Variation and co-variation of PM$_{10}$, particle number concentration, NO$_X$ and NO$_2$ in the urban air – Relationships with wind speed, vertical temperature gradient and weather type

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HIGHLIGHTS

- NO$_X$ was a good proxy of particle number concentration (PNC) in calm conditions.
- PM$_{10}$ was a weak proxy for PNC.
- Air pollution was strongly related to Lamb Weather Types (LWT).
- The PNC-NO$_X$ relationship prevailed on an hourly, daily and LWT basis.
- A seasonal variation existed for the PNC-NO$_X$ relationship, being weakest in summer.

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ABSTRACT

Atmospheric ultrafine particles (UFP; diameter < 0.1 μm) represent a growing global health concern in urban environments and has a strong link to traffic related emissions. UFP is usually the dominating fraction of atmospheric particle number concentrations (PNC) despite being a minor part of total particle mass. The aim of this study was to empirically investigate the relationship between PNC and other air pollutants (NO$_X$, NO$_2$ and PM$_{10}$) in the urban environment and their dependence on meteorology and weather type, using the Lamb Weather Type (LWT) classification scheme. The study was carried out in Gothenburg, Sweden, at an urban background site during April 2007–May 2008. It was found that daily average [PNC] correlated very well with [NO$_X$] ($R^2 = 0.73$) during inversion days, to a lesser extent with [NO$_2$] ($R^2 = 0.58$) and poorly with [PM$_{10}$] ($R^2 = 0.07$). Both PNC and NO$_X$ had similar response patterns to wind speed and to the strength of temperature inversions. PNC displayed two regimes, one strongly correlated to NO$_X$ and a second poorly correlated to NO$_X$ which was characterised by high wind speed. For concentration averages based on LWTs, the PNC-[NO$_X$] relationship remained strong ($R^2 = 0.70$) where the windy LWT W deviated noticeably. Exclusion of observations with wind speed >5 ms$^{-1}$ or $\Delta T < 0$ °C from LWTs produced more uniform and stronger relationships ($R^2 = 0.90$; $R^2 = 0.93$). Low wind speeds and positive vertical temperature gradients were most common during LWTs A, NW, N and NE. These weather types were also associated with the highest daily means of NO$_X$ (~30 ppb) and PNC (~10 000 # cm$^{-3}$). A conclusion from this study is that NO$_X$ (but not PM$_{10}$) is a good proxy for PNC especially during calm and stable conditions and that LWTs A, NW, N and NE are high risk weather types for elevated NO$_X$ and PNC.

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1. Introduction

Urban air contains a mix of pollutants from various sources, where two important constituents are particulate matter (PM) and nitrogen oxides (NO$_X$ = NO + NO$_2$). In the case of nitrogen oxides,
nitrogen dioxide (NO₂) is more often regulated, but sometimes air quality standards (AQs) are based on NOₓ. Nitrogen dioxide is known to cause adverse effects both on human health (WHO, 2006; Samoli et al., 2006; Chiusolo et al., 2011) and vegetation, e.g. epiphytic lichens (Hultgren et al., 2004; Gadsdon et al., 2010). In many European urban environments traffic is a dominant source for NOₓ and NO₂ exposure (Hak et al., 2010).

PM pollution is more complex, covering a large size range. It consists of a multi-component matrix originating from various sources and is subjected to several parallel atmospheric processes resulting in a dynamic quantity (Heal et al., 2012). In many urban areas, particle number concentration (PNC) is normally dominated by the ultrafine particles (UFP; diameter < 0.1 μm) fraction (Molinar et al., 2002; Charron and Harrison, 2003; Kitzleson et al., 2004; Kumar et al., 2011). In Gothenburg, 90% of the PNC was attributed to the UFP size fraction (Janzell and Hällquist, 2005). Generally, PNC or UFP in urban environments is dominated by particles from traffic exhaust emissions, especially diesel engines (HEL, 2013), while PM₁₀ often has large contributions from many other sources such as non-exhaust direct emissions from clutches, brakes and re-suspension of road dust from road gritting, road and tyre wear (Harrison et al., 2001; Ketzel et al. 2007; Johansson et al. 2007). The health effects of particles are well recognized but the recognition of how they link to size, composition and physical properties are unclear (Cassee et al., 2013). It has been suggested that UFPs formed by combustion in vehicle engines, may cause enhanced health effects. WHO recently upgraded diesel exhausts from ‘probably carcinogenic’ to ‘carcinogenic to humans’ (IARC, 2012), where UFPs make up an important component of the pollution mixture and act as carriers of adsorbed carcinogenic substances (IARC, 2013). UFPs are known to cause oxidative stress in the lung (Li et al., 2008) and have been suggested to pose a higher risk for cardiovascular disease due to their specific properties such as high surface area, large particle number, metal and organic carbon content (Delfino et al., 2005). Also an increased number concentration of UFPs has been associated with increased cardiovascular mortality (Stolzel et al., 2007). Furthermore, Seaton and Dennekamp (2003) proposed UFP exposure, proxied by NO₂, to be the cause of cardiovascular effects, even at low NO₂ concentrations.

To the extent that PNC (UFP) and NOₓ emanate from the same combustion processes (in vehicle engines), one could expect that atmospheric concentrations of PNC (UFP) and NOₓ are strongly related. In fact, it has been suggested to use NOₓ, NO or NO₂ as ‘proxies’ for particle pollution levels (Ketzel et al., 2003; Seaton and Dennekamp, 2003; Sardar et al., 2012; Bevvers et al., 2012). This assumption of a close relationship between PM and NOₓ or NO₂ needs more empirical evidence from different environments, and can be questioned in the case of any mass based measure, such as PM₁₀, while number based measures such as UFP can be expected to be more closely related to NOₓ or NO₂. Even if NO₂ rather than NOₓ is a more frequently and easily measured compound (e.g. using passive diffusion samplers) using it as the proxy for PM adds further uncertainty to any association with PM, including UFP. NO and NO₂ concentration is highly sensitive to the NO–NO₂–O₃ relationship (Leighton, 1961). The oxidation of NO with O₃, and the photolysis of NO₂, can strongly affect the urban NO₂ concentration, which thus varies with respect to variables that do not necessarily affect PM concentration. In addition, the fraction of NO₂ in the exhaust NOₐ emissions varies with the composition of the vehicle fleet (Carslaw et al., 2011). Diesel engines have a higher fraction of NO₂ and of certain types of particle, differentiated by large diesel vehicles emit higher fractions of NO₂ (Alvarez et al., 2008). Thus, there are several reasons to believe that NOₓ, rather than NO and NO₂, is a more reliable proxy for PM emanating from combustion in vehicle engines.

It is well established that weather conditions, such as wind speed and temperature inversion, strongly affect the degree of accumulation of air pollutants near emission sources such as traffic in urban environments (Rodriguez et al., 2007; Jones et al., 2010; Gründström et al., 2011; Pearce et al., 2011). For PM pollution the relationship is not as evident. The coarse particle fraction included in PM₁₀ can be enhanced during higher wind speed and atmospheric turbulence by facilitating re-suspension and reducing sedimentation (Harrison et al., 2001; Gradon, 2009).

Lamb Weather Types (LWTs) represent an effective method of characterising local meteorological conditions based on synoptic scale sea level pressure (Chen, 2000). The distribution of the sea level pressure provides information about the geostrophic wind and vorticity, which has been proven to be a useful summary of the local meteorological conditions (e.g. Tang et al., 2009).

The principal aim of this study was to investigate the relationships between PNC, NOₓ, NO₂ and PM₁₀ in the urban environment and how the relationships are affected by specific meteorological variables and the general weather conditions represented by LWT. A number of hypotheses were postulated:

- The first hypothesis was that NOₓ is a better proxy for PNC compared to NO₂ and especially PM₁₀, which can be motivated by the facts that 1) NOₓ is less sensitive to the NO–NO₂–O₃ relationship which obviously is important for NO and NO₂; 2) NOₓ and UFP represented by PNC are both mainly emitted from combustion, in contrast to PM₁₀ which mostly dominated by coarse particles emanating from a number of different sources.
- The second hypothesis was that NOₓ and PNC respond similarly to the variation of important meteorological variables such as wind speed and atmospheric stability. Both pollutants are expected to have high concentration during low wind speeds and strong atmospheric stability.
- The third hypothesis was that the response of the air pollutant concentrations to changing meteorological variables can be associated to LWTs where LWTs with a large fraction of low wind speeds and strong atmospheric stability would more often result in high levels of NOₓ and PNC.

2. Material and methods

2.1. Data

Monitoring of air quality and meteorological data was performed on a rooftop 30 m above ground level in the commercial district of Gothenburg city centre (“Femmen”; 57°42.522’N, 11°58.236’E). The site is located adjacent to the central terminal for bus and trains and approximately 300 m away from a busy traffic route (E45). Hourly measurements of NO and NO₂ (Tecan CLD 700 AL chemiluminescence instrument), PM₁₀ (TEOM - Tapered Element Oscillating Microbalance, Series 1400b), PNC (Condensation Particle Counter TSI 3775, size cut-off 4 μm), atmospheric pressure (Vaisala PA11A), air temperature and relative humidity (Campbell Rotronic MP101 thermometer/hygrometer), wind direction and wind speed (Gill ultrasonic anemometer) were carried out. The vertical air temperature gradient at two heights (3 m and 73 m above ground) was measured (RM Young platinum temperature probe model 41342) at a site located 8 km south of the city centre (“Järnbrott”; 57°38.8456’N, 11°55.6007’E). The difference in temperature between the two heights (Tₚmax – Tₚmin) represents a measure of the atmospheric stability and is signified by ΔT throughout this article. The measurement period for the study lasted from April 2007 to May 2008.
2.2. Lamb weather types

Daily mean sea level pressure (MSLP) for 16 grid points centred over the Gothenburg City centre (57°7’N, 11°97’E), were obtained from the NCEP/NCAR Reanalysis database 2.5 x 2.5° pressure fields (Kalnay et al., 1996). Circulation indices, u (westerly or zonal wind), v (southerly or meridional wind), \( \nu \) (meridional gradient of \( u \)), \( \xi \) (zonal gradient of \( v \)) and \( \xi \) (total shear vorticity) describing the geostrophic winds and Lamb weather types (Jenkinson and Collison, 1977) were calculated following Chen (2000). The classification scheme has 26 weather types: anticyclone (A), cyclone (C), eight directional types (NE, E, SE, ...), 16 hybrid types (ANE, AE, ASE, CNE, CE, CSE, ...). In this study, the 26 weather types were consolidated into 10 LWTs according to the directions of the geostrophic wind, eight directional: NE, E, SE, SW, W, NW, N, and two rotational: A and C.

2.3. Calculations

Air pollutant concentrations are expressed as mixing ratios (ppb) for NO2 and NOx, mass per volume (\( \mu g \) m\(^{-3} \)) for PM\(_{10}\) and number concentration (\( \# \) cm\(^{-3} \)) for PM\(_{10}\). Hourly and daily averages of PNC were correlated with NO\(_2\), NO\(_x\), and PM\(_{10}\) using regression analysis based on total least squares. Additionally, NO\(_2\), NO\(_x\), PM\(_{10}\) and PNC were averaged for intervals of wind speed (\( u \)) and \( DT \), using steps of 0.5 m s\(^{-1} \) and 0.5 °C, respectively. To assess the individual response of each pollutant to the meteorological variables the pollution concentration averages for each interval were correlated with \( u \) and \( DT \) using the least squares method. Days with a daily average of \( DT \) exceeding 0 °C, were defined as inversion days.

Further analysis was also made of the effect from \( u \) and \( DT \) on the proxy relationship found between PNC and NO\(_2\) (hourly values). For each LWT, averages of air pollutant concentrations were calculated and correlated with PNC. Additionally, time fractions of \( u \) below 1 ms\(^{-1} \) and \( DT \) above 0 °C were calculated for each LWT and correlated with each other using regression analysis. Finally, meteorological variables (atmospheric pressure, temperature, wind speed, relative humidity) were averaged for each LWT in order to characterise each weather type in terms of meteorology.

3. Results

3.1. Relationship of PNC with PM\(_{10}\), NO\(_2\) and NO\(_x\)

Hourly PNC had a weak (\( R^2 = 0.17 \)) positive relationship with PM\(_{10}\) with large scatter (Fig. 1a). On a daily basis the corresponding relationship was even weaker (\( R^2 = 0.08; \) Fig. 1b) and considering only inversion days (black marks), defined as daily \( DT \) averages > 0 °C, provided a relationship which was marginally weaker (\( R^2 = 0.11 \)). PNC showed a stronger relationship (\( R^2 = 0.50 \)) to [NO\(_2\)] on an hourly basis (Fig. 1c) and during inversion days [NO\(_2\)] explained 54% of the PNC variation (Fig. 1d). PNC showed the strongest positive relationship with [NO\(_x\)], explaining 55% of the PNC variation on an hourly basis (Fig. 1e), but providing an even stronger relationship (\( R^2 = 0.73 \)) for inversion days (Fig. 1f). Analysis was also conducted for PNC-NO\(_x\) which displayed similar but weaker relationship patterns in comparison with [NO\(_x\)] (not shown). For hourly averages the \( R^2 \) value for PNC-NO\(_x\) was 0.47 and for inversion days 0.67.

At low [NO\(_x\)] the PNC to [NO\(_x\)] variation was larger for both daily and hourly observations (Fig. 1e and f), indicating the importance of partly different sources for PNC and NO\(_x\), and of chemical/physical transformation processes. At high [NO\(_x\)] the relationship was more uniform and the highest [NO\(_x\)] and PNC occurred during temperature inversions signified by the black marks of Fig. 1f. There seems to exists a baseline relationship between [NO\(_x\)] and PNC representing a level of PNC it which principally never falls below (dotted line in Fig. 1f). This can be interpreted as the minimum daily level of PNC that will be present in the city for any given NO\(_x\) situation.

3.2. Dependence of NO\(_2\), NO\(_x\), PNC and PM\(_{10}\) on wind speed and atmospheric stability

Wind speed (\( u \)) had a strong influence on the concentrations of the analysed air pollutants. Both [NO\(_2\)] and [NO\(_x\)] decreased monotonically with increasing \( u \) calculated on an interval basis (Fig. 2a and b). These relationships were negative and strongly non-linear with much higher concentrations at \( u \) below 2 ms\(^{-1} \). Relatively low concentrations were observed for \( u \) higher than approximately 3 ms\(^{-1} \). A similar relationship was observed for PNC, where the highest concentrations were also observed for low \( u \) (Fig. 2c). At \( u > 3 \) ms\(^{-1} \), PNC reached a stable level only fluctuating slightly between 7000 and 7300 \( \# \) cm\(^{-3} \). [PM\(_{10}\)] showed a more complex relationship to \( u \) with initially decreasing concentrations at increasing \( u \) (Fig. 2d). However, concentrations increased again at \( u > 5 \) ms\(^{-1} \), which demonstrates the importance of the capacity of strong winds associated with large mechanical turbulence to carry and re-suspend coarser particles such as dust from roads and other surfaces.

Vertical mixing of the air is strongly linked to the temperature stratification near the ground. Fig. 3 shows air pollutants and their relationship to the temperature difference between 73 m and 3 m (\( DT \)). Strong linear relationships were observed for NO\(_x\) (\( R^2 = 0.96 \)), NO\(_2\) (\( R^2 = 0.96 \)) and PM\(_{10}\) (\( R^2 = 0.62 \)) (Fig. 3a, b, and d), while for [PNC] the relationship was more complex (Fig. 3c). Here, a negative relationship (\( R^2 = 0.95 \)) was observed for negative temperature differences (\( DT < 0 \) °C) and a positive relationship (\( R^2 = 0.98 \)) at positive temperature difference (\( DT > 0 \) °C). Observations with \( DT < -0.5 \) °C were characterised by high temperatures (average 11 °C and \( u \) often 78% of the time) in the range 2–6 ms\(^{-1} \) (average = 4.5 ms\(^{-1} \)). Situations with \( DT > 0.5 \) °C were characterised by lower temperatures (average 7 °C and \( u \) often 81% of the time) lower than 2 ms\(^{-1} \) (average 1.6 ms\(^{-1} \)).

High concentrations of all pollutants were observed when the temperature gradient was inverted (\( DT > 0 \) °C) and showed large variation when the temperature gradient was very strong (\( DT > 3 \) °C), indicating that extremely high levels of pollutants sometimes occur under strongly stable atmospheric conditions, during which the vertical dispersion is very limited.

Fig. 4 illustrates the hourly proxy relationships between [PNC] and [NO\(_x\)], [NO\(_2\)] and [PM\(_{10}\)], with consideration of the different degrees of dispersion expressed by \( DT \) or \( u \). The relationship between PNC-[NO\(_x\)] stood out and was most prominent at \( DT \geq 0.5 \) °C (\( R^2 = 0.85 \)) and low \( u \) (\( u \leq 2 \) ms\(^{-1} \); \( R^2 = 0.82 \)) (Fig. 4a and d). A second regime of high [PNC] (>20 000 \( \# \) cm\(^{-3} \)) during low [NO\(_x\)] (<70 ppb) was apparent at high \( u \) (\( u \geq 5 \) ms\(^{-1} \)), and the association between PNC and [NO\(_x\)] was weak (\( R^2 = 0.24 \)). These situations were also always associated with very unstable conditions occurring when \( DT \leq -0.5 \) °C, and a frequently occurring (60%) wind flow from the west. At stable and calm conditions (\( DT > 0.5 \) °C or \( u < 2 \) ms\(^{-1} \)) the PNC-[NO\(_x\)] relationship was also quite good (\( R^2 = 0.59 \) and \( R^2 = 0.62 \), Fig. 4b and e). PNC showed weak relationships to [PM\(_{10}\)], with the highest \( R^2 \) observed during stable (\( DT > 0.5 \) °C; \( R^2 = 0.27 \)) and calm conditions (\( u < 2 \) ms\(^{-1} \); \( R^2 = 0.29 \)).

3.3. LWT connection with meteorological and air quality parameters

LWTs were analysed with respect to different meteorological
variables prevailing on the surface/local scale in order to classify their meteorological character in greater detail (Table 1). The most common LWTs were A, SW, W, NW and C (combined representing ~75% of the time) and the least common were NE and SE (~5% combined). LWTs A, N and NW were generally calm and dry weather types, with high atmospheric pressure, low average $u$ and moderate to low temperatures and humidity. LWTs C, SW and W on the other hand were wet and turbulent with low atmospheric pressure, high average $u$ and mild temperatures. The fraction of low $u$ ($u < 2 \text{ m s}^{-1}$) was most common for LWTs A, NW, N and NE.

For each LWT, averages were calculated for [NOX], [NO2], PNC and [PM10] which can be seen in Table 2. The highest concentrations were normally found in LWTs A, NE and N with the exception of PM10 which showed high concentrations also in LWT W. Low concentration averages were generally found in LWTs SE, S, SW and W for NOx and NO2. PNC was low in S and C conditions while [PM10] was low in C, SE, SW and NW.

A correlation analysis was conducted for [NOx] and PNC averages based on LWT (Fig. 5). A strong ($R^2 = 0.70$) positive linear relationship (black line) was found (Fig. 5a). LWTs A, N and NE were associated with the highest levels for both pollutants. LWT W deviated from the fitted regression line and the relationship was tested with the exclusion of W (grey line) which resulted in a stronger linear relationship ($R^2 = 0.86$). The same analyses (not shown) was conducted for [NO2] and [PM10] and showed similar patterns but weaker relationships ($R^2 = 0.58$; $R^2 = 0.36$). Since windy and unstable situations resulted in a poorer association between PNC and [NOx], an analysis was conducted where such conditions were not included. In Fig. 5b, observations when $u > 5 \text{ m s}^{-1}$ were excluded from all LWTs and the PNC-[NOx]
relationship was improved \( R^2 = 0.90 \) and less scattered with LWT W better aligned. In Fig. 5c, observations with \( D_T < 0 \) were excluded and again the PNC-NOx relationship was improved \( R^2 = 0.93 \).

### 3.4. Seasonal and LWT variation of the PNC-NOx relationship

A seasonal influence on air pollution levels is expected due to the annual variation in e.g. temperature. Table 3 shows the relationship between NOx and PNC during four seasons. The strongest relationship \( R^2 = 0.74 \) was found during autumn (SON). The summer (JJA) months produced the poorest \( R^2 = 0.27 \) PNC-NOx relationship when the average temperature was high (16.6 °C). Evaporation of particles during warm temperatures (Bigi and Harrison, 2010) is a likely reason for reducing PNC in the summer hence reducing its association with [NOx]. Winter and spring produced relatively good relationships \( R^2 = 0.57; R^2 = 0.52 \). The winter of the studied period was 2.3 °C warmer and windier than the ten-year average.

We analysed the regression statistics of the PNC-NOx relationships for individual LWTs (Table 4). For all LWTs except SE (containing few data and with a very small negative intercept), the intercepts varied between 2028 and 5441 \( \pm m \). This means that there was a substantial, but not very large variation in the background level of PNC not related to NOx. The largest intercepts were found for LWTs A and NW, these weather types generally had high pollution levels, but it is hard to find a simple explanation for the pattern of intercept variation in the PNC-NOx relationships among LWTs. The correlation between PNC and NOx was strong and significant in all LWTs (Table 4).

### 4. Discussion

This study has shown that the variation in urban PNC had a strong positive relationship with [NOx] and the variation of both pollutants had strong and similar responses to the variation in \( u \) and also to \( D_T \) when positive. The relationship between PNC and [NOx] was also stable for concentration averages based on different LWTs, representing different weather situations.

All pollutants, apart from PM10, responded monotonically to increasing wind speed with non-linearly decreasing concentrations. [PM10] showed a negative relationship with \( u \) at low \( u \), but a weak positive response at \( u > 3 \text{ m s}^{-1} \). Wind speed affects dispersal of PM from the sources at street-level (Jones et al., 2010) and associated mixing with urban background air [PNC ~2000 \( \pm m \); Janhall and Hallquist, 2005] causes lower averages of [NOx] (~18 ppb) and PNC (~7000 \( \pm m \)) at higher \( u \), while higher \( u \) in addition increases the strength of some of its sources for [PM10] (e.g. re-suspension of road dust). This explains why [PM10] can be elevated both at low \( u \) by poor dilution, and at high \( u \) by stronger re-suspension. In London, re-suspension of particles has been
observed (Jones et al., 2010) and in Stockholm 90% of the PM$_{10}$ was attributed to road wear, i.e. not linked to vehicle exhaust emissions (Johansson et al., 2007). One may note that TEOM measurements of PM$_{10}$ can include some humidity and composition bias (Muir, 2000; Charron et al., 2004; Gehrig et al., 2005). However, the effects described above cannot be explained by such artefacts.

In response to $\Delta T$, [NO$_x$], [NO$_2$] and [PM$_{10}$] showed positive linear relationships, [PM$_{10}$] with a weaker slope. For PNC levels two regimes were apparent in response to increasing $\Delta T$, one regime where PNC decreased with $\Delta T$ (negative regime, at $\Delta T<0$ °C) and the second where PNC increased with $\Delta T$ (positive regime, at $\Delta T>0$ °C). Very high PNC levels were always observed in the positive regime coinciding with high [NO$_x$], indicating a strong link to traffic emissions accumulating under strong atmospheric stability. The negative PNC regime was not related with [NO$_x$] and was characterized by $u$ mostly between 2 and 6 ms$^{-1}$ representing both moderately calm and windier conditions. Unstable conditions defined by a negative $\Delta T$ are driven by solar heating of the ground and the resulting thermal turbulence can assist vertical transport of emissions from ground level and could be a plausible explanation for the increase in PNC and PM$_{10}$ observed at the rooftop. At negative $\Delta T$ [NO$_x$] levelled out while [NO$_2$] continued to decrease, which could potentially be due to increased photolysis of NO$_2$ at stronger solar radiation. As hypothesised, the response of [NO$_x$] and PNC was similar to $u$ and partly similar to $\Delta T$ (at positive $\Delta T$).

For the three categories of $\Delta T$ (Fig. 4a) the slope of the regression between PNC-NO$_x$ remained similar, despite their differing individual responses. This suggests that the proxy relationship per se is not very sensitive to $\Delta T$, but during large negative $\Delta T$, [NO$_x$] was a poorer proxy of PNC indicated by the lower $R^2$ value within this category. The high $u$ category (Fig. 4d), however, did affect the slope and weakened the PNC-NO$_x$ relationship, implying that the proxy relationship is sensitive to $u$ and that [NO$_x$] is a poorer proxy of PNC during windy conditions. Both average of [PM$_{10}$] (Fig. 2d) and the standard deviation of PNC (Fig. 2c) increased with stronger winds ($u > 3$ ms$^{-1}$) indicating a potential contribution from coarser particle fractions to the number count which are not related to NO$_x$ emissions. Another aspect further supporting this particle contribution is the fact that LWT W, obviously having a higher PNC:[NO$_x$] relationship than the other LWTs (Fig. 5a), was also frequently associated with windy conditions suggesting a contribution of marine salt particles transported from the sea located directly west of the city. Gustafsson and Franzen (2000) demonstrated significant sea salt aerosol transport across southern Sweden during strong westerlies. This shows that a different PM source is sometimes associated with high PNC:[NO$_x$] relationship than the other LWTs.

Fig. 3. Relationships between the vertical temperature difference between 73 m and 3 m ($\Delta T$) and the concentrations of (a) NO$_x$, (b) NO$_2$, (c) PNC and (d) PM$_{10}$. Each point of the relationships is an average for a temperature interval with steps 0–0.5, 0.5–1 °C and so on. The dotted lines show the standard deviation for each interval. The relationships are based on the least squares method and statistical significance is based on the F-test.
tested pollutants were a good proxy of PNC.

The noise caused by the source complexity of PM as described above, was also observed in the PNC-NOx relationship based on LWT. When excluding observations with \( u > 5 \text{ m s}^{-1} \) from the regression analysis, the overall scatter was reduced and the LWT W observation deviated less from the regression line. A possible explanation is that a potential source contribution to PNC from marine salt particles was reduced and thus improved the overall association between PNC and [NOx] on an LWT basis (Fig. 5b). Similar wind driven marine source attributions to particle number with PM size \( 13-800 \text{ nm} \) have been made in Barcelona due to easterly wind directions (Pey et al., 2009). However, to definitely verify a marine salt particle contribution to PNC in our study, data on particle size fractions and composition would be necessary.

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Fig. 4. Relationships between hourly averages of PNC and NOx (a and d), NO2 (b and e) and PM10 (c and f). The upper figures (a, b and c) show observations for three categories of the vertical temperature gradient. Light grey marks show hours when temperature difference between 73 m and 3 m (\( \Delta T \)) is negative (\( \Delta T < -0.5 \degree C \)), e.g. well mixed situations. Black marks show hours with positive temperature difference (\( \Delta T > -0.5 \degree C \)), e.g. limited vertical mixing situations. Dark grey marks show hours with both negative and positive temperature difference (\( -0.5 \degree C < \Delta T < 0.5 \degree C \)). The lower figures (d, e and f) show observations for three categories of wind speed (\( u \)). Light grey marks show observations during windy conditions (\( u > 5 \text{ m s}^{-1} \)), black marks show observations during calm conditions (\( u \leq 2 \text{ m s}^{-1} \)) and dark grey marks show observations during an intermediate wind speed category (\( 2 \text{ m s}^{-1} < u < 5 \text{ m s}^{-1} \)).
Despite the deviation by LWT W, the positive relationship between PNC and [NOx] for averages based on LWTs remained strong. LWTs with a high frequency of low wind speed (u < 5 m s⁻¹) and high degree of atmospheric stability (A, NE, N and NW) were associated with higher PNC and [NOx], while LWTs with a large frequency in windy and unstable conditions (C, SE, S, SW) appeared in the lower end. This supports the hypothesis that the meteorological properties governing high levels of both NOx and PNC are strongly linked to the occurrence of calm and stable conditions also when aggregated as LWT averages. Had the frequency of low wind speed and positive temperature gradient (ΔT > 0°C) been more evenly distributed among LWTs, the PNC-NOx relationship would probably have been weaker on an LWT basis.

At ground level stations in London (Bigi and Harrison, 2010) and Stockholm (Johansson et al., 2007), the relationship between PNC and [NOx] showed similar patterns to our investigation, with the exception of the wind driven PNC regime observed in this study.

<table>
<thead>
<tr>
<th>LWT</th>
<th>n hr LWT</th>
<th>f LWT</th>
<th>NO₂ (ppb) Mean</th>
<th>NO₂ (ppb) sd</th>
<th>NOx (ppb) Mean</th>
<th>NOx (ppb) sd</th>
<th>PM₁₀ (µg m⁻³) Mean</th>
<th>PM₁₀ (µg m⁻³) sd</th>
<th>PNC (# cm⁻³) Mean</th>
<th>PNC (# cm⁻³) sd</th>
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Fig. 5. Relationships between [PNC] and [NOx] for different LWTs. The grey regression line (a) excludes LWT W from the relationship, and the black regression line includes all LWTs. The relationship between [PNC] and [NOx] (b) only includes observations with low wind speed (u < 5 m s⁻¹) and (c) only includes observations with positive temperature gradient (ΔT > 0.5°C). All regressions are based on the total least squares method and statistical significance is based on the F-test.
Table 3
Relationship between hourly PNC and [NOx], and averages of temperature (T) and wind speed (u) for winter (DJF), spring (MAM), summer (JJA) and autumn (SON) during the studied period and 2000–2009. Statistical significance (***p < 0.001) is based on the F-test.

<table>
<thead>
<tr>
<th>Studied period</th>
<th>Season</th>
<th>Slope</th>
<th>Intercept</th>
<th>R²</th>
<th>Significance</th>
<th>T (°C)</th>
<th>u (ms⁻¹)</th>
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<td>MAM</td>
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<td>4806</td>
<td>0.52</td>
<td>***</td>
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<td>3.9</td>
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<td>JJA</td>
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<td>5711</td>
<td>0.27</td>
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<td>SON</td>
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<td>5052</td>
<td>0.74</td>
<td>***</td>
<td>8.4</td>
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</table>

Table 4
Statistics related to the relationship between hourly PNC and NOxs during different LWTs. Statistical significance (***p < 0.001) is based on the F-test.

<table>
<thead>
<tr>
<th>LWT</th>
<th>Intercept</th>
<th>Std. error intercept</th>
<th>Slope</th>
<th>Std. error slope</th>
<th>R²</th>
<th>Significance</th>
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<td>0.34</td>
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<tr>
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<td>0.62</td>
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<tr>
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<td>272.5</td>
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<td>0.33</td>
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<tr>
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Daily averages were used in Stockholm. This time resolution seems to hide a possible wind driven PNC regime, which was obvious in the present study when an hourly time resolution was used. Another possible explanation could be that the wind driven source of PNC influences particle concentrations to a lesser degree in Stockholm. Both intercept and slope of the PNC-NOx relationship was larger in Stockholm, most likely due to differences in the actual vehicle fleet composition affecting the two monitoring sites.

Since no data for particle size distribution were available during the period of these measurements, the extent to which PNC can be attributed to traffic emissions could not be fully established. However, previous measurement at the monitoring site used in the present study during a short winter time period illustrated a pronounced UFP peak during morning rush hours which coincided with peaks of NOx and CO (Janhäll et al., 2006). The number-size distributions peaked at 40 nm which is typical for combustion generated particles being the dominant source during winter and especially during temperature inversions (Olofson et al., 2009). Furthermore, measurements at numerous other places have confirmed that a majority of the PNC in urban environments are found in the ultrafine size range and originate from vehicle exhausts (Pey et al., 2009; Woo et al., 2010; Kumar et al., 2011). On most spatial scales (except for road tunnels), the dilution process has the fastest time scale for particle transformation in comparison with coagulation and deposition (Kumar et al., 2011), and is expected to have occurred to a considerable extent when the ground level emission plume has reached the roof-top. There are studies showing that PNC can be up to 5 times larger at street-level than roof-top levels (Vákevá et al., 1999; Kumar et al., 2008). Photochemically induced nucleation of new particles can be of importance for UFP concentrations (Rodriguez et al., 2007) and can be promoted by high u at roof-top level (Kumar et al., 2008). Freshly nucleated particles (UFP) may have added to the PNC in our study but is most probably of minor importance when only considering the strong association between PNC and [NOx] at stable conditions.

Urban air pollution monitoring normally only includes legally regulated gases and therefore long-term measurements of UFP or PNC are scarce. Indirectly, NOx gives an indication of vehicle exhaust particles, but different after-treatment equipment (with or without diesel particle filters) on diesel vehicles cause trade-offs between emissions of NOx and particles (Hallquist et al., 2013). Thus, to create a strategy for mitigating PNC and NOx and using the information presented in this paper the variability in exhaust composition between different vehicle types must be taken into consideration. The lack of UFP data in cities throughout the world prevents any direct assessment of the long term evolution of UFPs in the ambient air, which is problematic for studying epidemiological effects from UFP exposure. Incorporating situations giving rise to high [NOx] and PNC may be of help but still does not completely single out the direct UFP effect, which is important for setting up accurate exposure guidelines and legislation (Morawska et al., 2008). Furthermore, multi-pollutant exposure may be more relevant when determining health effects such as cardiovascular risk (Brook et al., 2010) and our study has shown that all pollutants analysed, although all having somewhat different relationships with u and ΔT, tend to reach the highest concentrations during stable atmospheric conditions represented by low u, positive ΔT and LWTs A, NE and N, which can be characterised as high risk weather types with respect to the air pollutants covered by this study.

5. Conclusions

- PNC had a positive relationship with all pollutants studied, where hourly [NOx] was the better proxy of PNC (R² = 0.55) as compared to [NO2] (R² = 0.50) and especially [PM10] (R² = 0.17). This is of large significance for the use of proxies in studies of the effects of urban pollutants on health.
- During inversion days (daily ΔT > 0 °C) the relationship between daily PNC and [NOx] (R² = 0.73) and [NO2] (R² = 0.54), respectively, was stronger. Low wind speeds (<2 m·s⁻¹) were associated with high levels of NOx. PNC and PM10. PM10 differed from the other pollutants in that concentrations increased again with wind speed when exceeding 3 m·s⁻¹.
- LWTs associated with a high fraction of very low wind speeds (<2 m·s⁻¹) were A, NW, N and NE. They all represented high levels of NOx, NO2, PNC and PM10. For PM10 the difference was small between low wind speed LWTs and the more turbulent LWTs.
• PNC had a weaker positive relationship ($R^2 = 0.24$) to $[NO_x]$ at stronger winds ($u > 5 \text{ m s}^{-1}$) frequently occurring during LWT W, possibly reflecting a substantial particle contribution from sea salt particles not associated with NOx emissions.

Acknowledgements

Thanks are due to the Environment Administration of the City of Gothenburg for providing air pollution and meteorological data from the monitoring sites Femman and Järnbrott. Thanks are also due to the Swedish Environmental Protection Agency and Country Board of Västra Götaland for financial support of the particle counter.

References


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