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Short communication

Influence of wind-speed on short-duration NO_2 measurements using Palmes and Ogawa passive diffusion samplers

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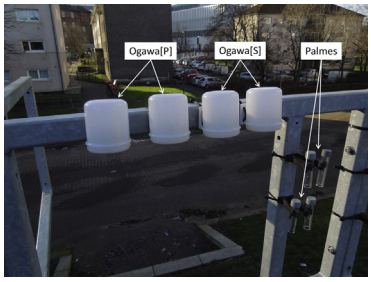
HIGHLIGHTS

- A variant on the standard Ogawa passive diffusion sampler was also tested.
- Wind-induced turbulence increased passive sampler uptake rates.
- In general, relationships between wind speed and uptake rates were linear.
- Estimation of wind speed variations allowed correction of wind speed effects.
- Wind protection of samplers appears necessary when wind speed variations are unknown.

GRAPHICAL ABSTRACT



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ABSTRACT

We assessed the precision and accuracy of nitrogen dioxide (NO_2) concentrations over 2-day, 3-day and 7-day exposure periods measured with the following types of passive diffusion samplers: standard (open) Palmes tubes; standard Ogawa samplers with commercially-prepared Ogawa absorbent pads (Ogawa[S]); and modified Ogawa samplers with absorbent-impregnated stainless steel meshes normally used in Palmes tubes (Ogawa[P]). We deployed these passive samplers close to the inlet of a chemiluminescence NO_2 analyser at an urban background site in Glasgow, UK over 32 discrete measurement periods. Duplicate relative standard deviation was <7% for all passive samplers. The Ogawa[P], Ogawa[S] and Palmes samplers explained 93%, 87% and 58% of temporal variation in analyser concentrations respectively. Uptake rates for Palmes and Ogawa[S] samplers were positively and linearly associated with wind-speed ($P < 0.01$ and $P < 0.05$ respectively). Computation of adjusted uptake rates using average wind-speed observed during each sampling period increased the variation in analyser concentrations explained by Palmes and Ogawa[S] estimates to 90% and 92% respectively, suggesting that measurements can be corrected for shortening of diffusion path lengths due to wind-speed to improve the accuracy of estimates of short-term NO_2 exposure. Monitoring situations where it is difficult to reliably estimate wind-speed variations, e.g. across multiple sites with different unknown exposures to local winds, and personal exposure monitoring, are likely to benefit from protection of these sampling devices from the effects of wind, for example by use of a mesh or membrane across the open end. The uptake rate of Ogawa[P] samplers was not associated with wind-speed resulting in a high correlation between estimated concentrations and observed analyser concentrations. The use of Palmes meshes in Ogawa[P]

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samplers reduced the cost of sampler preparation and removed uncertainty associated with the unknown manufacturing process for the commercially-prepared collection pads.

1. Introduction

Exposure to nitrogen dioxide (NO_2) has been associated with adverse effects on human health, including cardio-respiratory illness, hospital admissions and mortality (World Health Organization, 2013). Passive samplers, because of their relatively low cost and simplicity of deployment, have been used in studies to estimate outdoor NO_2 concentrations over large geographical areas (Cyrys et al., 2012; Gillespie et al., 2017, 2016; Lewné et al., 2004) and for indoor and personal exposure (Yu et al., 2008). However the temporal resolution of passive samplers is limited, and a number of potential issues may affect their accuracy and precision (Cape, 2009).

Passive samplers can be grouped into tube and badge designs (Cape, 2009; Tang et al., 2001; Yu et al., 2008). Tube samplers, including the commonly-used Palmes sampler (Palmes et al., 1976), have relatively long diffusion paths and low uptake rates, and are typically used for measuring concentrations over 1–5 week periods. Badge samplers, including Ogawa samplers (http://ogawausa.com/), have relatively short path lengths and higher uptake rates facilitating measurement of relatively low NO_2 concentrations and exposures over shorter intervals (e.g. 24 h).

Palmes samplers have often been observed to overestimate concentrations measured by automatic analysers during co-location studies (Cape, 2009). Possible reasons for such overestimations include: wind-speed induced turbulence effectively shortening the diffusion path; and chemical reactions within the diffusion path that result in misrepresentation of external photochemical conditions. Chamber and wind-tunnel studies have reported positive associations between wind-speed and sampler uptake rates for open tube samplers (Buzica et al., 2005; Martin et al., 2014; Plaisance et al., 2004). Field studies using wind shelters and/or protective meshes or membranes to minimise turbulence within the diffusion path have noted reduced sampler overestimation and higher correlations between sampler and analyser measurements (Bush et al., 2001; Martin et al., 2014; Plaisance et al., 2004). Concentrations of NO_2 determined using UV-transmitting quartz tubes have shown smaller overestimations than standard acrylic tubes suggesting reduction in NO_2 photolysis in the former (Heal et al., 1999, 2000), although this effect has been observed to only occur in summer (Kirby et al., 2000). Collectively there is limited observational evidence regarding whether a single factor is the dominant cause of the overestimations in NO_2 concentrations frequently observed by Palmes tubes, or if they are the consequence of multiple site-specific environmental factors.

The order-of-magnitude shorter diffusion path length in Ogawa samplers is anticipated to limit within-tube chemical effects. The manufacturer of the Ogawa samplers provides shelters to minimise the effect of wind on the relatively large face area of the badges. Temperature, absolute humidity, and wind-speed have been observed to be positively associated with the uptake rate of Ogawa samplers (Hagenbjörk-Gustafsson et al., 2010).

Our study deployed standard Palmes and Ogawa samplers (the latter hereafter referred to as Ogawa[S]) at an urban background monitoring site in Glasgow, UK. We also prepared and deployed modified Ogawa samplers with absorbent-impregnated stainless steel meshes normally used in Palmes tubes (hereafter referred to as Ogawa[P]) to: (a) eliminate one of the technical differences in our comparison between Palmes and Ogawa samplers; (b) reduce operational costs; and (c) eliminate uncertainty in our scientific description of the methods associated with the undisclosed preparation methods of the pre-coated collection pad sold by the manufacturer. The samplers were deployed for 2-day and 3-day exposure times; and 7-day exposure times matched to consecutive 2-day and 3-day periods. Potential influences of meteorological and atmospheric composition factors on agreement between sampler and reference chemiluminescence analyser measurements were investigated. The 2-day and 3-day deployments increased the range of meteorological and chemical conditions sampled by avoiding the reduction in variation of these conditions resulting from longer-term averaging, and allowed evaluation of the precision and accuracy of the samplers at these short exposure periods.

2. Methods

Duplicate Palmes, Ogawa[S] and Ogawa[P] samplers were deployed next to the inlet to reference gas analysers at the Townhead air quality monitoring site in Glasgow, UK (latitude: 55.866°, longitude: −4.243°) (Fig. 1). The Ogawa[S] and Ogawa[P] samplers were deployed under shelters purchased from the manufacturer. The Palmes tubes were unsheltered, as is standard practice. The Townhead site is in an urban background location, approximately 1 km north of the city centre and 122 m from the nearest road. Concentrations of NO_2 and O_3 were measured as hourly averages using a Teledyne-API 200A NO_x chemiluminescent analyser and a Thermo Scientific Model 49i O_3 analyser respectively. Both analysers undergo regular Quality Assurance and Quality Control assessments as part of the UK Automatic Urban and Rural Network (www.scottishairquality.co.uk/). The concentrations measured by the analysers at Townhead were averaged to the same time periods as the passive sampler exposures.

The passive samplers were mounted on a railing at a common height approximately 1 m horizontal distance from the analyser inlets. Temperature and relative humidity were measured at 1-min intervals using an Onset HOBO U23 Pro v2 External Data logger located on the railing under a solar radiation shield, from which hourly-average data were calculated. Hourly wind-speed data was obtained from the nearest Meteorological Office site at Glasgow airport (approximately 10 km west of the Townhead site). Both Glasgow airport and Townhead monitoring sites are in open locations, therefore the wind-speeds recorded at Glasgow airport were anticipated to provide a reasonably reliable indication of relative temporal changes in wind-speed at Townhead.

We made passive sampler measurements over 32 discrete periods, ranging in duration from 2 days to 8 days, between February 2015 and October 2015. Five of the week-long passive sampler exposure periods were contemporaneous with cumulative 2, 2 and 3 day exposure periods (Supplementary Information Table S1). The 2 and 3-day exposure times provided a wider range of field conditions to test the passive samplers as the impact of averaging over longer exposures was reduced. The ranges (and relative standard deviations) of exposure-averaged wind-speed for all 2 & 3-day and all 7-day exposure periods were 1.1–8.2 m/s (46%) and 2.1–5.4 m/s (29%) respectively.

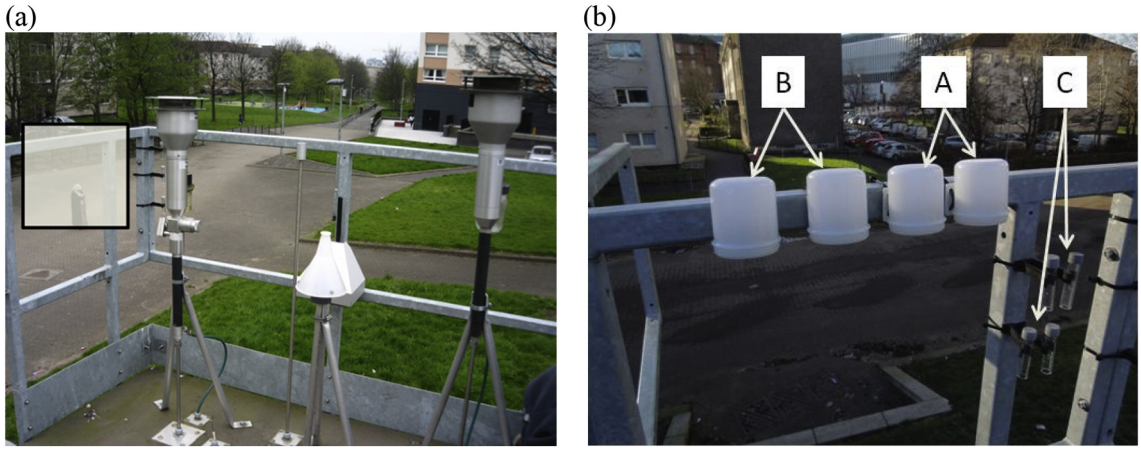

Fig. 1. Location of passive NO_2 samplers on the roof of Townhead automatic monitoring site, Glasgow. (a) Location of passive samplers (highlighted by grey square) close to the inlets of the automatic analyser. (b) Deployment of samplers: A = Ogawa[S]; B = Ogawa[P]; C = Palmes. Temperature and relative humidity were measured using HOBO sensors, located on the railing opposite the passive samplers.

We prepared Palmes samplers with two stainless-steel collection meshes dipped in a 1:1 triethanolamine (TEA):acetone solution (Heal, 2008). We assembled Ogawa[S] samplers using precoated TEA collection pads purchased from the manufacturer, and Ogawa[P] samplers using two Palmes meshes prepared using the same process as the Palmes samplers. Samplers were prepared in 8 batches and were stored in a refrigerator in sealed bags (Palmes) and containers (Ogawa) before deployment, and between deployment and laboratory analysis.

We analysed the 8 batches of samplers separately. Nitrite collected by Palmes samplers was extracted into aqueous solution and quantified by the Saltzman reaction and colorimetric absorption at 540 nm. The nitrite mass was converted to ambient concentration of NO_2 using the diffusion coefficient for NO_2 in air, the internal length and cross-sectional area of the tube, and the exposure time (Targa and Loader, 2008). The nitrite mass collected by Ogawa[S] samplers and calculation of ambient NO_2 were determined using aqueous extraction and colorimetric absorption following the manufacturer's protocol (Ogawa, 2006). The laboratory determination of nitrite mass collected by Ogawa[P] samplers followed the method in Targa and Loader (2008), while the subsequent conversion to ambient NO_2 used the Ogawa protocol. The volumetric mixing ratios (ppb) of NO_2 calculated from the Ogawa protocol were converted to gravimetric units ($\mu g/m^3$) using a factor of 1.9125 (conversion at 20 °C and 1013 mb) to match the reporting conditions of the reference analyser concentrations.

Duplicate laboratory blanks (for both Ogawa absorbent pads and Palmes coated meshes) were prepared with each batch of samplers and stored in the refrigerator during sampler deployments. The blanks were analysed in an identical manner to the samples and the average masses of nitrite in the blanks were subtracted from the appropriate samples prior to calculation of sampler NO_2 concentration.

The masses of nitrite collected by the Ogawa[P] sampler were lower than those collected by the Ogawa[S] sampler. Linear regression indicated that Ogawa[P] nitrite = 0.62 × Ogawa[S] nitrite (R^2 = 0.93) (Fig. S1). The slope of this regression line was of similar magnitude to the ratio of the area of the Palmes mesh to the area of the Ogawa[S] collection pad (0.916 cm^2/1.65 cm^2 = 0.56). Therefore the lower nitrite masses collected by the Ogawa[P] samplers was consistent with this difference in collection areas between the Ogawa[S] pad and Palmes mesh.

An empirical passive sampler uptake rate (UR) for each exposure was calculated from measured nitrite mass as follows:

$$UR\left(cm^3\,min^{-1}\right) = \left[\frac{nitrite\,mass\,(ng)}{\left([NO_2]\,(ng\,m^{-3}) \times t\,(min)\right)}\right] \times 10^6\left(cm^3\,m^{-3}\right) \quad (1)$$

where $[NO_2]$ = exposure-averaged analyser NO_2 concentration, and t = exposure duration. Associations between meteorological variables and uptake rates were examined using linear regression.

3. Results and discussion

3.1. Precision and limits of detection

The average Limit of Detection (LoD), calculated as three times the standard deviation of the blank concentration plus average blank concentration using the shortest exposure time in the calculation, was 1.1 $\mu g/m^3$ for the Ogawa samplers and 10.1 $\mu g/m^3$ for the Palmes sampler (Table 1). These LoDs were substantially lower than the minimum concentrations measured by the samplers.

The mean relative standard deviation (RSD) for duplicate measurements was <7% for all samplers and exposure durations (Table 1, Fig. S2). These mean RSD values for our measurements were within the 2.8%–11.0% range of published statistics for exposure periods of 1-week or greater (Bush et al., 2001; Buzica et al., 2005; Heal et al., 1999a, 1999, 2000; Kirby et al., 2000; van Reeuwijk et al., 1998; Vardoulakis et al., 2009), and were lower than the mean RSD of 12.6% reported by Heal et al. (1999a) for 2-day indoor Palmes measurements (this was the only study using Palmes tube exposures of less than 3-days that we located). Our good precision data highlight the potential for passive sampling to provide greater temporal resolution than the time periods normally used. In the remainder of this paper the duplicate mean is used as the NO_2 concentration for a given sampler and exposure period.

3.2. Sampler accuracy

Using the measured nitrite masses and standard protocols for computation of atmospheric concentrations described in the Methods section, concentrations derived from Palmes and Ogawa [S] samplers were generally higher than reference analyser observations, and concentrations from Ogawa[P] samplers were generally lower than the analyser observations (Fig. 2, Table 1). Our

Table 1
Limits of detection (LoD) and duplicate relative standard deviation (RSD) statistics for the three passive sampler types and their root mean square error (RMSE), normalised mean bias (NMB), regression forced through the origin (and 95% confidence interval) and R^2 statistics with respect to the analyser measurements. The RSD, NMB and RMSE statistics are presented for all studies, for exposures of 3 days and less, and for exposures of greater than 3 days. Statistics are presented for sampler NO_2 concentrations before and after correction of uptake rates (second and third panels respectively – see text for details of correction procedure).

	Palmes	Ogawa[S]	Ogawa[P]
LoD All (μg/m^3)	10.8	1.1	1.1
Mean duplicate RSD All (%)	5.6	2.5	5.9
Mean duplicate RSD $t \leq 3$ (%)	6.0	2.2	6.4
Mean duplicate RSD $t > 3$ (%)	4.7	3.0	4.5
Data using theoretical uptake rates:			
RMSE sampler *vs.* analyser All (μg/m^3)	9.6	4.8	8.9
RMSE sampler *vs.* analyser $t \leq 3$ (μg/m^3)	11.1	5.6	8.9
RMSE sampler *vs.* analyser $t > 3$ (μg/m^3)	4.9	2.3	8.8
NMB sampler *vs.* analyser All	0.28	0.11	−0.33
NMB sampler *vs.* analyser $t \leq 3$	0.30	0.17	−0.33
NMB sampler *vs.* analyser $t > 3$	0.20	−0.04	−0.32
Regression slope (95% CI)	1.25 (1.15–1.35)	1.11 (1.06–1.17)	0.67 (0.64–0.69)
R^2 sampler *vs.* analyser All	0.59	0.87	0.93
Data using empirical uptake rates:			
RMSE sampler *vs.* analyser All (μg/m^3)	3.9	3.4	2.7
RMSE sampler *vs.* analyser $t \leq 3$ (μg/m^3)	4.5	3.2	3.1
RMSE sampler *vs.* analyser $t > 3$ (μg/m^3)	2.4	3.7	1.1
NMB sampler *vs.* analyser All	0.03	0.02	0.02
NMB sampler *vs.* analyser $t \leq 3$	0.05	0.08	0.03
NMB sampler *vs.* analyser $t > 3$	−0.01	−0.11	−0.02
Regression slope (95% CI)	1.06 (1.00–1.09)	1.05 (1.00–1.09)	1.03 (0.99–1.07)
R^2 sampler *vs.* analyser All	0.90	0.92	0.93

observation of Palmes sampler overestimation of analyser concentrations was consistent with the previous studies reviewed in Section 1. Closer inspection of the Ogawa[S] data showed that while the 2 and 3-day Ogawa[S] exposures overestimated analyser concentrations, the 7-day exposures underestimated, as has been noted previously (Hagenbjörk-Gustafsson et al., 2010; Mukerjee et al., 2008; Sather et al., 2006, 2007; van Reeuwijk et al., 1998). Overall, however, Ogawa[S] samplers had the lowest Root Mean Square Errors (RMSE) and Normalised Mean Bias (NMB) values, while the Palmes samplers had the largest deviations from the analyser (Table 1). The Ogawa[P], Ogawa[S] and Palmes samplers explained 93%, 87% and 58% of temporal variation in analyser concentrations respectively. Preparation of the Ogawa[P] meshes according to standard procedures (Heal, 2008; Targa and Loader, 2008) eliminated scientific uncertainty associated with the unspecified preparation method for the commercially-available collection pads used in Ogawa[S] samplers, and reduced the cost of sampler preparation.

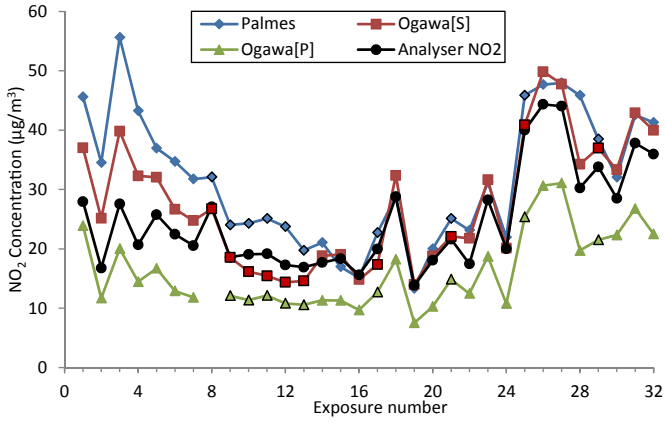

Fig. 2. Concentrations of NO_2 measured by automatic analyser and by Palmes, Ogawa [S] and Ogawa[P] samplers (prior to correction for observed wind-speed effects) for 32 separate exposure periods. Symbols with a dark border are measurements from exposures of greater than 3 days.

3.3. Long-term vs. cumulative short-term measurements

The time-weighted weekly average from the three cumulative short-term exposures showed close agreement with the corresponding simultaneous 1-week exposure (Fig. S3). Our results are consistent with Heal et al. (1999a) who did not observe significant differences between cumulative 2 or 3-day and 1-week indoor exposure measurements. In contrast, significantly lower concentrations have been observed between 1-month measurements and cumulative 1 or 2 week measurements in parallel, which have been attributed to loss in the long term of absorbed NO_2 from the TEA absorbent (Bush et al., 2001; Heal et al., 1999a, 1999, 2000; Kirby et al., 2000).

3.4. Correction of sampler uptake rates by wind-speed

We examined correlations between empirical sampler uptake rate, calculated using Equation (1), and the following meteorological and atmospheric composition variables (Table 2) previously reported to be associated with passive sampler uptake rate: air temperature; relative and absolute humidity (Cape, 2009; Hagenbjörk-Gustafsson et al., 2010); wind-speed (Bush et al., 2001; Buzica et al., 2005; Martin et al., 2014; Plaisance et al., 2004); atmospheric NO_2 concentration; and an atmospheric chemistry metric representing the potential for within-tube formation of additional NO_2 [ratio of analyser NO_2 plus minimum of analyser NO or O_3, to analyser NO_2 ($Ratio(Min(NO,O_3)+NO_2)/NO_2$)] (Heal et al., 1999).

Palmes sampler uptake rates were correlated with temperature and absolute humidity in the opposite direction to that expected from the literature (Cape, 2009) (Table 2). This likely resulted from confounding by negative correlations between temperature and wind-speed, and between absolute humidity and wind-speed (Fig. S4). The empirical Ogawa[S] sampler uptake rate was also

Table 2
Pearson correlation coefficients for bivariate relationships between passive sampler empirical uptake rates and exposure-averaged observed meteorological and atmospheric composition variables.

	Palmes_UR	*Ogawa[S]_UR*	*Ogawa[P]_UR*
T	−0.69**	−0.48**	−0.22
RH	0.32	0.51**	0.46**
AH	−0.62**	−0.31	−0.04
WS	0.78**	0.40*	0.04
NO_2	−0.15	0.20	0.41*
Ratio(*Min*(*NO*,O_3)+NO_2)/NO_2	−0.39*	−0.04	0.18

Variables are exposure means of: air temperature (*T*, °C); relative humidity (*RH*, %); absolute humidity (*AH*, g/m^3); wind-speed (*WS*, m/s); analyser NO_2 (NO_2, ppb), ratio of analyser NO_2 plus minimum of analyser NO (ppb) or O_3 (ppb) to analyser NO_2 (*Ratio*(*Min*(*NO*,O_3)+NO_2)/NO_2); uptake rates (*UR*) for Palmes, Ogawa[S] & Ogawa[P] samplers. *Correlation coefficient significant at $P < 0.05$; **Correlation coefficient significant at $P < 0.01$.

correlated with temperature in the opposite direction to that expected (Hagenbjörk-Gustafsson et al., 2010). Similarly, the positive correlations between Ogawa[S] and Ogawa[P] sampler uptake rates and relative humidity were contradictory to expectations (Cape, 2009; Hagenbjörk-Gustafsson et al., 2010).

The correlations between the empirical Palmes and Ogawa[S] uptake rates and wind-speed were significant. The general pattern of increased sampler uptake rate as wind-speed increased (Fig. 3a) is consistent with increasing wind-speeds reducing effective diffusion path length (and hence increasing effective uptake rate) because of induced turbulence, and consistent also with similar patterns noted in previous field measurements (Bush et al., 2001; Buzica et al., 2005; Martin et al., 2014; Plaisance et al., 2004). The reduced, but still positive, correlation between the Ogawa[S] sampler uptake rate and wind-speed (Fig. 3c) suggested that the wind shelter provided by the manufacturer might not fully protect the sampler from wind effects. On the other hand, there was negligible correlation between Ogawa[P] sampler uptake rate and wind-speed (Fig. 3e), despite both types of sampler being deployed under the same type of shelter.

For wind-speeds > 2.3 m/s, the empirical uptake rates for the Palmes sampler were greater than the theoretical uptake rate of 1.2 cm^3/min calculated from sampler geometry (Fig. 3a), resulting in large overestimations of NO_2 concentrations at these wind-speeds (Fig. 3b). The empirical uptake rates calculated for the Ogawa[S] sampler (Fig. 3c) were mostly smaller than the theoretical uptake rate of 12.1 cm^3/min calculated from sampler geometry (Tang et al., 2014) but larger than the uptake rate of 9.3 cm^3/min calculated using manufacturer conversion factors (conversion factor of 56 ppb min/ng for NO_2 at 20 °C and 70% RH – see Supplementary Information for details).

From the above analyses of our observations, wind-speed was the variable with the most consistent and pronounced correlation with sampler uptake rate in the anticipated direction (Table 2). Therefore, we corrected sampler uptake rate for wind-speed influence following a similar approach to that used in an evaluation study of Ogawa samplers in Sweden (Hagenbjörk-Gustafsson et al., 2010). We calculated the linear regression between empirical uptake rate (computed from Equation (1)) and exposure-period-average wind-speed across the set of measurement periods (Fig. 3a, c, e). This regression line was used to correct the uptake rate using the measured average wind-speed for each exposure period, and the corrected uptake rate then used to correct the estimates of atmospheric concentrations from measured nitrite mass and exposure time by rearrangement of Equation (1). We then compared the corrected NO_2 concentrations to analyser measurements using linear regression (Fig. 3b, d, f). Following reasoning given by Martin et al. (2014) and Pfeffer et al. (2010) we forced the regression lines through the origin because of insignificant laboratory blank concentrations for our passive samplers and incomplete temporal coverage by the reference analyser (resulting from analyser calibration and/or maintenance activities).

After we corrected uptake rates for wind-speed we observed a 30% increase in the explained variation in the bivariate relationship between the corrected Palmes concentrations and analyser concentrations (Fig. 3b). We noted a smaller (~5%) increase in explained variation for Ogawa[S] after wind-speed correction (Fig. 3d). The absence of substantial correlation between the Ogawa [P] sampler uptake rate and wind-speed (Fig. 3e) meant that correction was only appropriate by adjusting the uptake rate to the average empirical uptake rate of 5.9 cm^3/min, which was approximately half of the theoretical Ogawa uptake rate because of the approximately factor 2 smaller Ogawa[P] sampler NO_2 capture surface area noted in Section 2.

The above observations highlight the importance of evaluation of samplers under field conditions and suggest that it may be beneficial to calibrate uptake rates for the Palmes and Ogawa samplers to the conditions under which measurements are made. Our study used wind-speed data from a single meteorological station, at an open site at the edge of the urban conurbation containing the pollution monitoring site, to correct the passive sampler data. Ideally we would have made wind speed measurements at the pollution monitoring site, however we anticipate the meteorological station data provided a reasonably reliable indication of relative temporal changes in wind-speed at the similarly open monitoring site, and any systematic difference in wind-speed between the two locations would have been accommodated by the empirical nature of the corrections that we developed.

In some exposure assessment situations the influence of wind-speed can be dealt with by the type of calibration we describe in this paper using measured or estimated wind-speeds (e.g. where passive diffusion samplers are used to record relative temporal changes in gas concentrations at a single site).

In other situations the correction required may be more difficult to implement, for example when the objective is to compare pollution concentrations at multiple sites with different exposure to prevailing wind conditions. In this latter type of situation it would be necessary to record wind measurements at the multiple sites or use a weather model to estimate the wind-speeds to allow site-specific correction of the sampler uptake rates. If the passive samplers were to be used over multiple sites without reliable information on wind speed variations, or in personal sampling to monitor in individuals with different levels and types of physical activity patterns (*e.g.* comparison of pollution exposures in cyclists, pedestrians and car drivers where the passive sampling device will have different relative speeds compared to the surrounding air), our observations suggest that it appears necessary to use field calibrated passive sampling devices with some form of modification to prevent wind-induced turbulence within the diffusion path. Previous studies have attempted to reduce the effect of wind-speed on sampler precision and accuracy through use of shelters over sampler inlets (Bush et al., 2001; Martin et al., 2014; Plaisance et al., 2004). However, shelters may increase the risk of vandalism by their conspicuous appearance; air under the shelter may be of a different composition to ambient air (Kirby et al., 2000); and for personal sampling it may be difficult to expose the samplers under a shelter. The use of a mesh or membrane across the open end of the diffusion sampler is an alternative, and perhaps more practical, modification to the samplers to reduce the effect of wind-speed turbulence on sampler precision and accuracy.

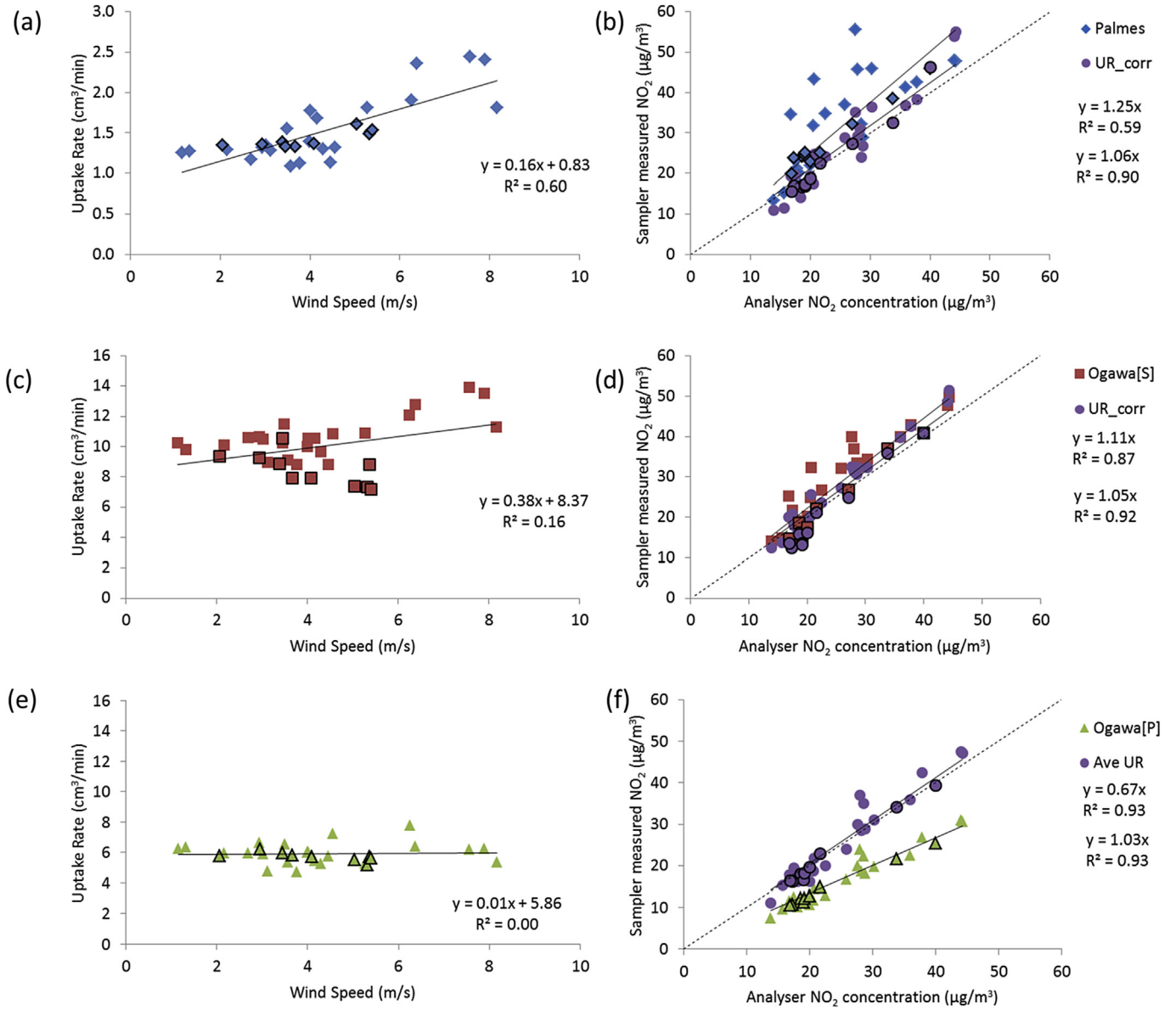

Fig. 3. Correction of NO_2 passive sampler measurements using average wind-speed measured during each exposure period for Palmes and Ogawa[S] samplers; and using an average uptake rate (5.9 cm^3/min) for Ogawa[P] samplers. The uptake rate for each sampler (calculated from the nitrite mass collected by individual samplers divided by the product of exposure time and average analyser concentration) was plotted against wind-speed (Graphs: a; c; e). The linear regression lines were used to derive a corrected uptake rate for the samplers for the average wind-speed during a given exposure period. The corrected uptake rate was then used to calculate a corrected passive sampler NO_2 concentration which was plotted against the automatic analyser concentration, alongside the concentration of NO_2 calculated using the standard method for each sampler (Graphs: b; d; f). Symbols with a dark border indicate measurements from exposures of greater than 3 days.

4. Conclusions

We used standard (open) Palmes tubes, standard Ogawa[S] samplers with commercially-available absorbent pads, and modified Ogawa[P] samplers with TEA-impregnated meshes normally used in Palmes tubes to measure NO_2 at an urban background automatic monitoring site in Glasgow for exposure periods ranging from 2 days to 1-week.

Duplicate relative standard deviation was <7% for all passive samplers for both short ($t \leq 3$ days) and long ($t > 3$ days) exposures demonstrating good potential for application of passive NO_2 sampling at finer temporal resolution than the time periods commonly used.

The Ogawa[P], Ogawa[S] and Palmes samplers explained 93%, 87% and 58% of temporal changes in analyser concentrations respectively. Palmes and Ogawa[S] sampler uptake rates were positively and linearly correlated with wind-speed, which enabled empirical correction of the uptake rates and subsequent re-estimation of corrected NO_2 concentrations. After these corrections the Palmes and Ogawa[S] sampler estimates explained a larger proportion (additional 30% and 5% respectively) of variation in analyser concentration, with regression lines closer to 1:1. Our observations suggest that if Palmes and Ogawa[S] samplers are exposed in windy environments (e.g. >2 m/s) field calibrated uptake rates appear to be necessary to account for the effect of wind-speed on sampler concentration estimates.

The Ogawa[P] uptake rate was not correlated with wind-speed and explained a slightly higher proportion of variation in analyser

concentrations than the Ogawa[S] sampler. After adjustment of individual Ogawa[P] uptake rates to the average observed Ogawa[P] uptake rate (5.9 cm^3/min) the regression between the Ogawa[P] and analyser NO_2 measurements was closer to the 1:1 line and maintained a high R^2 value ($R^2 = 0.93$). Therefore, the use of Palmes meshes in Ogawa samplers was a successful adaptation of the Ogawa sampler providing a reduction in cost of sampler preparation with specified preparation protocols. Further field-testing will help to establish if this observed average uptake rate for the modified Ogawa[P] sampler allows accurate estimation of analyser concentrations at other times and locations.

This research has highlighted that passive samplers require field evaluation at automatic pollution monitoring station to calibrate uptake rates to environmental conditions. In particular Palmes and Ogawa[S] sampling uptake rates were substantially influenced by wind-speed and we have suggested a method to correct the sampler uptake rates when estimates of wind-speed variations are available. Monitoring situations where it is difficult to reliably estimate wind-speed variations, e.g. across multiple sites with different unknown exposures to local winds; or in personal exposure monitoring; are likely to benefit from protection of the sampling device from the effects of wind, for example by placing a mesh or membrane across the open end prior to field calibration.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.04.008.

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