



# A new flow-through directional passive air sampler: design, performance and laboratory testing for monitoring ambient nitrogen dioxide

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## ABSTRACT

A new type of passive air sampler for monitoring trace air pollutants in ambient air is introduced. It has a rotatable upper part that can turn into the prevailing wind direction. Pollutants from different directions are transported through a specially-shaped air channel in the upper part and retained on different parts of a sample carousel in the fixed lower part. Pollution sources are trackable by examining the pollutant distribution in the carousel. The design of this new directional passive air sampler (DPAS) is described. Wind tunnel tests show the DPAS responding to wind direction changes at wind velocities as low as  $0.9 \text{ m s}^{-1}$ . Measurements of wind velocities inside and outside the DPAS revealed good correlation for potential quantitative results. The DPAS was tested at a wind velocity of  $2.0 \text{ m s}^{-1}$  using stainless steel meshes impregnated with triethanolamine (TEA) for nitrogen dioxide ( $\text{NO}_2$ ). The source direction was clearly identifiable. Further tests and field trials are advocated.

### Keywords:

Directional passive air sampling  
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## 1. Introduction

It has long been recognised that air quality has a strong link with human health and well-being. The World Health Organisation (WHO) has been publishing and updating air quality guidelines for common air pollutants like particulate matter (PM), ozone ( $\text{O}_3$ ), nitrogen dioxide ( $\text{NO}_2$ ) and sulphur dioxide ( $\text{SO}_2$ ) since 1987, to provide information on reducing the health impacts of air pollution. In order to ensure compliance with these guidelines, it is necessary to continuously monitor the air concentrations of these pollutants at sites representative of population exposures (WHO, 2006).

In the UK, automatic monitoring of the key air pollutants started in the 1970s. For example, the Department of Environment, Food and Rural Affairs (DEFRA) has been funding the UK Automatic Urban and Rural Air Quality Monitoring Networks (AURN) to continuously monitor  $\text{NO}_2$  levels in ambient air using chemiluminescent analysers at nearly 100 monitoring sites (NSCA, 2007; DEFRA, 2007b). Although capable of making accurate real-time measurements of pollutants in ambient air, these continuous monitors are restricted from being more widely applied due to their requirements for an uninterrupted power supply, space to accommodate bulky instruments and their protective housings, and regular site visits by specialist staff for calibration and maintenance purposes. Consequently, continuous monitoring is relatively costly and only performed at key monitoring stations. Moreover, the large amount of finely time-resolved monitoring

data generated by continuous monitors require human and machine time to analyse, which may not always be necessary. As an alternative to such continuous monitoring, it is therefore important to develop passive techniques for time-integrated measurements of air pollutants, based on samplers that do not require regular visits by specialist staff, and are reliable, compact and easily-deployed.

One of the important alternatives to continuous monitors is passive samplers designed to take up air pollutants without the need for a pump or power supply. Tube and badge type diffusive samplers for work-place monitoring were first introduced in the 1970s, together with the first attempt to mathematically describe the uptake process using Fick's Law of diffusion (Palmer and Gunnison, 1973; Palmer et al., 1976; Tompkins and Goldsmith, 1977; Moore, 1986). Since these diffusive samplers are inexpensive, lightweight and easy to use, they are suitable for deployment almost anywhere to form a high density monitoring network for large scale air-quality surveys and pollution source mapping. For example, ground-level  $\text{NO}_2$  concentrations are measured with diffusion tubes at  $\sim 1200$  urban background and roadside sites throughout the UK, compared to the  $\sim 100$  continuous samplers deployed across the country (NSCA, 2007; DEFRA, 2007b).

Diffusive passive sampling is cheap and samplers can be deployed at many sites simultaneously. However, uptake rates and performance may be subject to variability, caused by environmental factors (Campbell et al., 1994; Gair and Penkett, 1995;

DeSantis et al., 1997), and long exposure/deployment times [e.g. typically some weeks for NO<sub>2</sub> (Palmer et al., 1976)] are required under ambient conditions to give a sufficient mass for detection.

New legislation increasingly requires investment in environmental monitoring and pollution control that will deliver the greatest added value to regulatory bodies, by reducing costs and targeting the most culpable sources. Directional analysis of monitoring data obtained with either continuous or passive sampler networks can help with identifying pollution sources, inferring emission strengths, validating emission inventories, quantifying spatial patterns of emissions and assessing pollution impacts in the networked areas.

Currently, directional analysis of air pollution is usually done by plotting ambient pollution levels measured at a single monitoring site against azimuth as a “pollution rose”. With this method it is sometimes possible to identify contributions from particular individual sources (e.g., stacks) or sectors (e.g., an industrial estate or an urban area), although there have been no systematic procedures for doing so and directional data therefore tend to be used descriptively rather than quantitatively.

It is our contention that there is therefore a need and opportunity to develop an additional sampling tool or approach. This would combine the benefits of cheap, passive sampling, the benefits of directional sampling for source identification and attribution, and the benefits of more rapid (kinetic passive) sampling using channelled wind flows to bring pollutant to the sampler surface. A comparison of the practical characteristics of continuous monitors, diffusive samplers and the conceived directional passive air sampler (DPAS) is given in Table 1.

A new design of a cost-effective, rotatable, directional passive air sampler is described here. It was tested in a wind tunnel, to understand its basic performance in response to wind direction and wind velocity. NO<sub>2</sub> was selected as the pollutant to test the new sampler prototype. NO<sub>2</sub> is a commonly-occurring pollutant, and its adverse effects on human respiratory systems and the environment have been reported (WHO Regional Office for Europe, 2003; DEFRA, 2007a; DEFRA, 2007b). Triethanolamine (TEA) is widely used to sample NO<sub>2</sub> in conventional diffusion tubes, and was therefore used in the new flux-based prototype as the absorbing reagent. Following this prototype design and preliminary testing, suggestions are made for improvements and further trials.

## 2. Desirable Features of a DPAS

Before presenting the new sampler design, some important features regarding both performance and practicalities expected in a DPAS are introduced in this section. These features were kept in mind throughout the development process, and tested in this study to confirm that the design had incorporated these required features.

### 2.1. Responsiveness to wind direction changes

A DPAS differs from a conventional passive diffusive sampler in that it is capable of recording direction-resolved monitoring data. To achieve this, different parts of the sampling medium in a DPAS should be designated to capture pollutants from different directions. If there is a moving part in the DPAS to guide air through to a specific part of the sampling medium, it should move with as little friction as possible and be responsive to changes in wind direction, even if the wind velocity is relatively low.

### 2.2. Sensitivity

Because wind directions keep changing in the real environment, any specific angular sector of the sampling medium in the DPAS may only be exposed for a short period. Also, in contrast to a continuous monitor, a DPAS does not rely on a pump or any other active means to sample a large volume of air; this implies that the amount of pollutant available for capture could be very limited. In order to collect sufficient pollutant for analysis, the DPAS should either have a very sensitive sampling medium that responds quickly to record the increment in pollution, or have an alternative means to enhance the uptake rate and be coupled with a sensitive method of detection. Considering that there may not be much to increase in the sensitivity of the sampling medium, and an over-sensitive sampling medium could be subject to interferences, it may be easier to increase the overall sensitivity of a DPAS by using flux-based techniques to enhance the uptake rate. In this way, the overall deployment time of the DPAS can also be effectively shortened, in comparison to the time needed to sample the same level of pollution by a conventional passive diffusive sampler.

### 2.3. Resolution

It is desirable that a DPAS used alone or in combination with others can accurately suggest the geographical location of pollution sources. For this purpose, the sampler needs to be able to distinguish between narrow sectors having impacts from localised sources (e.g., point sources like stacks), and broader sectors having impacts from more extended sources (e.g., area and line sources such as landfills, roads, stockpiles and other fugitive sources). Moreover, it should also be able to distinguish sectors containing few sources and therefore only background levels of pollution. Thus the DPAS needs to have good resolution in terms of both angular discrimination and in terms of the ratio of detected source signals to background levels.

### 2.4. Flexibility/Versatility

It would be preferable if the DPAS design can be used to sample different pollutants in different campaigns. This could effectively lower the complexity and costs of designing and manufacturing different types of DPAS. If changes are necessary to accommodate various pollutants, it is desirable to have a modular design so that only parts of the DPAS need to be replaced, thereby avoiding any major modification to the deployment system.

**Table 1.** A comparison of practical characteristics of continuous monitors, diffusive samplers and the conceived directional passive air sampler (DPAS)

Characteristics	Type of sampler		
	Continuous monitor	Diffusive sampler	DPAS
Diffusive sampling	Negligible	Major	Minor
Kinetic/flux-based passive sampling	Negligible	Minor	Major
Turbulence exposure	From the pump	From wind (minor)	From wind (major)
Wind direction measurement	Measured separately	Measured separately	Inherent
Power supply	Required	Not required	Not required
Calibration before deployment	Required	Not required	Not required

## 2.5. Reliability

A DPAS should be capable of performing consistently throughout the deployment period. To achieve this, both the deployment system and the sampling medium should be relatively stable to resist the impacts of environmental factors such as temperature, humidity, and wind-induced vibration.

## 2.6. Robustness

It is anticipated that the sampler may encounter different conditions in the real environment. Therefore, a DPAS should be robust, to reduce the number of site visits and maintenance. Durable materials should be used for the outside body of the sampler and for the internal sampling medium matrix, and necessary sheltering should be considered and provided for the sampling medium.

## 2.7. Integrity

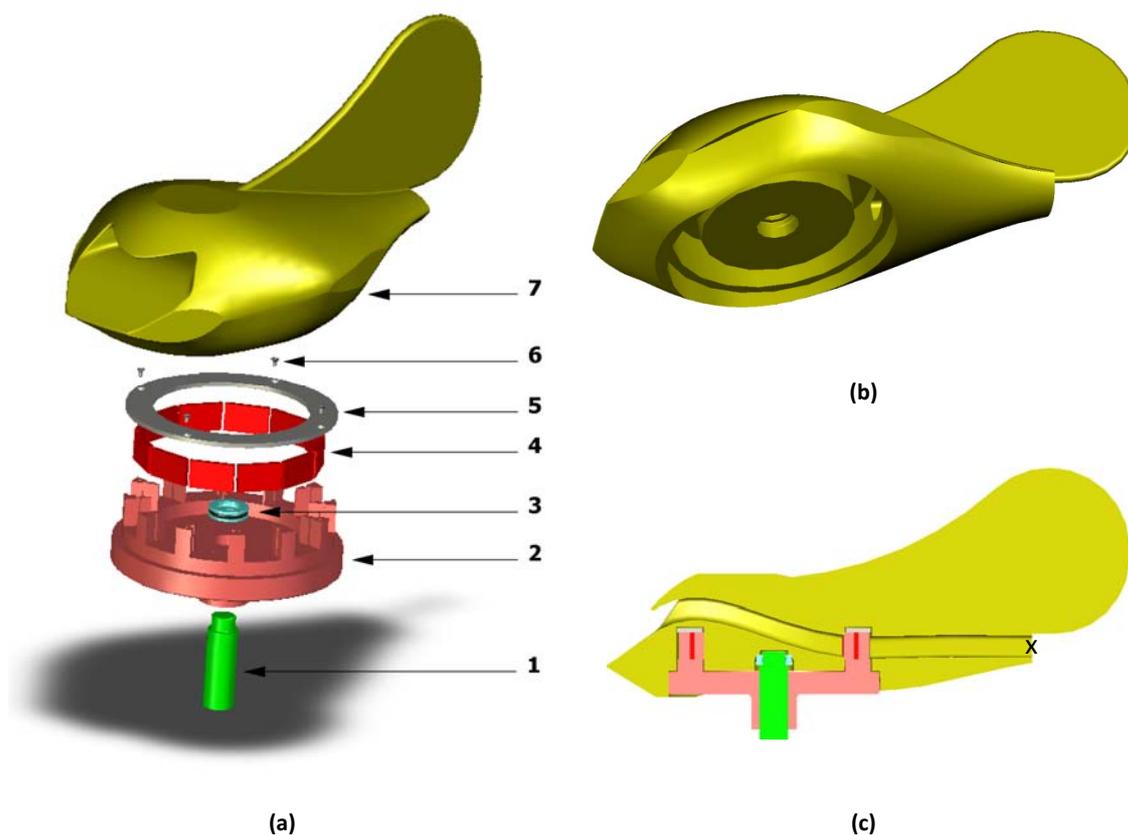
It is important that the pollutant record is retained on the sampling medium after exposure, that there is no loss via degradation or volatilisation, and that there is minimal “leakage” of pollutants to sheltered portions of the sampling media that are not being exposed to the wind in line with the wind direction at any given time.

## 2.8. Ease of use

Although a DPAS could be more complex than conventional passive diffusive samplers, it should still be relatively easy to use, so that protocols of deployment and analysis of the sampler can be standardised to achieve satisfactory repeatability and reproducibility under the same conditions. It should not require specialist staff to deploy or collect the sampler.

## 2.9. Cost-effectiveness

The greatest advantage of passive sampling techniques lies in that they can provide satisfactory monitoring results at much lower costs than continuous monitors. The overall cost of manufacturing and analysing a DPAS needs to be kept low, even if it might be more complex than conventional passive diffusive samplers. In this way, affordable networks of such samplers can be maintained. Compared with networks formed by conventional passive diffusive samplers, the DPAS network would be better able to determine the geographical positions and the emission strengths of pollution sources, by triangulation. The monitoring results can also be used to evaluate the differential impacts of particular sources by comparing pairs of relevant samplers lying upwind and downwind of a particular source.



**Figure 1.** The rotatable DPAS and its components. (a) the exploded scheme of the  $\text{NO}_2$  rotatable DPAS: 1 – the supporting pole (static), 2 – the sample carousel (static,  $\Phi \approx 13.6$  cm), 3 – the bearing supporting the upper part (rotates), 4 – sampling media (static), 5 – sampling medium cover ring (static,  $\Phi \approx 12.1$  cm), 6 – screws, 7 – the upper part of the rotatable DPAS ( $L \approx 34.5$  cm); (b) the upper part of the rotatable DPAS, in which there is a circular ditch sheltering the sampling media and restricting air movement to the air channel; (c) the YZ Plane cross section view of the assembled rotatable DPAS revealing the specially-shaped channel in the upper part of the rotatable DPAS leading the ambient air to go through one of the twelve sampling media (the red vertical line on the right in the air channel) fitted in the sampling medium tray while sheltering the others (the red vertical line on the left under the air channel) in the circular ditch in the upper part of the rotatable DPAS. “x” marks the position of outlet velocity measurement as discussed in “Testing the Sampler Performance” Section.

### 3. Description of the Sampler Design

The flow-through rotatable DPAS for ambient air sampling developed in this study and its components are shown in Figure 1.

The DPAS can be simply divided into an upper and a lower part detachable from each other. The upper part is a whole piece with a streamlined design and a vane at its rear (Figure 1a, Part 7), which enables the upper part to turn into the prevailing wind direction when supported by a central pole (Figure 1b). Inside the upper part there is a 7 mm wide circular ditch (Figure 1b) for accommodating the sampling media, which are held by the lower part with a specially-shaped channel leading ambient air through them (Figure 1c). The lower part can be further broken down into three main components – the sample carousel (Figure 1a, Part 2), the sampling media (Figure 1a, Part 4) and the sampling medium cover ring (Figure 1a, Part 5). The sampling media used in this prototype are in the form of twelve sections, each being 2.10 cm wide by 1.80 cm high (Figure 1a, Part 4). These are fitted into the twelve slots aligned in a circle on the sample carousel to form a sampling medium ring. A sampling medium cover ring (Figure 1a, Part 5) is then fixed with screws on the top of the pillars forming the slots to restrain the possible movement of the sampling media at high wind velocities. When assembling the rotatable DPAS, the sample carousel is fixed through its central hole on the supporting pole, on top of which sits the upper part of the rotatable DPAS with a bearing fitted in its centre hole at the bottom. There is no contact but a very narrow gap between the upper and the lower parts of the rotatable DPAS, so that the lower part remains static, to record pollution from different directions, while the upper part rotates freely with the prevailing wind direction. The thickness of the pillars forming the slots on the sample carousel is adjusted to closely fit the width of the ditch. This effectively blocks the individual sampling units from each other so that they form separate sampling windows. Together with the help of the sampling medium cover ring, any extra space inside the ditch is greatly reduced to avoid air movement from one sampling window to another. When the upper part of the rotatable DPAS is facing a specific wind direction, the air is let into the channel with a cross section slightly smaller than that of each sampling medium (Figure 2). The air bypasses the sheltered sampling windows on the sampling medium ring (Figure 1c), and only impinges on to the one that is exposed in the airway. In this way the air from a particular direction is funnelled onto a particular part of the sampling medium ring, and is well-separated from other parts of it. There is flexibility to adjust the number of sampling windows or, indeed, to have a continuous sampling medium strip around the diameter of the ditch – depending on the analyte/ sampling matrix.

### 4. Testing the Sampler Performance

#### 4.1. Start-up and line-up wind velocities

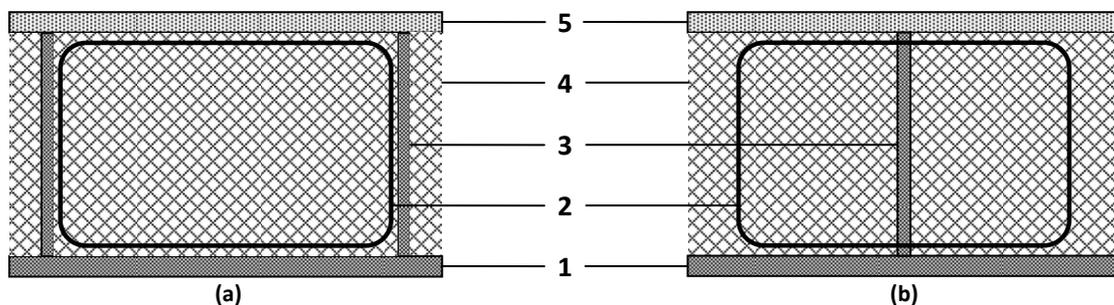
As the purpose of the rotatable DPAS is to collect airborne pollutants from different directions by turning its upper part to the prevailing wind direction, it is important to know how sensitive it is in responding to winds with different velocities. The lowest wind velocities required for positioning the rotatable upper part to the wind direction were measured by placing the rotatable DPAS in the middle of a wind tunnel (40 cm × 40 cm cross-section, Plint & Partners, UK). The front of the DPAS was positioned at varying angles across the wind direction and, by gradually increasing the velocity, the wind velocities at which the DPAS first started to turn to the wind direction and at which it was fully aligned to the wind direction were noted, to give an indication of its responsiveness to wind velocity and direction changes.

#### 4.2. Wind velocity attenuation and the choice of the sampling medium

It is reasonable to expect that air would slow down as it passes through the rotatable DPAS, because of the aerodynamic features of the air channel in the upper part of the rotatable DPAS and of the sampling medium inside the channel. Tests were performed to see the relationship between the wind velocities measured outside and inside the DPAS using a hot wire anemometer. By correlating these external and internal velocities it is possible to estimate the air volumes “sampled” by the DPAS.

Depending on the sampling medium used, the degree of resistance to air flows inside the chamber will vary. Hence, different media/configurations were tested. Passive sampling might be conducted using coated meshes, polyurethane foams or vials of sampling solutions exposed to the air flow. Hence, tests were performed as follows:

A piece of stainless steel mesh (wire diameter 0.25 mm with aperture size 0.94 mm × 0.94 mm), together with another two types of stainless steel meshes (wire diameter 0.13 mm with aperture size 0.13 mm × 0.13 mm and wire diameter 0.51 mm with aperture size 1.54 mm × 1.54 mm) and a piece of 2 mm thick polyurethane foam (PUF, 0.035 g cm<sup>-3</sup>, Klaus Ziemer GmbH, Germany) were fitted into the DPAS to determine the wind velocity changes before and after the air passed through the rotatable DPAS. Wind velocities immediately at the outlet of the air channel were measured as the internal wind velocities when the external wind velocity in the wind tunnel was varied from 1.0 to 20.0 m s<sup>-1</sup>.



**Figure 2.** Cross section view of different sampling situations. 1 – the sample carousel in the lower part of the DPAS, 2 – the air channel in the upper part, whose cross-sectional area is slightly smaller than that of an individual sampling window, 3 – pillars on the sample carousel forming separated sampling windows, 4 – individual sampling media, 5 – sampling medium cover ring. (a) Only one sampling window is exposed in the airway; (b) more than one sampling window is exposed in the airway, under which circumstance the minimised width of the pillars separating the individual sampling media helps reduce the impact on sampling and source direction attribution.

To evaluate the impact of sampling media on the flow rate, a control experiment with no sampling medium fitted into the rotatable DPAS was also conducted. The results from these experiments were examined to select the sampling medium that produced the lowest drop in velocity, whilst maintaining a stable correlation between the internal and external wind velocities.

#### 4.3. Directional sampling simulation in the wind tunnel

Since the wind tunnel used in this study could only generate wind from one fixed direction, it was considered that the best way to test the directional sampling capability of the rotatable DPAS was to fix the rotatable upper part of the DPAS to face the wind direction. The inlet was aligned to expose only one sampling medium in the continuous air flow whilst leaving the other media sheltered. Amounts of NO<sub>2</sub> recorded on the exposed and sheltered media were then compared with NO<sub>2</sub> in ambient air that was drawn into the wind tunnel from the room outside. Separate sampling confirmed the stability of ambient NO<sub>2</sub> levels in the sampling environment.

For these trials, stainless steel meshes were soaked in 5% Decon 90 Milli-Q water solution for 24 h, thoroughly rinsed with Milli-Q water and then dried at 70 °C in a DC1000 drying cabinet (Genlab Limited, UK) over night. The clean meshes were numbered and weighed on a Mettler AT 250 micro balance before being soaked in 50% (v/v) TEA acetone solution (both chemicals were supplied by Fisher Scientific, UK) in capped Petri dishes for 30 min. Excess absorbent solution was then removed by placing the meshes between layers of filter papers, and the meshes were then weighed again to record the amount of absorbent retained. Freshly prepared meshes were stored individually in air-tight polystyrene vials prior to deployment.

On deployment, twelve sampling media were fitted into the numbered slots in the DPAS with stainless steel tweezers, once in the wind tunnel. Another three meshes were left in unopened storage vials to act as field blanks. Sampling Slot 1 was aligned to the air channel and secured in position with tape. The DPAS was then set up with the air channel inlet directly facing the wind direction. The wind velocity was maintained at ~3.3 m s<sup>-1</sup> (externally) and ~2.0 m s<sup>-1</sup> (internally), and was monitored every 15 min with a RS327-0641 handheld hot-wire anemometer (RS Components Ltd, UK). The DPAS was left in the continuous air flow in the wind tunnel for 8 h. After deployment, the meshes were returned to the original storage vials for transportation to the laboratory for chemical analysis.

#### 4.4. Chemical analysis of the directional samples

The chemical analytical method is similar to that mentioned in other studies (Palmes et al., 1976; Shooter, 1993; Campbell et al., 1994). 3.000 ml 2% (w/v) solution of sulphanilamide (AnalaR, VWR International Ltd., England) in 5% (v/v) ortho-phosphoric acid (85%, BDH Laboratories, England) and 0.150 ml 0.14% w/w solution of N-(1, naphthyl)ethylenediamine dihydrochloride (NEDA) (AnalaR, VWR International, Ltd.) were added into each acrylic vial containing the individual meshes. The vials were then re-capped, shaken vigorously for half a minute, and left to stand for 5 min before the extracts were analysed on a UV/vis-spectrophotometer (CE 1011, CECIL Instruments, UK) for light absorbance at a wavelength of 540 nm. The amount of NO<sub>2</sub> (µg) trapped on each individual sampling medium was determined against calibration on nitrite standard solutions prepared with sodium nitrite (100.04%, Fisher Scientific, UK) against their light absorbance at the same wavelength.

For ease of viewing, the amounts of NO<sub>2</sub> and TEA on the twelve individual sampling media were plotted in the form of radar charts. This enabled correlations between the amounts of TEA and

NO<sub>2</sub> to be made, as well as comparisons of the exposed and sheltered sampling media.

#### 4.5. QA/QC

The retrieved sampling media were analysed within 24 h of the collection time, and fresh nitrite standards were prepared for each analysis. Before the analysis, the small polystyrene vials for containing the prepared and the used sampling media, together with their caps, and the cuvettes used for the colorimetric analysis were soaked in 5% v/v Decon 90 Milli-Q water solution overnight and thoroughly rinsed with Milli-Q water.

The three unexposed sampling media used as field blanks were analysed along with the deployed ones. Readings from the deployed sampling media were corrected with those from the field blanks. The lower detection limit of the method was calculated as three times the standard deviation of the three blanks.

### 5. Results & Discussion

#### 5.1. Start-up and line-up wind velocities

As the upper part of the current rotatable DPAS has a certain mass, it needs some momentum from the wind to turn itself to the wind direction. The wind velocities required to start up the upper part of the rotatable DPAS moving to align it with the wind are listed in Table 2, for different initial angles between the DPAS vane and the wind tunnel flow.

**Table 2.** Wind velocities at which the upper part of the rotatable DPAS started to turn into the wind direction. Wind velocity values are means of triplicate measurements

Initial position (°, from the wind direction)	External wind velocity (m s <sup>-1</sup> )	
	Start-up	Line-up
10	3.1 ± 0.2	5.8 ± 1.8
20	2.4 ± 0.2	7.9 ± 0.4
30	2.2 ± 0.1	7.8 ± 0.0
40	2.5 ± 0.3	8.6 ± 2.9
50	2.3 ± 0.7	12.0 ± 2.6
60	1.7 ± 0.1	9.8 ± 0.4
70	1.0 ± 0.0	10.5 ± 1.3
80	0.9 ± 0.1	11.9 ± 0.1
90	1.6 ± 0.3	14.0 ± 0.0

The data show that the upper part of the rotatable DPAS could start aligning itself at wind velocities ranging from 0.9 to 3.1 m s<sup>-1</sup>, meaning that it is relatively easy to get the rotatable DPAS to work (the average wind velocity at 1.5 m in Lancaster, U.K. is typically 4–5 m s<sup>-1</sup>, for example). It can also be seen that the greater the angle between the vane and the wind tunnel flow, the easier it is to start the sampler turning into the wind.

It was observed during the experiment that winds at the start-up velocities were only sufficient to align the upper part of the DPAS to within a 5° tolerance of the real wind direction, whereas stronger winds were needed to truly position the rotatable upper part to the wind direction. These “line-up values” are also listed in Table 2.

The irregular values seem to suggest that it is relatively difficult to align the upper part of the DPAS exactly to the wind direction, which limits the precision of the sampler for determining the arrival directions of the wind/pollutants. For example, the DPAS may only be aligned to within a 5° tolerance of the real wind direction at the lower wind velocities. However, this is considered

an acceptable level of precision, because (as configured here) each individual sampling medium in the rotatable DPAS is responsible for 30° sampling, and would be chemically analysed as a whole unit, so any details of a finer resolution than 30° would be ignored. Also, as an indicative tool, it is the pollutant distribution recorded on the whole sampling medium ring that will be used to track the pollution source. Therefore, a slight deviation (1/6 of the sampler's resolution) on any single sampling medium should not effectively change the tracking result. Improvements may be possible in later prototypes.

## 5.2. Wind velocity attenuation and the choice of the sampling medium

Figure 3 shows the “internal” wind velocities measured with different sampling media fitted, plotted against those measured in the wind tunnel (external wind velocities).

In all cases, the internal velocity was lower than that measured externally. This decrease was found to be ~40% for the medium and the wide aperture meshes, ~55% for the fine aperture mesh and ~85% for the PUFs. The relationships of internal wind velocity versus external wind velocity were slightly curvilinear. However, Figure 3 also shows that if linear relationships were assumed,  $R^2$  values were greater than 0.9. Due to the possible incursion of particulate matter and problems arising from humidity, the medium aperture mesh was selected for further experiments.

## 5.3. Directional sampling simulation in the wind tunnel

There is effectively no emission source of  $\text{NO}_2$  inside the laboratory where the wind tunnel was located, but the laboratory air did contain typical background levels of  $\text{NO}_2$  for indoor air. Daily monitoring studies using diffusion tubes carried out in this laboratory suggested that  $\text{NO}_2$  level in the indoor air was  $23 \pm 2 \mu\text{g m}^{-3}$ .

For each of the twelve sampling segments, Figure 4 shows the amounts of (a)  $\text{NO}_2$  captured and (b) TEA initially on the segment.

The sampling medium in Slot 1 which was exposed in the airway for 8 h can be very easily identified in Figure 4 (a), as the absolute amount of  $\text{NO}_2$  trapped on it is much higher (typically about five times) than those on the sheltered ones. Ideally, all the sheltered sampling media should only receive pollutants by

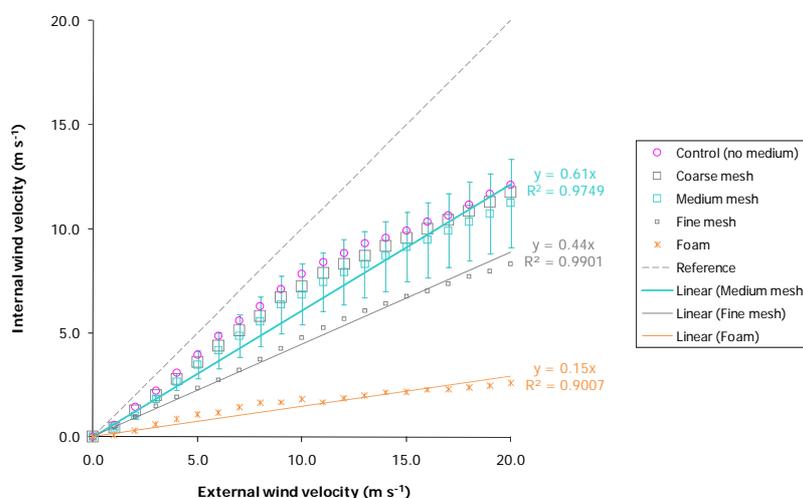
molecular diffusion, so they should have about the same level of  $\text{NO}_2$  trapped on them, given a sufficiently long period of time and assuming that the amounts and surface areas of TEA were similar for all media. However, although sampling media in Slots 12, 2, 11 and 3 have less  $\text{NO}_2$  trapped on them than the directly exposed Sampling Medium 1 does, they still captured slightly more  $\text{NO}_2$  than their deeply sheltered counterparts 9, 8, 7, 6 and 5 did, with an averaged  $\text{NO}_2$  amount of  $0.35 \pm 0.06 \mu\text{g}$  against  $0.25 \pm 0.05 \mu\text{g}$  from the latter. This is presumably due to air leakage from Slot 1 to its neighbouring Slots 12, 2, 11, 3.

In summary, the difference in mass of  $\text{NO}_2$  trapped between the exposed mesh and the sheltered meshes (i.e. the “signal-to-noise ratio”) needs to be maximised for successful deployment of the DPAS. This can be achieved by better isolation of the sheltered meshes and/or longer deployment times, but the studies here clearly showed the potential of the sampler for directional discrimination.

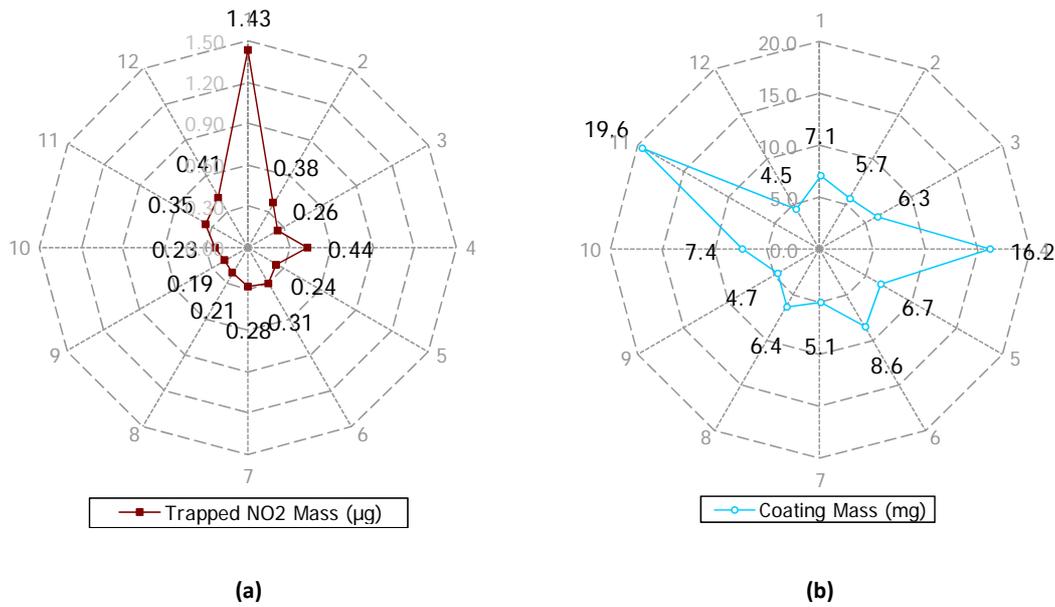
Given the generally decreasing trend in the amounts of  $\text{NO}_2$  on the sheltered sampling media from front to back, the relatively large amount of  $\text{NO}_2$  on the sampling medium in Slot 4 was suspected to be caused by the relatively large amount of TEA absorbed on it (Figure 4b). Therefore, a bivariate Spearman's  $\rho$  correlation analysis between the amounts of TEA absorbent coated onto Sampling Media 2 – 12 and the  $\text{NO}_2$  trapped on them was carried out, but the result only showed very poor correlation between the two variables ( $R = 0.182$ ,  $p = 0.593$ ). Considering that the amount of  $\text{NO}_2$  trapped on a certain sampling medium may depend more on the amount of TEA absorbent coated on it when the sampling is by molecular diffusion, and that due to the potential air leakage from Slot 1, sampling media next to Slot 1 might have been sampling at a higher rate than they did by diffusion only, the same correlation analysis was carried out again only on Sampling Media 3 – 11. This time a strong correlation between the two concerned variables was revealed ( $R = 0.810$ ,  $p = 0.015$ ). This supports the theory that leaked air from Slot 1 could be affecting neighbouring Slot 2 and 12.

## 5.4. Estimation of the $\text{NO}_2$ air concentration

As the above correlation suggests that the sheltered Sampling Media 3 – 11 might have taken up  $\text{NO}_2$  by molecular diffusion only, it was attempted to estimate the  $\text{NO}_2$  air concentration by using Fick's First Law of diffusion and the amounts of  $\text{NO}_2$  collected on the sheltered Sampling Media 3 – 11.



**Figure 3.** Correlations between the external and internal wind velocities with different sampling media fitted in the rotatable DPAS. Data points are means of triplicate measurements. Blue error bars are standard deviations of triplicate measurements for the medium mesh. Standard deviations for the other media are not shown for ease of viewing.



**Figure 4.** Trapped NO<sub>2</sub> and the original TEA absorbent on each individual sampling medium. **(a)** The amounts of NO<sub>2</sub> captured on each individual sampling medium. 1 is the one directly exposed to the 2 m s<sup>-1</sup> internal wind for 8 h, while the others were sheltered in the narrow pitch in the upper part of the rotatable DPAS; **(b)** the amounts of TEA absorbent on each individual sampling medium.

When assuming the NO<sub>2</sub> air concentration to be zero in the close vicinity of the meshes due to the absorption in TEA, Fick's First Law of diffusion can be simplified as:

$$F = D \frac{c}{z} \tag{1}$$

in which case *F* is the diffusive flux of NO<sub>2</sub>; *D* is the diffusion coefficient of NO<sub>2</sub> in the air; *c* is the NO<sub>2</sub> air concentration and *z* is the length of the diffusion pathway (Palmes et al., 1976).

As the amount of NO<sub>2</sub> trapped on a single mesh *Q* can be expressed as:

$$Q = FA t \tag{2}$$

where *A* is the cross-sectional area of the diffusion pathway and *t* is the exposure time.

Therefore, the NO<sub>2</sub> air concentration *c* can be derived by combining Equations (1) and (2) as:

$$c = \frac{z}{DA} \frac{Q}{t} \tag{3}$$

In this study, the diffusion pathway length *z* is regarded as the distance between the mesh and the inside wall of the ditch in the upper part of the rotating DPAS, in which case is ~2.95 mm; the diffusion coefficient for NO<sub>2</sub> in the air *D* under the condition of study is 0.154 cm<sup>2</sup> s<sup>-1</sup>; as there are comparatively wide openings on the sampling media (the meshes) reducing the effective cross-sectional area of the diffusion pathway, *A* is calculated as the sampling window area (18.10 mm × 17.65 mm) minus the total area of the openings on the mesh (~240 mm<sup>2</sup>), i.e., ~79 mm<sup>2</sup>; the sampling period *t* is 8 h. If these values are inserted together with the amounts of NO<sub>2</sub> trapped on Sampling Media 3 – 11 (*Q*) into Equation (3), the NO<sub>2</sub> air concentration is calculated as 23 ± 6 µg m<sup>-3</sup>. This estimation agrees very well with the separately monitored value of 23 ± 2 µg m<sup>-3</sup> in the same laboratory. This calcula-

tion therefore supports the suggestion that the sheltered sampling media were taking up NO<sub>2</sub> by molecular diffusion only.

### 5.5. Sampling efficiency of the mesh design

A simple calculation was done to evaluate the efficiency of the meshes used in this study as the sampling medium for NO<sub>2</sub> in the ambient air. In this case the efficiency of interest is the proportion (or percentage) of NO<sub>2</sub> entering the sampler that is collected by the relevant exposed sampling medium. The effectively sampled air volume (*V<sub>sampled</sub>*) can be estimated as follows with the amount of NO<sub>2</sub> collected on Mesh 1 (*m<sub>NO2</sub>*) and the indoor NO<sub>2</sub> concentration measured separately (*c<sub>NO2</sub>*):

$$V_{sampled} = \frac{m_{NO_2}}{c_{NO_2}} = \frac{1.43 \mu g}{23 \mu g m^{-3}} \approx 0.062 m^3$$

While the volume of the air passing through the sampling window (*V<sub>through</sub>*) during the 8 h could be calculated from the area of the sampling window (*A<sub>window</sub>*), the air flow rate (*v<sub>air</sub>*), and the exposure time (*t*), as follows:

$$V_{through} = A_{window} v_{air} t = 18.10 mm \times 17.65 mm \times 2.0 m s^{-1} \times 8 h \approx 18.4 m^3$$

Therefore, the sampling efficiency (*E<sub>sampling</sub>*) can be calculated as the proportion between the two volumes as:

$$E_{sampling} = \frac{V_{sampled}}{V_{through}} \times 100\% = \frac{0.062 m^3}{18.4 m^3} \times 100\% \approx 0.34\%$$

It can be seen that a very small portion (less than 1%) of the through flow was needed to generate this directional sampling result, which proves that this prototype of the rotatable DPAS was sufficiently sensitive.

NO<sub>2</sub> is relatively abundant in the atmosphere and coupled with sensitive analytical methods – a low sampling efficiency does not hamper its analysis using this DPAS configuration. However,

other pollutants may require configuration of sampler/matrix designed to achieve greater sampling efficiency.

## 6. Future Needs and Directions

It has been demonstrated that the new rotatable directional passive air sampler responds to low wind velocities and is capable of directional sampling, with a clear signal-to-noise ratio obtained after just 8 h exposure. The relationship between the wind velocities inside and outside this prototype within the range of 1.0 – 20.0 m s<sup>-1</sup> can be approximated by a linear relationship. This will aid in the estimation of air concentration from the mass sampled.

Sampling tests in the wind tunnel, under controlled conditions, showed that the rotatable DPAS in this study could distinguish the direction of a NO<sub>2</sub> source. In order to further infer the NO<sub>2</sub> air concentration, the effectively sampled air volume ( $V_{sampled}$ ) is needed. This could be done with a full calibration against a continuous monitor to obtain the sampling efficiency ( $E_{sampling}$ ) under different conditions. The volume of the air passing through the DPAS ( $V_{through}$ ) from a certain direction could be calculated using a record of the wind velocities occurring during the deployment. Then  $V_{sampled}$  could be derived with the method described in the discussion section.

Under the tested conditions, the DPAS prototype only retained NO<sub>2</sub> from < 1% of the air passing through its air channel to generate the directional sampling result. This sensitivity is encouraging, although, saturation of the absorbent/sampling media (TEA in this study) is a limitation to longer-term sampling campaigns. Various configurations can be used in future to vary sampling efficiency and analyte storage capacity.

Although the current prototype was designed for monitoring NO<sub>2</sub> in the ambient air, with small modifications using different sorbents/trapping media, the new design should be capable of sampling other airborne pollutants.

In complex real-world situations, exposure times to air from different directions, and from potentially multiple sources in those different directions, will combine to supply the masses of pollutants retained by the DPAS. In these situations it may be necessary to deploy several DPASs in order to distinguish between different sources by triangulation. A future challenge will therefore be to develop approaches which enable the pollutant signals obtained from several DPASs to be interpreted in terms of impacts from individual sources.

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