NO_x also explained 70 % of the spatial variation in Cu and Ni in Glasgow but not in London. Weekly NO_2 measurements derived from passive diffusion tubes were also shown to correlate well with increments in PNC. A high temporal correlation between PNC and 1,3-butadiene and benzene (which can also be measured by passive sampler) implies that passive sampler measurements may be a straightforward tool for deriving long-term spatial patterns in PNC.

Keywords: particle number concentration, nitrogen oxides, transition metals, air pollution, Glasgow, London

1 Introduction

Epidemiological studies have shown consistent associations between health outcomes and exposure to airborne particulate mater (PM) (Hoek et al., 2002; Pope et al., 2004). Toxicological studies suggest that specific components within particles and the number of particles, more than particle mass alone, are responsible for these health effects. Particle-bound transition metals (especially Fe, Cu, Ni, V, and Zn) and ultrafine particles have been associated with inflammatory responses in human cells (Jiménez et al., 2000; Wilson et al., 2002, Donaldson et al., 2005; and Monteiller et al., 2007). Ultrafine particles are better characterized by the particle number concentration (PNC) rather than by particle mass concentration, as they dominate the former but contribute negligibly to the latter.

PNC and particle-bound metals are expensive and time-consuming to measure and, except for a few specific metals, their ambient levels are not currently subject to regulation. They are therefore not routinely monitored in air quality networks. Consequently there is limited epidemiology on their health effects. Sulphates of Fe, Ni and Zn in $PM_{2.5}$ were associated with mortality in a time-series study of 8 cities in Canada from 1986 to 1996 (Burnett et al., 2000). The effect of the metals was greater than for the mass alone. In contrast, a study in Edinburgh (UK) did not show stronger associations between metals and adverse acute cardiopulmonary health outcomes after adjustment for PM_{10} mass (Heal et al., 2009). A growing number of studies have reported associations between ultrafine particles and cardiovascular disease (von Klot et al., 2005, Lanki et al. 2006, Nicklas et al. 2009, Hoek et al., 2010) and mortality (Hoek et al., 2010).

It would be useful, for epidemiological studies in particular, if other easier and less expensive to measure pollutant metrics (e.g. NO, NO_2 or PM optical absorption) could be used as quantitative relative measures of the concentrations of transition metals and PNC. Total metal content in PM_{10} has been found to correlate with NO_x, PNC and PM light absorption (Harrison et al., 2003; Götschi et al., 2005). Less attention has been paid to the water-extractable fraction, despite its likely greater bioavailablity in the human respiratory system (Costa et al., 1997; Adamson et al., 2000). Heal et al. (2005) reported significant correlations between the water-extractable fraction of metals in PM_{10} and $PM_{2.5}$ and black smoke (equivalent to filter darkness) at an urban background site in Edinburgh.

The aim of this study was to examine the spatio-temporal associations of transition metals and PNC with traffic-related air pollutants at paired kerbside and urban background sites in two cities with a view (1) to investigate a 'simple tracer' for transition metals and PNC, (2) to determine the extent of between and within site inter-pollutant correlations to facilitate better interpretation of epidemiological studies of the health effects of traffic-related air pollution.

2 Experimental methods

2.1 Sampling sites

Associations between traffic-related air pollutants were evaluated for central Glasgow and central London. Both are large, congested cities in which road traffic is the major contributor of local PM_{10}, NO_2, CO, benzene and 1,3-butadiene, and which have nearby kerbside and urban background monitoring stations. This enables comparison of the extent of consistency in within-site inter-pollutant relationships across locations with differing levels of air pollution and of the inter-pollutant relationships in the roadside increments of the pollutants (concentrations at the kerbside site with the concentrations at the background site subtracted).

All monitoring sites are part of the UK national Automatic Urban & Rural Network (AURN). The Glasgow sites were located at:

- Hope St. (kerbside, 55° 51′ 30″ N, 4° 15′ 11″ W): Hope St. is a busy road with two carriageways each way and average traffic flow of around 25,000 vehicles per day comprising mostly buses and taxis. The street is orientated NS and forms a 30 m high (20 m wide) symmetric canyon with the monitoring site located on the E side of the street. A junction ~10 m S of the monitoring station is subject to frequent congestion during peak traffic periods. The monitor inlets are ~1 m from the kerb and 3 m above the ground. The monitoring station is located on the downwind side of the street.
- St. Enoch Sq. (now designated urban background but formerly designated urban centre, 55° 51′ 84″ N, 4° 15′ 45″ W): St. Enoch Sq. is a pedestrian area surrounded by commercial premises. The nearest road is ~20 m N from the site and is orientated WE with typical traffic

flows up to 20,000 vehicles per day. The monitor inlets are ~3 m above the ground. The site is only ~300 m E of the kerbside site in Hope St. and is therefore a good background site for evaluating the contribution of traffic to pollutant concentrations at the latter.

- Montrose St. (urban background, 55º 51′ 22″ N, 4º 14′ 44″ W): monitor inlets at this site are located on the second floor of Glasgow City Chambers ~12 m above ground level facing south. Montrose St. is a symmetric street canyon of depth ~30 m, but width ~10 m, with typical traffic flows in the range 8,000-15,000 vehicles per day.

The London sites were located at:

- Marylebone Rd. (kerbside, 51º 31′ 21″ N, 0º 9′ 17″ W): Marylebone Rd. is a very congested road with three carriageways in both directions and carrying around 80,000 vehicles per day. The carriageway adjacent to the monitoring station is bus and taxi only. The surrounding area forms an asymmetrical street canyon orientated in a NE-SW direction with the monitoring station on the E side of the street. The canyon width is ~40 m and the average building height is ~25 m, comprising educational and commercial buildings plus housing. The monitor inlets are ~1 m from the kerb and ~3 m above the ground and located on the upwind side of the street.

- North Kensington (urban background, 51º 31′ 15″ N, 0º 12′ 49″ W): this site is in a residential area in the grounds of a school, 4 km S of Marylebone Rd. The inlets are 3 m above the ground.

Further information on the monitoring sites can be found at http://uk-air.defra.gov.uk/.

2.2 Sampling instrumentation

Instrumentation and data sources at each site are summarised in Table 1. Sampler operation and gravimetric determination of filter masses at the London sites was undertaken as part of the London Air Quality Network. Sampler operation in Glasgow was carried out as part of this project with the exception of the butanol-based condensation particle counter (CPC), which was operated by National Physical Laboratories as part of the UK network. Filters collected in London where shipped to Glasgow for the optical and chemical analyses. Samples for metal analysis were collected using a Partisol 2025 (Rupprecht & Patashnick Co. Inc.) with a PM_{10} size-selective inlet at Glasgow (on to Zefluor PTFE membrane filters) and a

$PM_{2.5}$ inlet at London (on to quartz filters). Filters were changed automatically at midnight and total daily volume of air sampled was 24 m^3. In Glasgow, the Partisol sampler was operated in accordance with guidance specified by the USEPA (1998); pre- and post-exposed filters were conditioned for 24 h in a temperature and humidity controlled room before being weighed three times on an analytical balance of 1 µg precision (Sartorius MC5) equipped with anti-static ionising blower. A set of 6 blank filters were weighed together with the pre- and post-exposed filters and their mean mass change used to correct the mass change of the sample filters.

The optical absorbance of the sample filters (PM_{10} and $PM_{2.5}$) was determined by measuring sample reflectance, *R*, with an EEL Model 43D reflectometer (Diffusion Systems Limited, London, U.K), and converting to an absorption coefficient, α (m^{-1}), with the relationship $\alpha = \frac{A}{2V}\ln\left(\frac{R_0}{R}\right)$, where R_0 is the reflectance of an unloaded filter (100%), *A* the exposed area of the filter (m^2) and *V* the volume of air sampled (m^3).

PNC at Hope St. and Montrose St. in Glasgow were measured using a water-based, CPC (TSI Model 3785, minimum detectable D_{50} particle diameter: 5 nm) operated according to manufacturer instructions. A butanol-based CPC (TSI Model 3022A; minimum detectable D_{50} particle diameter: 7 nm) was used at St. Enoch Sq. and at the London sites. PNC data were recorded at 1 min and 15 min resolution for the water- and butanol-CPCs, respectively, and averaged as required.

Hourly concentrations of nitrogen oxides (NO, NO_2 and NO_x), CO, PM_{10} as measured by TEOM, 1,3-butadiene and benzene, and daily black smoke (BS), were obtained from the UK Air Quality Archive (http://uk-air.defra.gov.uk/). The gases 1,3-butadiene and benzene are not measured at St Enoch Sq. and North Kensington and BS is only measured at Marylebone Rd.

One-week averaged NO_2 was also measured at St. Enoch Sq. using Palmes-type diffusion tubes (PDTs). Tubes were prepared and analysed colorimetrically, as described by Heal et al. (1999). Tubes were exposed in duplicate together with a field blank.

Hourly meteorological data were obtained from the British Atmospheric Data Centre (www.badc.nerc.ac.uk) for the Bishopton site ~18 km W of Glasgow city centre and for Heathrow Airport ~16 km and 20 km W of the London North Kensington and Marylebone Rd. sites, respectively.

In Glasgow a total of 16/17 days of metal data were collected between 8 June and 31 August 2006. Individual pollutants had longer time series measurements. NO_2 PDTs data was collected over 12 weeks. In London 26 days in 2006 were chosen on the basis of providing the maximum pairs of pollutant concentrations at both sites simultaneously. These days were: 13, 15, 16 May; 23, 24, 25, 26 June; 24, 25, 26, 31 October; 3, 8, 11, 12, 13, 17, 23, 27 November; 4, 6, 8, 10, 12, 14, 15 December.

2.3 Chemical analysis

The Glasgow PM_{10} filters were sequentially extracted for polycyclic aromatic hydrocarbons (PAHs) and water-soluble metals following a method reported by Piñeiro-Iglesias et al. (2003). Each filter was first digested in 2.5 mL of 1:1 v/v hexane:acetone in an ultrasonic bath for 30 min to extract the PAHs. D-10 acenaphtene and D-12-indenol (1,2,3-c,d) were added as internal standards to yield a final concentration of 10 ng mL^{-1}. Extracts were concentrated to 0.1 µL with a flow of N_2. Filters were then digested in 7 mL of ultrapure water (18.4 MΩ) in an ultrasonic bath for 1 h following a protocol described by Heal et al. (2005). The first extracts were analysed for (benzo(b,k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indenol(1,2,3-cd)pyrene) by gas-chromatography mass spectrometry (GC-MS) at the Natural Environment Research Council (NERC) facility at the University of Bristol. Concentrations for all PAHs were below the limit of detection (LOD) and are therefore not discussed further here. The second extracts were analyzed for V, Cr, Mn, Fe, Ni, Cu, As, Cd and Pb by inductively coupled plasma mass spectroscopy (ICP-MS, Thermo PlasmaQuad instrument) at the NERC facility at Kingston University. The $PM_{2.5}$ filters from the London sites were subject only to the extraction step for metal determination, but otherwise the procedure was as described above.

3 Quality Control

3.1 Limits of detection

The LOD for PM_{10} was calculated as 3 times the mean standard deviation (SD) of day-to-day mass change of blank filters × $\sqrt{\frac{n+1}{n}}$, divided by the nominal sampling volume, as defined by Vaughan et al. (1989), and was 0.1 µg m^{-3}.

The LODs for each metal were defined as three times the standard deviation of the concentrations in the field blanks (Table 2). The median concentration of the field blanks was subtracted from the concentration measured in the exposed filters.

The LOD for NO_2 PDT measurement, defined as the mean of the field blank tubes plus three times the SD of the blanks, was calculated to be equivalent to 6.4 µg m^{-3}. NO_2 measurements were also field blank corrected with the corresponding blank for each week and site.

All PM_{10} and NO_2 measurements were above their LODs. There were only three instances of metal concentration below its LOD, one each for Ni and Cd at Hope St. and one for Ni at St. Enoch Sq., and these were retained in the dataset as recommended by Brown et al. (2008).

3.2 Precision

The precision of the PDTs expressed as the coefficient of variation (CV) from duplicate measurements was 8.8%. The temporal correlations of the PDTs and the co-located chemiluminescence analyser was high, with R values of 0.79 (n=12).

An inter-comparison study at St. Enoch Sq. between the water-CPCs showed a CV of 7% and $R = 0.98$ ($n = 624$, 15-mins average). The comparison of the two water-CPC and butanol-CPCs showed CVs of 25% and 28%. The water-CPC read lower than the butanol-CPC for PNC >30,000 particles cm^{-3} (as measured by the butanol-CPC), possibly because of reduced condensation efficiency in the particle growth tube in the water-CPC. Results from the inter-comparison study are shown elsewhere (Sánchez Jiménez, 2010).

3.3 Metal losses during PAH extraction

To examine potential losses of particle-bound metal during the PAH extraction step of the PM_{10} filters, parallel determinations were undertaken on filters undergoing both extractions or the metal extraction step only. Six filters (F) were cut in half (h), (F_1h_1, F_1h_2, F_2h_1, F_2h_2…) and two halves of different filters underwent extraction together so that the metal concentration in F_1h_1&F_2h_1 was the same as the metal concentration in F_1h_2&F_2h_2 (assuming the metals were distributed homogeneously in the filters). Although loss of metal during the PAH extraction step could be substantial (5-60%), it was systematic as indicated by the large correlation (R = 0.97) between the metal concentration in the pairs of filters undergoing either one or two extraction steps. Therefore, although metal concentrations in the Glasgow data have been underestimated this does not affect the strength of the correlations in the relationships between metals and co-pollutants.

4 Statistical analysis

Pollutant measurements were averaged to produce 24 h concentrations, as this is the averaging period used in time-series epidemiology with these metrics. Daily and hourly data were not normally distributed so non-parametric Spearman correlation coefficients were used to describe the strength of the correlation. Hourly and daily correlations were examined to determine which averaging period predicted better the PNC. In addition, the inter-pollutant correlations between daily averages was examined to determine whether PNC and metals can act as confounders or collinear pollutants on the associations between health outcomes and nitrogen oxides and PM. Analyses were conducted using SPSS 16.0. Correlation coefficients between 0.50-0.69 were referred to as moderate, above 0.69 as high and below 0.50 as low.

The inter-pollutant relationships, including those between roadside increments, were examined using reduced major axes regression which allows for statistical uncertainty in both variables (Ayers, 2001). Coefficients of determination (R^2) were used to describe the strength of the association.

5 Results

5.1 Pollutant concentrations

A summary of the pollutant concentrations at each location is given in Table 3. Direct comparison between the pollutant concentrations at London and Glasgow is compromised because the sampling periods and sample sizes were different for both cities. The data from London were selected to maximise the range of observed pollutant concentrations. The datasets were also of insufficient duration to represent intra-annual and inter-annual variations. Nevertheless, concentrations of PM and gaseous pollutants were much higher at the kerbside sites (Hope St. and Marylebone Rd.) than at the background sites (North Kensington, St. Enoch Sq. and Montrose St.) because of the major impact of nearby traffic at the former sites. The variability of pollutant concentrations, expressed as the inter quartile range (IQR), was higher at the London sites than in Glasgow, likely because the data for London were from 26 days spread through winter and summer whereas in Glasgow the data were from a consecutive period in summer only.

5.2 Correlations of the same pollutant measured at different sites

Individual pollutants showed low to moderate correlations between kerbside and background sites in each city (Table 4). Correlations between Hope St. and St. Enoch Sq. in Glasgow were greater for PM_{10} (R = 0.67 and 0.73, for hourly and daily averaged data, as measured by TEOM) than for PNC (R = 0.47, 0.43) and NO_x (R = 0.52, 0.33). The contrast in absolute pollution concentrations between the kerbside and background sites was greater in London than in Glasgow but between-site correlation coefficients for the particle metrics PM_{10} (R = 0.50, 0.23) and PNC (R = 0.58, 0.46) were similar. The correlation of NO_x between the two London sites was lower, particularly for daily averages (R = 0.43, 0.06) which appears to be driven by the much greater local NO_x source strength at the highly polluted Marylebone Rd. site. Concentrations of NO at North Kensington (background) were very low (<5 $\mu g\ m^{-3}$) except on the 3 November where concentrations reached 200 $\mu g\ m^{-3}$ (data points deviating from the general trend in the scatter plot in Table 4). On this day, PM_{10} concentrations in North Kensington were also higher (scattered points in Table 4). This was probably the result of the bonfires that took place to celebrate Guy Fawkes' Night, which fell on the following Sunday (5 November). When data for this day were removed from the dataset, correlation coefficients did not change substantively.

PM_{10}, PNC and constituent NO_x species correlated more strongly between the two background sites in Glasgow (Montrose St. and St. Enoch Sq.), particularly NO_x, NO_2 and NO (*R* values ≈0.8) (Table 4), than between kerbside and background sites, as expected given the absence of strong kerbside source influences at the background sites.

CO concentrations were more weakly correlated between sites, if at all, with the exception of between Hope St. and Montrose St. but the low variability in CO concentrations at St. Enoch Sq. (Table 4) reduces the numerical 'discrimination' in statistical calculations.

The averaging period did not significantly influence the correlation coefficients between the Glasgow sites. However, for the London sites, hourly averaging yielded greater correlation coefficients than daily averaging, especially for NO_x, NO_2 and NO.

For particle-bound metals, correlations between the kerbside and background sites in London were highly significant ($P < 0.01$) for each metal measured (Table 5). In Glasgow, between kerbside and background site correlations were high for V and As ($R > 0.7$), moderate for Mn ($R = 0.5$) but low for the remaining metals quantified (Table 5). The lower between-site correlations between metals in Glasgow may be due to greater inaccuracies in the metal concentration because of losses during the sequential extraction.

5.3 Correlations of different pollutants measured at the same site

At all sites in this study, PNC and NO_x were the pollutant pair with the greatest and most consistent inter-pollutant correlations ($R = 0.60$-0.90, Tables 6-8). Generally, there were no substantive differences between correlations derived from daily and hourly averaged data (hourly data not shown), with the exception of Hope St. At this site daily averaged data had greater *R* values than their hourly counterparts, presumably due to the underestimation at high PNCs by the water-CPC.

Correlations between PNC and PM_{10} were high only at Hope St. ($R = 0.74$). At the other sites the correlation coefficients were <0.5.

In Glasgow, correlations between PNC and optical absorbance of PM_{10} were low ($R = 0.47$ and 0.35 at St. Enoch Sq. and Hope St., respectively) (Table 6). In contrast, in London, PNC was more strongly correlated with $PM_{2.5}$ optical absorbance at the more polluted site (Marylebone Rd., $R = 0.87$) than at the background site (North Kensington), $R = 0.34$ (Table 8).

Correlations between PNC and 1,3-butadiene or benzene were moderate to high ($R = 0.71$ and 0.55, respectively) at Hope St. (Table 6) and high ($R = 0.81$ and 0.78, respectively) at Marylebone Rd. (Table 8).

Correlations between PNC and CO varied substantially across the sites ($R = 0.27$-0.70, Tables 6-8).

In Glasgow, the strength of the correlations of metals with PNC were generally greater than with PM_{10} or with PM_{10} optical absorbance. Correlations between metal concentrations and NO_x or NO_2 were high at St. Enoch Sq. but not at Hope St. At St. Enoch Sq., Mn, Fe, Cu, As, Cd and Pb were significantly correlated with NO_2 and NO_x ($R = 0.6$-0.7), PNC ($R = 0.7$-0.8), PM_{10} ($R = 0.5$-0.8) and PM_{10} optical absorbance ($R = 0.5$-0.8) (Table 6). Cr was also significantly correlated with PNC and NO_x and NO_2 ($R \approx 0.7$) but not with PM_{10} and PM_{10} optical absorbance ($R \approx 0.4$), and Ni showed moderate correlation with PNC and PM_{10} ($R \approx 0.6$) but not with nitrogen oxides and PM_{10} optical absorbance ($R = 0.3$-0.4). CO did not show significant correlation with any of the metals.

A different pattern of inter-pollutant correlations was present at Hope St. For example, unlike at St. Enoch Sq., Fe, As, Cd, and Pb were not significantly correlated with PNC, NO_x or NO_2 (Fe was significantly but negatively correlated with NO_x and NO_2). However, V Cr, Mn, Ni and Cu were significantly correlated with PNC ($R = 0.7$-0.9), Ni and Cu were significantly correlated with PM_{10} ($R = 0.58$ and 0.70, respectively) and Ni was also highly correlated with

NO_2 (R = 0.75) (Table 8). None of the metals were correlated with PM_{10} optical absorbance except Cd (R = 0.50). Concentrations of 1,3-butadiene and benzene (available only at Hope St.) were moderately correlated with Cu (R = 0.58 and 0.52, respectively), but not with the other metals (Table 8).

At Marylebone Rd. (Table 8) there was no significant correlation between any of the particle-bound metals and NO_x, NO_2, PNC and optical absorbance of $PM_{2.5}$, except for V and Ni with PM_{10} (R = 0.48 and 0.44, respectively) and for Mn and Fe with $PM_{2.5}$ (R = 0.54 and 0.48, respectively). Curiously, Cu concentrations were significantly negatively correlated with NO_x, NO_2, PNC, BS and optical absorbance of $PM_{2.5}$.

At North Kensington (Table 8), Fe, Cu, Zn, As, Cd and Pb were moderately to highly correlated with NO_x and NO_2 ($R \approx$ 0.5-0-8). These metals (except for Cu) were also moderately to highly correlated with $PM_{2.5}$ ($R \approx$ 0.6-0.8) and moderately correlated with PM_{10} ($R \approx$ 0.5). Metal concentrations did not correlate with PNC. A few metals, Cu, As, Cd and Pb, had low positive correlations with CO ($R \approx$ 0.5).

5.4 Effects of wind on pollutant correlations

In both cities the prevailing wind direction was W-SW as is usual in the UK. At Marylebone Rd. the monitoring station was located at the upwind side of the street so southerly winds (perpendicular to the street) may induce a recirculation vortex blowing pollutants against the station. This might explain the observed increase in the increments in pollutant concentrations (i.e. the on road emissions at Marylebone Rd.). In contrast, Hope St. was located on the downwind side of the street, relative to westerly winds. Therefore, wind blowing in this direction dilutes pollutant concentration resulting in a decrease of the increments and absolute concentrations.

At the background sites, St. Enoch Sq. and North Kensington, wind speed was negatively correlated with all pollutants. At the street canyon sites pollutant concentrations varied in their response to wind speed. PNC was positively correlated with wind speed at Marylebone Rd. (R = 0.40) but negatively correlated at Hope St. (R = –0.52). PM_{10} was not correlated with wind speed at Marylebone Rd. (R = –0.02), and showed a moderate but not significant negative association at Hope St. (R = –0.40). Metal concentrations decreased with increasing wind speed at both sites. NO_x and NO_2 showed a small positive association with increasing wind speed at Marylebone Rd. (R = 0.36 and 0.41), and a moderate negative correlation at Hope St. (R = –0.47 and –0.51, respectively).

5.5 Regressions of roadside increments of pollutants

Table 9 summarises the relationships between the increments in pollutant concentrations at the kerbside sites (Hope St. and Marylebone Rd.) and their respective background sites (St. Enoch Sq. and North Kensington). The increments in NO_x explained 79% and 78% of the variance in the increments in PNC in Glasgow and London, respectively. At St. Enoch Sq., NO_2 as measured by the PDTs explained 70% (n = 12) of the variance in the weekly averaged PNC.

The increments in PM_{10} explained 70% of the variance in the increments in PNC in Glasgow and 55% in London (p <0.05 in Glasgow and p <0.001 in London). The increments in CO explained less than 50% of the variance in both cities indicating CO cannot be used as a surrogate for PNC.

The increments in NO_x and NO_2 were in general not strongly associated with the increments in metal concentrations (Table 10). Only in Glasgow the increments in NO_2 explained 47% of the variance in Ni and 67% of the variance in Cu. The increments in NO_x explained 65% of the variance in Cu. The increments in PNC showed a strong correlation with the increments in Cu and Ni in Glasgow, explaining 66% and 76% of the variance, respectively. In London explanatory power between the remaining metals and co-pollutants was below 40% and are not shown.

6 Discussion

6.1 Spatial variability of air pollutants

Direct comparisons between the concentrations at London and Glasgow have to be made with caution because sampling periods and sample sizes were different in the two cities.

A metal enrichment at the kerbside compared to background site St. Enoch Sq. was observed in Glasgow, reflecting the contribution of traffic to metal concentrations. That this trend was not observed at the London sites, where concentrations of V, Pb, As and Ni at North Kensington were higher than at Marylebone Rd. could be the result of a local contribution of metals in water-soluble form at North Kensington. These emissions could originate from a Ni refinery located 3.2 km NW from North Kensington (data retrieved from the UK Environment Agency). It could be that on the timescale in which the air reaches Marylebone Rd. these metals are oxidised and therefore insoluble in water.

6.2 Correlations between air pollutants

Nitrogen oxides showed the most consistent associations with PNC across all the studied sites in Glasgow (R = 0.7-0.8) and London (R = 0.6-0.9) for hourly and daily averaging periods and therefore would be the best surrogate for PNC. The averaging period, hourly and daily did not significantly influence the strength of the correlation coefficients, suggesting that correlations are mostly driven by the diurnal pattern of traffic flows. If the correlations between pollutants were mainly driven by meteorology and long-transport, then correlations between daily averages would be higher than their hourly counterparts, since the homogenising effects of meteorology and long-transport are more noticeable over an entire day rather than on an hourly basis. The slightly higher correlation coefficients at the London sites for hourly data is attributed to the larger contrast in the pollutant concentrations, compared to Glasgow, which result in a higher statistical power. Daily averages are principally reported here as this is the relevant exposure period for time-series epidemiological studies.

Pollutants were highly correlated at locations close to traffic source but considerably less so a few tens of metres away from the traffic source, which supports the supposition that correlations are driven by traffic sources.

6.2.1 Correlations of the same pollutant measured at different sites

The correlations of PNC between sites observed in this study are lower than those reported elsewhere in Europe. For example, Aalto et al. (2005) reported correlation coefficients for daily PNC between urban background and traffic sites of 0.67, 0.69 and 0.84 in Rome (n = 293), Stockholm (n = 534) and Barcelona (n = 89), respectively, and Puustinen et al. (2007) reported correlation coefficients in the range of 0.67-0.76 between background sites and high and low traffic sites in Amsterdam, Athens, Birmingham and Helsinki for the years 2002 to 2004. The correlation coefficients for hourly averaged data were lower (0.56-0.66). However, different studies have different characteristics such as distance between monitoring sites, sample sizes, and, in particular, meteorological influences. Higher correlation between background and roadside sites likely reflects the dominance of the homogenising effect of meteorology, whereas lower correlation indicates that local, traffic-related sources of the pollutant are important at the roadside site. The moderate to low correlations of PNC between paired sites in this study suggest the latter. The between-site correlations for PM_{10} and NO_2 in this study show site dependence: for example, correlation coefficients for NO_2 ranged from 0.37 between the two sites in London to 0.5-0.8 between pairs of sites in Glasgow. These results indicate that measurements of these pollutant metrics at one site may not well represent daily variations at other locations, so assigning PNC, PM_{10} and NO_2 data from a single monitoring site as the exposure for a large urban population in epidemiological studies may lead to exposure misclassification.

PNC did not show higher correlations between the background sites compared to background vs. traffic site in Glasgow, as observed for nitrogen oxides. This indicates that nitrogen oxides are more homogeneously distributed than PNC, suggesting meteorological factors affect in a different way the formation and dispersion of both pollutants. In addition PNC do not only depend on traffic emissions but also on particle formation processes, nucleation of particles by condensation of pre-existing vapours and condensation of vapours into existing particles (Kulmala et al., 2004). These can be different at each site, resulting in a lower concentration between sites compared to NO_x and NO_2 which mostly originate from traffic and follow the same pattern across sites.

6.2.2 Correlations between PNC and nitrogen oxides measured at the same site

The within-site correlation coefficients observed in this study between PNC and NO_x or NO_2 were higher at the roadside sites, where concentrations are driven by traffic emissions, than at the urban background sites, where concentrations can be influenced by local sources resulting in weaker correlations.

Harrison and Jones (2005) in a study that examined the correlations between hourly PNC vs. NO_x at five UK sites including St. Enoch Sq., North Kensington and Marylebone Rd. reported similar correlations to those found in this study at North Kensington and Marylebone Rd. (0.51, 0.76, respectively) and slightly lower at St. Enoch Sq. ($r=0.42$).

The higher correlations found at the roadside compared to the background sites suggest that the use of daily NO_x and NO_2 concentrations as surrogates for daily PNC is appropriate at trafficked sites but not at background sites.

6.2.3 Correlations between water-soluble metals and other traffic-related air pollutants

The large correlation coefficients between paired sites for metals reveal that the day-to-day variation in metal concentration is similar at both sites. The low correlation coefficients of Fe and Cu between the London sites, compared with those for V and As, and the lack of correlation of Cr, Ni and Pb between the Glasgow sites could be the result of the higher uncertainty on the calculation of the concentrations of these metals, as their concentrations were close to their respective LODs. The high correlation between metals but not $PM_{2.5}$ concentrations between the London sites suggests different dispersion processes for both pollutants. This is partly supported by the fact that metals were negatively correlated with wind speed at both sites, whereas $PM_{2.5}$ was negatively correlated with wind speed at North Kensington but not at Marylebone Rd.

The different pattern of correlations between metals and PNC between background sites and street canyon, and between both cities, is attributed to the different dispersion in open spaces compared with street canyons. Dispersion of on-road emissions within street canyons is a function of the orientation of the canyon relative to wind direction. The wind regimes at both sites influence the dispersion of pollutant in different ways, as indicated by the different correlations between wind speed and pollutant concentrations at each site. Therefore, the position of the monitoring station in the canyon becomes very important when measuring the concentration of pollutants. Results from this study showed that for open spaces but not for street canyons NO_2 appear to represent well the temporal variations of water-soluble metals. However, in the street canyons the relationships found in this study may not translate to other urban locations. Harrison et al. (2005) also found low correlations for PNC vs. NO_x at street canyon sites. Noble et al. (2003) found better correlation between PNC vs. CO, PM_{10} and nitrogen oxides at wind speeds below 3 m s^{-1}. These earlier findings together with those from this study suggest that correlation between pollutants seem to be affected by small-scale variations in pollutant dispersion induced by the wind regimes created within street canyons and therefore results found at one location cannot be generalised.

The high correlations between NO_2 and metals (Fe, Cu, As Cd, Pb) at St. Enoch Sq. and North Kensington, which are sites representative of population exposure, means that metals are a potential confounding factor for the health effects associated with NO_2 in time-series epidemiological studies based on data from a single exposure site. Further studies are required to investigate whether personal exposures of metals and NO_2 are also correlated.

The lack of correlation between PNC and metals at North Kensington is attributed to the fact that metal concentrations were possibly influenced by long range transport of particles, as opposed to traffic sources, as all metals except Cu correlated with PM_{10}, which at background sites is largely influenced by background air masses. This is confirmed by the low correlation between PM_{10} and NO_x ($r=0.38$). In contrast, at St. Enoch Sq. PM_{10}, was highly correlated to both NO_x and metals, suggesting a common traffic source.

6.3 Potential surrogates for PNC

The increments in daily NO_x and NO_2 concentrations between trafficked and background sites have shown to be a simple and novel surrogate for daily spatial variation of PNC. The increments in NO_x explained 78-79% of the variance in PNC at the paired sites in both Glasgow and London. Likewise, weekly NO_2 PDT values have been shown to be a good relative measure of weekly variability in PNC, explaining 70% of the variability of the latter.

The different relationship between PNC and nitrogen oxides is partly attributed to the fact that PNC do not depend only on traffic emissions but also on particle formation processes, as discussed above. Therefore, particles can still be formed in the atmosphere in the absence of traffic emissions leading to high background concentrations and the different relationships with nitrogen oxides, as observed in this study. This reduces the value of nitrogen oxides as a surrogate for PNC as a different relationship has to be derived for each location.

Benzene and 1,3-butadine were also highly correlated with PNC and are therefore also potentially useful surrogates for PNC. Further examination of the relationships between the increments in benzene and 1,3-butadine vs. increments in PNC are required. In addition, benzene and 1,3-butadine can be measured by passive samplers, which therefore suggests a relatively non-technical and inexpensive surrogate for determining long time-averaged spatial patterns of PNC.

The particle size fraction dominating the PNC metric contributes comparatively little to the particle mass measured by PM_{10}. Therefore unless PM_{10} at a site is overwhelmingly dominated by the ultrafine fraction, correlation between PNC and PM_{10} is not expected to be high, and this is what is observed in this study. The low correlation between PNC and PM_{10} at Marylebone Rd. has been noted previously and is attributed to the large contribution of resuspended particles at this site (Charron and Harrison, 2003). The use of PM_{10} as a surrogate for PNC is therefore not appropriate.

The PM_{10} and $PM_{2.5}$ optical absorbance is a measure of black carbon (BC) (Cyrys et al. 2003), and has been found to correlate strongly with PNC in some previous studies (Zhu et al. 2002, Ketzel et al. 2003, Noble et al. 2003). In this study, PM optical absorbance was strongly correlated with PNC at Marylebone Rd. (R = 0.87) but not at the other sites (R <0.5). Marylebone Rd. has substantial heavy goods vehicle and bus traffic, considerably more even than Glasgow Hope St. The optical 'blackness' depends not only on the BC content but also on the size of the particles (decreasing for smaller sizes) and the degree of dilution of optically absorbing particles with non-absorbing/transparent particles: the absorption of BC increases considerably when it is included in a large transparent particle, due to the lower density (Horvath, 1986). Particle size distributions shift to larger sizes and become compositionally mixed as they disperse (Ketzel et al., 2003; Gidhagen et al., 2005), changing their optical properties. Therefore, it is not surprising that at background sites the optical properties of the mix of particles collected over a day is not correlated with average PNC. The lack of correlation at Hope St., where BC concentrations may be expected to be high remains unclear.

6.4 Limitations

This study clearly had some major limitations. The relationships are derived from a relatively small data set and may not represent the annual trend. Only one pair of sites was studied in each city. Measurements at paired sites in a given urban area over longer periods are needed to confirm the relationships found in this study. However, the different slopes and intercepts between NO_x, NO_2 and PNC suggest that for each location a different relationship has to be derived. Despite this limitation NO_x and NO_2 are a simple and non expensive method to represent PNC.

7 Conclusions

One of the mayor challenges in epidemiological studies of air pollution and health is the lack of data on spatial variability on PNC. This study has shown the potential for using NO_2 and NO_x increments between background and street sites to represent daily variations in PNC and water-soluble metals: increments in NO_x explained 78-79% of the variance in PNC at the paired sites in both Glasgow and London. The increments in NO_x also explained in 70 % of the spatial variation in Cu and Ni at Glasgow but not at London. Weekly NO_2 measurements derived from passive diffusion tubes were also shown to correlate well with increments in weekly PNC

The corollary of the high correlation between NO_2 and PNC and water-soluble metals at the background sites is that the latter pollutants may act as cofounders for health effects attributed to NO_2 data from such sites. Concentrations of CO cannot be used as a surrogate for PNC.

Further validation on the geographical extension of these relationships is necessary. This could be achieved for example by examining the spatio-temporal relationships of aggregated data on the increments of a reference site and different additional sites (with different influence of traffic sources). A high correlation would mean that air pollution maps derived from NO_2 could be used to represent spatial and temporal variations in PNC and water-soluble metals. There is a need of regulating PNC. The relationships derived from these validated studies could be use to estimate the PNC which correspond to the EU limit value for NO_2 as a guide to establish a threshold value for PNC.

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Table captions

Table 1: Sampling equipment used at each monitoring site and data source.

Table 2: Limits of detection (ng m^{-3}) for metal concentrations derived from 24 h Partisol samples of PM10 on PTFE filters and of $PM_{2.5}$ on quartz filters.

Table 3: Descriptive statistics of traffic-related air pollutants at Glasgow (Hope St: Kerbside/street canyon, St:Enoch Sq., urban centre and Montrose St: background/street canyon) and London (Marylebone Rd: street canyon, North Kensington: urban background).

Table 4: Spearman correlation coefficients (p-values and sample sizes) between concentrations of the same pollutant measured at paired sites.

Table 4: Spearman correlation coefficients (*p*-values and sample sizes) of water-soluble metal concentrations in PM_{10} between Hope St. and St. Enoch Sq. in Glasgow and in $PM_{2.5}$ between Marylebone Rd. and North Kensington in London.

Table 6: Spearman correlation coefficients (and sample sizes) between daily-averaged air pollutant measurements at Hope St. (upper table) and St. Enoch Sq. (lower table).

Table 7: Spearman correlation coefficients (and sample sizes) between daily-averaged air pollutant measurements at Montrose St. (urban background).

Table 8: Spearman correlation coefficients (and sample sizes) between daily-averaged traffic-related air pollutants at Marylebone Rd. (upper table) and North Kensington (lower table).

Table 9: Slope, intercept and R^2 values for Reduced Major Axis regressions of the increments in particle number concentrations (PNC) vs. increments in other pollutant measures for the paired sites Hope St vs. St. Enoch Sq. in Glasgow and Marylebone Rd vs. North Kensington in London. Particle optical absorbance (absPM) is for PM_{10} in Glasgow and $PM_{2.5}$ in London.

Table 10: Slope, intercept and R^2 values for Reduced Major Axis regressions of the increments in Cu and Ni vs. the increments in particle number concentrations (PNC) and nitrogen oxides at Hope St. vs. St. Enoch Sq. in Glasgow.

Table 1 Sampling equipment used at each monitoring site and data source.

Pollutant	Equipment	Monitoring sites				
		Glasgow			London	
		Hope St.	St. Enoch Sq.	Montrose St.	Marylebone Rd.	North Kensington
PM_{10}	PARTISOL	√	√		NAQA	NAQA
$PM_{2.5}$	PARTISOL				NAQA	NAQA
BS	BS monitor				NAQA	
PNC	water based-CPC	√	√	√		
	butanol based-CPC		NAQA		NAQA	NAQA
Absorbance PM	measured on PM_{10} PARTISOL filters	√	√		√	√
Metals	extracted from PM_{10} PARTISOL filters	√	√		√	√
NO_2	PDTs	√	√			
	Chemilumiscence Analyser	NAQA	NAQA	NAQA	NAQA	NAQA
CO	Infra Red Analyser	NAQA	NAQA	NAQA	NAQA	NAQA
Benzene & 1,3-butadiene	Ultra Violet Analyser	NAQA			NAQA	

√: measured as part of this project; NAQA: provided by the National Air Quality Archive ;BS:Black Smoke; PNC: particle number concentration;CPC: condensation particle counter; PDTs: passive diffusion tubes.

Table 2 Limits of detection (ng m^{-3}) for metal concentrations derived from 24 h Partisol samples of PM_{10} on PTFE filters and of $PM_{2.5}$ on quartz filters.

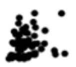
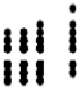
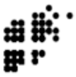
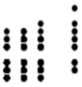
Metal	V	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb
Quartz filters (London sites) n=6	0.017	1.52	0.106	3.02	0.123	0.630	0.006	0.005	0.053
PTFE filters (Glasgow sites) n=2	0.013	0.113	0.128	2.67	0.325	0.538	0.004	0.013	0.232

Table 3 Descriptive statistics of traffic-related air pollutants at Glasgow (Hope St: kerbside/street canyon, St:Enoch Sq., urban centre and Montrose St: background/street canyon) and London (Marylebone Rd: street canyon, North Kensington: urban background).

	Hope St.			St. Enoch Sq.			Montrose St.			Marylebone Rd.			North Kensington		
	n	Median	IQR	n	Median	IQR	n	Median	IQR	n	Median	IQR	n	Median	IQR
PNC (particles cm^{-3})	35	23,564	10,475	79	12,851	3,128	63	11,095	2,940	26	109,953	35,393	26	23,407	9,784
PM_{10} PARTISOL (µg m^{-3})	31	32.9	12.0	24	21.6	12.5	-	-	-	26	45.0	9.00	26	25.5	10.8
$PM_{2.5}$ PARTISOL (µg m^{-3})	-	-	-	- -	-	-	-	-	-	26	30.0	7.00	26	15.5	7.00
BS (µg m^{-3})	-	-	-	- -	-	-	-	-	-	26	57.0	28.2	-	-	-
AbsPM*(10^{-5} m^{-1})	31	2.65	2.39	24	1.47	1.05	-	-	-	26	12.0	2.00	26	6.96	0.61
NO_x (µg m^{-3})	63	157	132	81	35.7	15.2	83	66.0	27.4	26	389	157	26	34.3	15.2
NO_2 (µg m^{-3})	63	50.1	31.9	81	22.4	9.65	83	39.2	13.4	26	133	37.4	23	28.8	13.7
NO (µg m^{-3})	63	71.0	60.7	81	8.04	4.91	83	17.3	9.72	26	167	79.8	26	3.51	3.11
CO (mg m^{-3})	75	0.296	0.133	54	0.191	0.061	83	0.248	0.124	26	0.974	0.34	26	0.240	0.083
1,3- Butadiene (µg m^{-3})	31	0.077	0.082	-	-	-	-	-	-	19	0.463	0.157	-	-	-
Benzene (µg m^{-3})	33	0.563	0.313	-	-	-	-	-	-	21	2.35	1.32	-	-	-
V (ng m^{-3})	17	0.202	0.354	17	0.183	0.565	-	-	-	26	1.20	2.00	26	1.49	2.06
Cr (ng m^{-3})	17	0.190	0.187	17	0.141	0.328	-	-	-	-	-	-	-	-	-
Mn (ng m^{-3})	17	0.428	1.23	17	1.57	1.46	-	-	-	26	0.723	0.802	26	0.352	0.488
Fe (ng m^{-3})	17	24.4	15.9	17	26.0	16.5	-	-	-	26	6.91	11.1	26	5.04	5.91
Ni (ng m^{-3})	17	0.392	0.675	17	0.473	0.593	-	-	-	26	0.429	0.473	26	0.803	0.97
Cu (ng m^{-3})	17	9.54	4.85	17	3.06	3.401	-	-	-	26	2.60	1.81	26	1.56	1.32
Zn (ng m^{-3})	-	-	-	-	-	8.468	-	-	-	26	11.2	7.66	26	7.73	11.3
As (ng m^{-3})	17	0.070	0.094	17	0.040	0.135	-	-	-	26	0.440	0.300	26	0.524	0.519
Cd (ng m^{-3})	17	0.057	0.033	17	0.054	0.036	-	-	-	26	0.058	0.042	26	0.061	0.078
Pb (ng m^{-3})	17	1.32	0.894	17	0.714	1.51	-	-	-	26	1.96	2.22	26	2.44	3.45
Wind speed	84	5.54	3.43	84	11.7	4.69	84	5.54	3.43	25	11.7	3.25	25	11.7	4.69

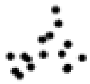
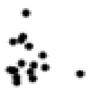
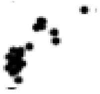
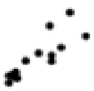
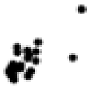
PNC: particle number concentration; BS: black smoke; Wind speed data in Glasgow sites was measured at Bishopton (circa 18Km from the sites) and in London at Heathrow Airport (circa 16 km from North Kensington and 20 Km from Marylebone Rd.

Table 4 Spearman correlation coefficients (*p*-values and sample sizes) between concentrations of the same pollutant measured at paired sites.

		Hope St. vs St. Enoch Sq.	Marylebone Rd. vs. North Kensington	Hope St. vs Montrose St.	Montrose St. vs St.Enoch Sq.
PNC	Hourly	__0.47**__ 0.000 717 	__0.58**__ 0.000 609 	__0.56**__ 0.000 828 	__0.57**__ 0.000 1349 
	Daily	__0.43*__ 0.017 30 	__0.46*__ 0.018 26 	__0.55**__ 0.002 35 	__0.41**__ 0.002 57 
PM$_{10}$ TEOM	Hourly	__0.67**__ 0.000 1386 	__0.50**__ 0.000 608 	NA	NA
	Daily	__0.73**__ 0.000 56 	0.23 0.267 25 	NA	NA
PM$_{10}$ PARTISOL	Daily	0.34 0.158 17 	0.34 0.094 25 	NA	NA
PM$_{2.5}$ PARTISOL	Daily	NA	0.35 0.080 26 	NA	NA
AbsPM*	Daily	0.43 0.082 17 	-0.03 0.900 26 	NA	NA
NO$_x$	Hourly	__0.52**__ 0.000 1552 	__0.43**__ 0.000 611 	__0.63**__ 0.000 1551 	__0.78**__ 0.000 1967 
	Daily	__0.33**__ 0.000 62 	0.06 0.766 26 	__0.55**__ 0.001 63 	__0.72**__ 0.000 81 
NO$_2$	Hourly	__0.50**__ 0.000 1552 	__0.37**__ 0.000 611 	__0.62**__ 0.000 1551	__0.80**__ 0.000 1967 
	Daily	__0.49**__ 0.000 62 	0.05 0.819 26 	__0.61**__ 0.000 63 	__0.80**__ 0.000 81 
NO	Hourly	__0.47**__ 0.000 1552 	__0.45**__ 0.000 611 	__0.61**__ 0.000 1551 	__0.74**__ 0.000 1967 
	Daily	__0.33**__ 0.009 62 	0.036 0.860 26 	__0.47**__ 0.000 63 	__0.61**__ 0.000 81 
CO	Hourly	__0.26**__ 0.000 1168 	__0.33**__ 0.000 605 	__0.58**__ 0.000 1817 	__0.27**__ 0.000 1326 
	Daily	0.17 0.257 47 	0.06 0.766 26 	__0.64**__ 0.000 75 	0.17 0.227 54 

PNC: particle number concentration; * AbsPM$_{10}$ at Glasgow sites and AbsPM2.5 at London sites; NA: not available;
**Correlation is significant at the 0.01 level.

Table 5 Spearman correlation coefficients (*p*-values and sample sizes) of water-soluble metal concentrations in PM_{10} between Hope St. and St. Enoch Sq. in Glasgow and in $PM_{2.5}$ between Marylebone Rd. and North Kensington in London.

		Hope St. vs St. Enoch Sq.		Marylebone Rd. vs. North Kensington	
V	Correlation Coefficient	**0.89****		**0.94****	
	Sig. (2-tailed)	0.000		0.000	
	N	17		26	
Cr	Correlation Coefficient	0.126			
	Sig. (2-tailed)	0.629		NA	
	N	17			
Mn	Correlation Coefficient	**0.53***		**0.79****	
	Sig. (2-tailed)	0.035		0.000	
	N	17		26	
Fe	Correlation Coefficient	0.25		**0.49***	
	Sig. (2-tailed)	0.350		0.010	
	N	17		26	
Ni	Correlation Coefficient	-0.01		**0.77****	
	Sig. (2-tailed)	0.955		0.000	
	N	17		26	
Zn	Correlation Coefficient			**0.67****	
	Sig. (2-tailed)	NA		0.000	
	N			26	
Cu	Correlation Coefficient	0.42		**0.45****	
	Sig. (2-tailed)	0.092		0.010	
	N	17		26	
As	Correlation Coefficient	**0.85****		**0.85****	
	Sig. (2-tailed)	0.000		0.000	
	N	17		26	
Cd	Correlation Coefficient	0.17		**0.57****	
	Sig. (2-tailed)	0.552		0.002	
	N	17		26	
Pb	Correlation Coefficient	0.36		**0.63****	
	Sig. (2-tailed)	0.172		0.001	
	N	17		26	

** Correlation is significant at 0.01 level (2 tailed);* Correlation is significant at 0.05

Table 6 Spearman correlation coefficients (and sample sizes) between daily-averaged air pollutant measurements at Hope St. (upper table) and St. Enoch Sq. (lower table).

Hope St. (Kerbside)	V	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb	PNC	PM_{10}P	Abs PM_{10}	NO_x	NO_2	CO
PNC	**0.76****	**0.71****	**0.93****	0.661	**0.92****	**0.94****	0.54	0.22	0.35	1					
	11	11	10	10	11	11	10	10	11	35					
PM_{10}P	0.29	0.21	0.46	0.07	**0.58***	**0.70****	0.33	0.08	0.02	**0.74****	1				
	17	17	16	16	17	17	16	16	17	25	25				
Abs PM_{10}	0.06	0.13	0.23	-0.09	0.20	0.29	0.47	**0.50***	0.13	0.35	0.28	1			
	17	17	16	16	17	17	16	16	17	25	25	25			
NO_x	-0.17	0.05	-0.27	**-0.70***	0.32	0.55	-0.32	-0.29	-0.57	**0.87****	**0.85****	**0.53***	1		
	9	9	9	9	9	9	9	8	9	19	17	17	63		
NO_2	0.12	0.29	-0.23	**-0.59***	**0.75***	0.48	-0.09	0.07	-0.29	**0.85****	**0.83****	**0.45***	**0.90****	1	
	9	9	9	9	9	9	9	8	9	19	17	17	63	63	
CO	0.20	0.22	0.25	-0.26	**0.55***	**0.66***	0.20	0.22	0.04	**0.64****	**0.76****	**0.43***	**0.78****	**0.60****	1
	14	14	13	13	14	14	14	13	14	25	22	22	63	63	75
1,3-Butadiene	0.20	0.00	0.29	-0.39	0.41	**0.58***	0.31	0.38	-0.09	**0.71****	**0.71****	**0.54****	**0.95****	**0.91****	**0.89****
	15	15	14	14	15	15	15	14	15	33	23	23	19	19	25
Benzene	0.15	0.05	0.25	-0.23	0.41	**0.52***	0.06	0.02	-0.04	**0.55****	**0.76****	0.32	**0.93****	**0.88****	**0.93****
	15	15	14	14	15	15	15	14	15	33	23	23	19	19	25
Wind speed	**-0.55***	-0.45	**-0.81****	-0.49	-0.48	**-0.84****	**-0.68****	0.09	-0.28	**-0.52****	-0.40	**-0.62****	**-0.47***	**-0.51***	**-0.51***
	16	16	16	16	15	16	15	14	16	34	24	24	19	19	24

St. Enoch Sq. (Urban background)	V	Cr	Mn	Fe	Ni	Cu	As	Cd	Pb	PNC	PM_{10}P	Abs PM_{10}	NO_x	NO_2	CO
PNC	0.52	**0.62***	**0.81****	**0.73****	**0.57***	**0.83****	**0.81****	**0.70****	**0.72****	1					
	17	17	17	17	17	17	17	17	17	17					
PM_{10}P	0.13	0.44	**0.77****	**0.56***	**0.55***	**0.60***	**0.52***	**0.53***	**0.53***	0.29	1				
	17	17	17	17	17	17	17	17	17	23	24				
AbsPM_{10}	**0.69****	0.41	**0.49***	**0.61****	0.23	**0.69****	**0.76****	**0.55***	**0.52***	**0.47***	0.23	1			
	17	17	17	17	17	17	17	17	17	23	24				
NO_x	0.52	**0.71****	**0.66***	**0.75****	0.42	**0.74****	**0.76****	**0.59***	**0.72****	**0.65****	**0.64****	0.415	1		
	15	15	15	15	15	15	15	15	15	75	20	20			
NO_2	0.51	**0.67***	**0.62***	**0.71****	0.39	**0.74****	**0.76****	0.53	**0.65***	**0.52****	**0.69****	**0.49***	**0.91****	1	
	15	15	15	15	15	15	15	15	15	75	20	20	81		
CO	0.31	0.12	0.19	0.00	-0.10	0.05	0.12	-0.31	-0.24	**0.34***	0.26	-0.28	**0.49****	**0.40****	1
	10	10	10	10	10	10	10	10	10	49	11	11	54	54	54
Wind	**-0.57***	**-0.63****	-0.49	**-0.51***	-0.38	**-0.61***	**-0.64***	-0.43	**-0.59***	**-0.30****	**-0.51***	-0.35	**-0.47****	**-0.57****	**-0.38****
	17	17	17	17	17	17	17	17	17	78	23	23	80	80	53

Significant correlations are in bold; **Correlation is significant at the 0.01 level (2-tailed), *Correlation is significant at the 0.05 level (2-tailed).
PNC: particle number concentration; PM10 P: PM_{10} concentrations measured with a Partisol sampler

Table 7 Spearman correlation coefficients (and sample sizes) between daily-averaged air pollutant measurements at Montrose St. (urban background).

	PNC	NO_x	NO_2	CO
NO_x	**0.62****	1		
	61	83		
NO_2	**0.66****	**0.93****	1	
	61	83	83	
CO	**0.67****	**0.65****	**0.74****	1
	61	83	83	83
Wind speed	**-0.45****	**-0.30****	**-0.42****	**-0.44****
	62	82	82	82

**Correlation is significant at the 0.01 level (2-tailed);
PNC: particle number concentration.

Table 8 Spearman correlation coefficients (and sample sizes) between daily-averaged traffic-related air pollutants at Marylebone Rd. (upper table) and North Kensington (lower table).

Marylebone Rd. (Kerbside)	V	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb	PNC	PM_{10} P	$PM_{2.5}$ P	BS	Abs $PM_{2.5}$	NO_x	NO_2	CO	1,3-butadiene	Benzene	Wind speed
PNC	-0.12	-0.24	-0.21	-0.24	**-0.60****	-0.26	-0.26	-0.36	-0.08	1.00										
	26	26	26	26	26	26	26	26	26	26										
PM_{10} P	**0.48***	0.31	0.12	**0.44***	-0.18	0.25	0.02	-0.03	0.10	**0.40***	1.00									
	25	25	25	25	25	25	25	25	25	25	25									
$PM_{2.5}$ P	0.38	**0.54****	**0.48***	0.34	0.03	0.36	0.24	0.19	0.19	**0.47***	**0.71****	1.00								
	26	26	26	26	26	26	26	26	26	26	25	26								
BS	-0.03	-0.26	-0.28	-0.19	**-0.49***	-0.25	-0.14	-0.33	-0.14	**0.71****	0.35	0.28	1.00							
	26	26	26	26	26	26	26	26	26	26	25	26	26							
Abs $PM_{2.5}$	0.07	-0.13	-0.23	-0.06	**-0.54****	-0.14	-0.27	**-0.39***	-0.07	**0.87****	**0.60****	**0.47***	**0.75****	1.00						
	26	26	26	26	26	26	26	26	26	26	25	26	26	26						
NO_x	-0.08	-0.28	-0.35	-0.21	**-0.67****	-0.20	-0.27	**-0.39***	-0.03	**0.90****	**0.57****	**0.40***	**0.73****	**0.93****	1.00					
	26	26	26	26	26	26	26	26	26	26	25	26	26	26	26					
NO_2	0.03	-0.22	-0.29	-0.10	**-0.63****	-0.17	-0.29	-0.34	-0.07	**0.87****	**0.67****	**0.49***	**0.68****	**0.92****	**0.97****	1.00				
	26	26	26	26	26	26	26	26	26	26	25	26	26	26	26	26				
CO	**0.44***	0.20	0.14	**0.39***	-0.18	0.11	0.29	0.25	-0.07	0.27	**0.49***	**0.56****	0.24	0.23	0.26	0.30	1.00			
	26	26	26	26	26	26	26	26	26	26	25	26	26	26	26	26	26			
1,3-butadiene	-0.02	-0.27	-0.27	-0.17	-0.61	-0.21	-0.24	-0.29	0.05	**0.81****	**0.67****	**0.45****	**0.69****	**0.74****	**0.87****	**0.83****	**0.50****	1.00		
	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19		
Benzene	-0.04	-0.19	-0.13	-0.19	-0.55	-0.18	-0.25	-0.31	0.16	**0.78****	**0.62****	**0.47****	**0.74****	**0.72****	**0.83****	**0.77****	0.45	**0.98****	1.00	
	21	21	21	21	21	21	21	21	21	21	20	21	21	21	21	21	21	19	21	
Wind speed	-0.26	**-0.53****	**-0.46***	-0.27	**-0.57****	**-0.52****	**-0.86****	**-0.48***	**-0.40***	**0.40***	-0.02	-0.20	0.12	0.32	0.36	**0.41***	-0.26	0.18	0.17	1.00
	25	25	25	25	25	25	25	25	25	25	24	25	25	25	25	25	25	18	20	25

North Kensington (Urban background)	V	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb	PNC	PM_{10} P	$PM_{2.5}$ P	Abs $PM_{2.5}$	NO_x	NO_2	NO	CO	Wind speed
PNC	-0.32	-0.25	-0.12	**-0.53****	0.24	0.19	0.25	0.20	0.32	1.00								
	26	26	26	26	26	26	26	26	26	26								
PM_{10} P	**0.44***	**0.58****	**0.59****	**0.54****	0.21	**0.47***	**0.55****	**0.63****	**0.49***	0.03	1.00							
	26	26	26	26	26	26	26	26	26	26	26							
$PM_{2.5}$ P	**0.48***	**0.72****	**0.77****	**0.63****	0.34	**0.64****	**0.69****	**0.81****	**0.64****	-0.12	**0.82****	1.00						
	26	26	26	26	26	26	26	26	26	26	26	26						
Abs $PM_{2.5}$	0.31	**0.60****	**0.74****	0.25	**0.58****	**0.71****	**0.64****	**0.64****	**0.74****	0.34	**0.55****	**0.65****	1.00					
	26	26	26	26	26	26	26	26	26	26	26	26	26					
NO_x	0.04	0.35	**0.56****	-0.04	**0.64****	**0.68****	**0.61****	**0.57****	**0.71****	**0.60****	0.38	**0.44***	**0.89****	1.00				
	26	26	26	26	26	26	26	26	26	26	26	26	26	26				
NO_2	0.06	0.34	**0.54****	-0.04	**0.62****	**0.69****	**0.63****	**0.56****	**0.74****	**0.59****	0.37	**0.42***	**0.89****	**0.98****	1.00			
	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26			
CO	-0.20	0.08	0.08	-0.36	**0.46***	0.34	**0.45***	**0.47***	**0.54****	**0.70****	0.09	0.16	**0.48***	**0.59****	**0.61****	**0.54****	1.00	
	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	26	
Wind	-0.17	**-0.64****	**-0.75****	-0.35	**-0.63****	**-0.75****	**-0.66****	**-0.69****	**-0.64****	0.06	**-0.52****	**-0.69****	**-0.70****	**-0.62****	**-0.65****	**-0.55****	-0.23	1.00
	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25

Significant correlations are in bold; * Correlation is significant at the 0.05 level (2-tailed);** Correlation is significant at the 0.01 level (2-tailed). Wind data was measured at Heathrow Airport (circa 20 Km from the monitoring site). Data were provided by the British Atmospheric Data Centre (BADC).

Table 9 Slope, intercept and R^2 values for Reduced Major Axis regressions of the increments in particle number concentrations (PNC) vs. increments in other pollutant measures for the paired sites Hope St vs. St. Enoch Sq. in Glasgow and Marylebone Rd vs. North Kensington in London. Particle optical absorbance (absPM) is for PM_{10} in Glasgow and $PM_{2.5}$ in London.

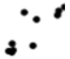
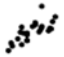
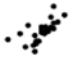
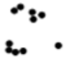
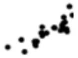
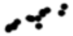
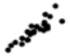
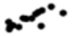
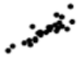
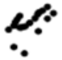
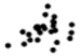
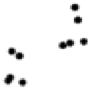
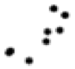
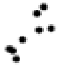
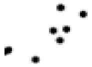
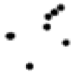
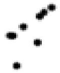
	Hope St. - St. Enoch Sq.					Marylebone Rd. - North Kensignton				
Relationship	N	intercept	slope	R^2		N	intercept	slope	R^2	
ΔPNC vs. ΔPM_{10}	10	-15,408	1,273	0.70		25	26,073	3,078	0.55	
ΔPNC vs. $\Delta PM_{2.5}$	NA	NA	NA			26	37,570	3,520	0.43	
ΔPNC vs. ΔAbsPM*	10	-10,980	8,657	0.03		26	-22,769	21,533	0.71	
ΔPNC vs. ΔNO_x	14	7,408	42.3	0.79		26	732	233	0.78	
ΔPNC vs. ΔNO_2	14	6,880	155	0.59		26	-12,534	933	0.74	
ΔPNC vs. ΔCO	19	1,881	75,842	0.30		26	652	119,440	0.08	

Table 10 Slope, intercept and R^2 values for Reduced Major Axis regressions of the increments in Cu and Ni vs. the increments in particle number concentrations (PNC) and nitrogen oxides at Hope St. vs. St. Enoch Sq. in Glasgow.

Relationship	N	intercept	slope	R^2	
ΔCu vs. ΔPNC	11	3.63	4.0E-04	**0.66**	
ΔCu vs. ΔNO_x	8	0.499	0.037	**0.65**	
ΔCu vs. ΔNO_2	8	0.739	0.151	**0.67**	
ΔCu vs. ΔNO	8	0.696	0.072	**0.59**	
ΔNi vs. ΔPNC	9	0.018	5.3E-05	**0.76**	
ΔNi vs. ΔNO_x	8	-2.33	0.014	0.19	
ΔNi vs. ΔNO_2	8	-2.24	0.055	0.47	

$R^2 > 0.5$ are in bold