Effectiveness of Green Infrastructure for Improvement of Air Quality in Urban Street Canyons

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The effectiveness of green infrastructure to improve urban air quality

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Abstract

Street-level concentrations of nitrogen dioxide (NO_2) and particulate matter (PM) exceed public health standards in many cities, causing increased mortality and morbidity. Concentrations can be reduced by controlling emissions, increasing dispersion, or increasing deposition rates, but little attention has been paid to the latter as a pollution control method. Both NO_2 and PM are deposited onto surfaces at rates that vary according to the nature of the surface; deposition rates to vegetation are much higher than those to hard, built surfaces. Previously, city-scale studies have suggested that deposition to vegetation

can make a very modest improvement (<5%) to urban air quality. However, few studies take full account of the interplay between urban form and vegetation, specifically the enhanced residence time of air in street canyons. This study shows that increasing deposition by the planting of vegetation in street canyons can reduce street-level concentrations in those canyons by as much as 40% for NO_2 and 60% for PM. Substantial street-level air quality improvements can be gained through action at the scale of a single street canyon or across city-sized areas of canyons. Moreover, vegetation will continue to offer benefits in the reduction of pollution even if the traffic source is removed from city centers. Thus, judicious use of vegetation can create an efficient urban pollutant filter, yielding rapid and sustained improvements in street-level air quality in dense urban areas.

Introduction

Outdoor air pollution causes 35 000-50 000 premature deaths per year in the UK [1], and more than 1 million worldwide[2], in addition to increased morbidity[3]. The pollutants mostly harmful in cities in the developed world are nitrogen dioxide (NO_2), ozone, sulfur dioxide and particulate matter with aerodynamic diameter less than 10 μm (PM_{10}), all of which cause or exacerbate pulmonary and cardiac diseases[4,5]. Attempts to reduce concentrations of these air pollutants have been ongoing for several decades, with much progress being made[3]. Methods usually center on the reduction of pollutant emissions, an increase in atmospheric dispersion, or the locating of high emitters away from existing pollution hotspots or areas of high population. Yet concentrations of air pollutants in many urban areas still consistently exceed public health standards, with mean concentration trends that are near-zero or even increasing[6]. Furthermore, there is a growing body of evidence that there is no safe threshold for exposure to air pollutants, especially PM[7, 8], so strategies are required to continue to drive concentrations down. Air quality management is particularly needed in poorly ventilated street canyons[61].

This study focuses on NO_2 and PM_{10}, which are the dominant pollutants in most urban areas, where they are largely derived from vehicle emissions (e.g. ~50% of NO_2 and ~80% of PM_{10} in Central

London, U. K.[9]). Although vehicular pollutants are reduced by dispersion, this is limited at the street-level by in-canyon air recirculation and low wind speeds. Pollutant concentrations can also be reduced by increasing dry deposition to surfaces. Compared to controlling emissions or enhancing dispersion, relatively little attention has been paid to deposition as a pollution control measure. An effective and accessible means of achieving an enhancement in pollutant deposition is to plant additional vegetation.

Dry deposition reduces pollutant concentration (C_i) through a first-order process,

$$\frac{dC_i}{dt} = -\frac{V_{d,i}}{z} \cdot C_i\,, \qquad (1)$$

where $V_{d,i}$ is the deposition velocity and z is the height through which the pollutant is well-mixed. $V_{d,i}$ depends on the pollutant species, i, and the nature of the surface, and is generally higher to vegetation than to other urban surfaces due to metabolic uptake by the plant, the 'stickiness' of the leaf surface, the large surface area of plants and their aerodynamic properties[10].

Previous estimates of the effect of dry deposition to urban vegetation suggest that it makes small reductions in NO_2 and PM_{10} concentrations on the city-scale[11-15,57,58,59]. For example, in Chicago, reductions of less than 1% are estimated based on current vegetation cover and less than 5% if the urban area was totally covered by trees[11]. These studies are based on relatively large domains of 12-3350 km^2, and use aggregate variables to describe the city or sub-regions of a city. Thus these estimates fail to take account of how the complex geometry of the urban surface affects street-level concentrations, where people are primarily exposed, in particular through the occurrence of street canyons Street canyons are virtually ubiquitous in dense urban areas such as central London, Paris, Rome or Manhatten. Within street canyons, overturning eddy circulations are largely isolated from the urban boundary layer (UBL) above, leading to greatly increased residence times of air within the canyon[16-20] (Fig. 1a). Residence times increase substantially as the aspect ratio (height/width; h/w) of the canyon increases, and as the above-roof wind speed decreases[16,17]. Where street canyons contain a pollutant source (e.g. traffic), the increased residence time within the canyon acts to increase street-level pollutant concentrations. Deposition in street canyons acts to reduce pollutant concentrations, and is more effective than deposition from the UBL, because of (i) the increased surface-to-volume ratio in the canyon as compared with the UBL, (ii) the decreased volume into which the pollutant is initially mixed, and (iii) the higher concentrations found within the street canyon, especially at low wind speeds (Fig. 1b). All these effects could be exploited for pollution control by enhancing deposition velocities to in-canyon surfaces. "Green walls" and street trees offer two means to achieve this enhancement.

Here, a model of street-canyon chemistry and deposition was used to show that judicious use of enhanced-deposition surfaces in concert with the urban form can very substantially reduce pollutant concentrations in one of the parts of the atmosphere where people are most likely to be exposed, i.e. at street level in street canyons. The model results were evaluated against available measurements. They demonstrate that vegetation can be an important component of pollution control strategies in dense urban areas, but only if it is applied with due regard to in-canyon air recirculation and the spatial distribution of emission sources. Urban greening initiatives whose focus is purely to increase urban tree coverage will fail to achieve their maximum air quality potential, and may even worsen air quality in street canyons. By taking into account the particular characteristics of street canyons the potential for air quality improvements could be greatly enhanced.

Experimental

Model formulation

The tortuous flows in street canyons can be simulated using computational fluid dynamic (CFD) models[16,18-20] or deduced from measurement studies[17]. Although some of the modeling studies have used simple chemical schemes to study reacting pollutants, such simulations are very expensive computationally, limiting the scope for sensitivity studies. Therefore, the atmospheric chemistry model CiTTyCAT[21] has been enhanced to simulate mixing and dry deposition within street canyons.

Conceptually, the urban form consists of two compartments, the lower of which can represent either a single street canyon or every street canyon within a city. In this model, CiTTy-Street (Fig. 1c), deposition velocities for roofs, canyon walls and floors can be assigned separately. Emissions of NO_x,

PM_{10} and volatile organic compounds (VOCs), including, if necessary, biogenic VOCs, are input to the lower compartment. Mixing, *M*, between the two compartments is parameterized using dimensionless air exchange rates (*E*) for different canyon aspect ratios[16] for the case of a perpendicular wind and modified by *h* and above-roof wind speed, *u*:

$$M = E \cdot \frac{u}{h}. \quad (2)$$

Concentrations in the upper compartment are refreshed using background concentrations at a rate dependent on *u* and the assumed horizontal length scale of the compartment (*f*). By varying *f*, CiTTy-Street can simulate either a single street canyon, or a series of generic street canyons. When considering exposure to the population across a whole city, the appropriate model output is an average of the canyon and overlying box, weighted by the proportion of the urban population exposed within the urban canyons. Similarly, the effects of parkland and other land-use variations can be accommodated by a weighted average of emissions and deposition in the overlying box. By changing deposition velocities to surfaces in the lower and upper compartments, deposition to different surface types is simulated.

Based on the available literature, it is currently not possible to draw a firm conclusion as to how *E* varies for above-roof wind directions that are not perpendicular to the canyon axis, or indeed the effects of junctions (see supporting information). It was assumed here that for a large area of street canyons the air exchange rates of Liu et al.[16] are valid for all wind directions, although the exact value of *E* for a particular street or set of streets remains a significant uncertainty, and one that may be sensitive to small features of canyon geometry or downwind fetch. For the case of single street canyons under a non-perpendicular wind horizontal ventilation is highly uncertain, but may be substantial (see supporting information). Thus the exchange rates applied in this study must be taken as a first approximation to the generic street canyon situation, and extrapolations to specific canyons must be carried out with caution.CiTTy-Street was evaluated against measurements made in and above street canyons in Hanover, Berlin and Copenhagen[22,23]. It was able to simulate successfully the magnitude of in-canyon NO_2 concentrations in a non-vegetated canyon given information on NO_2 and O_3 concentrations in the

UBL, traffic emission rates, photolytic flux and above-roof wind speed (Fig. S2). The simulated change in anomaly between canyon and UBL concentrations with above-roof wind speed fell between that measured at leeward and windward walls in these canyons (Fig. 1b and Fig. S1). This indicates that the lower compartment represented the canyon-average anomaly well. Full details of the model formulation and evaluation are given in the supporting information.

CiTTy-Street, was used to calculate the effects of urban vegetation on pollutant concentrations, taking central London, UK, as a case study. One control and three green wall/green roof scenarios were considered (Table 1), and each was evaluated for both a single canyon (f = 40 m) and for a large area of street canyons (f = 10 000 m). Note that the latter study does not represent a true simulation of central London, but rather a scaling-up of the single canyon run to represent a large area of generic street canyons. In the following, green walls are considered as a proxy for any in-canyon vegetation which minimally affects in-canyon residence time. Street trees are addressed later, as they have the potential to substantially lengthen canyon air residence times, and so increase street-level pollution concentrations[24,56]. The model results and conclusions we present below are sensitive to *h/w*, but not to canyon volume or cloud cover (see supporting information).

Deposition velocities

In this study, green walls can refer to any type of wall greening, from *Hedera spp.* (ivy) to a complete vertical canopy of grass or broadleaved plant species. Coverings of ivy are commonly found on old buildings in the UK and USA, whereas pilot studies using specially designed vertical canopies have been installed at several locations (e.g. Greenwich Dome, London; Grosvenor House, Luton). A reasonable value for the single-sided leaf area index (LAI) of a green wall is 1-2 m^2 leaf m^{-2} wall[25]. Green roofs can vary from a covering of grass to shrubs and small trees, and thus may have LAI varying from 2 to >5 [26].

NO_2 and O_3 deposition velocities for brick and concrete surfaces are taken from Grøntoft and Raychaudhuri[27]. Literature values for NO_2 deposition velocities for grasses and broadleaf species, i.e.

those species likely to be used for green walls and roofs, generally lie in the range 0.2-0.4 cm s^{-1} [14,28-33], although velocities as high as 1.3 cm s^{-1} have been calculated over tropical pasture[34]. Likewise O_3 deposition velocities for the same species types vary from 0.06 to 1.8 cm s^{-1} [14,35-39]. Given the wide range of candidate species for green walls/roofs, and the substantial overlap in measured deposition velocities for NO_2 and O_3 for different plant types and LAI, it was chosen not to identify a particular species for consideration. Rather, the study was kept general by using deposition velocities in the middle of the most commonly reported values in the literature: 0.3 cm s^{-1} for NO_2, 1.0 cm s^{-1} for O_3 (simulations are carried out during daytime when leaf stomata are likely to be open).

Reported deposition velocities for PM_{10} to vegetation vary by about three orders of magnitude: i.e. from ~0.01 to ~10 cm s^{-1} [25]. In addition, Freer-Smith et al.[40] have reported deposition velocities exceeding 30 cm s^{-1} for particles less than 1 μm in diameter, although to the knowledge of the authors these measurements have not yet been replicated elsewhere. Particle deposition rates are strongly dependent on the surface properties and orientation of the surface, and the wind speed, with higher wind speeds producing greater impaction rates, and hence yielding higher deposition velocities. As leaves typically present favorable surfaces for particle capture, but wind speeds in canyons and immediately above roofs are likely to be low relative to the above-roof mean wind speed, the relatively conservative value of 0.64 cm s^{-1} used by Nowak[11,12] is adopted. Use of this commonly-used deposition velocity aids comparison of the results herein with those of previous studies. However, this V_d of 0.64 cm s^{-1} is considered suitable for this study because it is comparable with that predicted by the process-based model of Petroff and Zhang[41] for deposition to grass (LAI 1-2; the same as the assumed LAI for a green wall) for PM_{10} mass distributions measured in polluted street canyons (mass distribution peaking at 3-10 μm)[42,43], and broadly comparable (although smaller) than the ~1 cm s^{-1} measured for particles of comparable size over moorland by Nemitz et al.[44]. The considerable uncertainty in this deposition velocity should be emphasized, and the deposition velocity may need to be re-evaluated if a different mass size distribution is assumed (see supporting information for further discussion). Secondary processes such as resuspension and possible deposition limitation due to leaf PM_{10} loading are not explicitly modelled. Both these processes would act to decrease overall deposition rates, but the uncertainties are much less than those in the initial choice of $V_{d,PM10}$. Modeled PM_{10} deposition fluxes are compared to measurements below.

Results

Simulating adoption of green walls across large areas of street canyons in CiTTy-Street reduced in-canyon concentrations of NO_2 and PM_{10} by as much as 15% and 23% respectively at u=1 m s^{-1} and h/w=1 (Fig. 2; for results in terms of absolute concentrations, please refer to the supporting information). These reductions were strongly dependent on residence time (i.e. wind speed and canyon geometry) and fraction of canyon wall greening (Table 1), but not on the initial pollutant concentration (see supporting information). The net pollutant flux out of the canyon was itself reduced by 2-11% for NO_x (Fig. S6 left) and became inward for PM_{10}, leading to small concentration reductions in the UBL above the canyon. As cities are a major regional source of air pollutants, for cities with large areal coverage of street canyons (e.g. London, Paris) this is expected to make an important difference to pollutant transport and regional-scale photochemistry, but this aspect is not pursued further here. Release of VOCs from urban trees can influence regional-scale photochemistry[14], but did not significantly alter the NO_2 and PM_{10} budgets in the canyon in this study.

Area-for-area — and for surfaces with comparable leaf-area indices (LAI) and, hence, comparable deposition velocities — the model results showed that greening of in-canyon surfaces is more effective than greening of roofs at reducing street-level pollutant concentrations because it acts directly upon the relatively small volume of air in the canyon, rather than indirectly via the UBL (Figs. 2 and S6 right). Further, the model calculations indicated that canyon greening can actually increase the pollutant sink, area-for-area, relative to a rural vegetated surface (by 15-70% for NO_2 for 100% green wall coverage at h/w=1, Fig. S7, see supporting information).

Modeled PM_{10} deposition rates were evaluated by comparing the modeled deposition flux per unit leaf area, $F_{L,i}$, with measurements, where $F_{L,i}$ was calculated from the deposition velocity and the modeled concentration:

$$F_{L,i} = \frac{V_{d,i}}{LAI} \cdot C_i \, . \qquad (3)$$

Assuming a single-sided LAI of 2, the modeled $F_{L,PM10}$ varied from 6 - 9 mg m^{-2} (leaf area) day^{-1} for wind speeds from 0.5 to 5 m s^{-1}. This is well within the range of available measurements. For roadside trees $F_{L,PM10}$=11-119 mg m^{-2} (leaf area) day^{-1} has recently been measured[46]. Another study measured mean $F_{L,PM}$ for particles with aerodynamic diameter greater than 0.45 μm as 25 mg m^{-2} (leaf area) day^{-1} to trees alongside a major road over a 14-day period in summer, similar deposition rates were observed to leaves in central London[47].

Pollutant concentration reductions were strongly dependent upon canyon residence time, and hence wind speed. To evaluate urban greening effects over a realistic wind climatology, a year (2008) of daily average wind speeds from Kew Gardens, London, were used[48]. The concentration change indicated by CiTTy-Street for each wind speed was multiplied by the probability of that wind speed occurring. In an idealized city of uniform street canyons with h/w=1, annual average concentrations of in-canyon NO_2 and PM_{10} were reduced by 9% and 13% by greening of canyon walls across large areas of street canyons. Despite implementation of considerable pollution control measures, UK roadside NO_2 concentrations have changed little over the period 1997-2010 [49], an effect attributed to an increased proportion of NO_x being emitted directly as NO_2 [6]. In-canyon greening could be an effective tool to reduce street level concentrations of NO_2 and other pollutants throughout dense urban areas.

Currently it is believed that large-scale tree planting across the city is required for vegetation to make discernible improvements to street-level air quality. Contrary to this, the results presented herein show that, because the air within a street canyon is, to a degree, isolated from the air in the UBL and all the other street canyons[16-20], greening in one canyon may have a profound effect on air quality in that canyon, and will have a small effect elsewhere through reductions in UBL concentrations (Table 1 and

Fig. 2). The street-level reductions were slightly smaller than for greening of large areas of street canyons, because actions in a single street canyon did not significantly reduce UBL pollutant concentrations. Using the 2008 Kew Gardens wind speed climatology produced reductions over a year for action in a single canyon (h/w=1) of 7% and 11% for NO_2 and PM_{10} concentrations respectively. This increased to 20% and 31% respectively when h/w=2. Note that when considering single-canyons, along-street ventilation may also be important when the above-roof wind is not near-perpendicular to the along-canyon axis (see supporting information). Counter-intuitively, increasing h/w for green street canyons reduced absolute concentrations at low wind speeds (Fig. S4), as the increased overall deposition rate more than compensated for the greater pollution-trapping effect at high h/w. This implies that there may be a case for artificially increasing the aspect ratio of some streets in conjunction with greening activities, perhaps by the addition of living vegetation (green) "billboards" on top of existing buildings.

At low wind speeds, when the effect of in-canyon vegetation was enhanced, the greening of canyon walls offered considerable potential of reductions in the frequency of exceedence of air quality limit values. In these circumstances, reductions in NO_2 and PM_{10} concentration of as much as ~40% and ~60% respectively were predicted by the model (Table 1 and Fig. S4). This indicates that street canyon vegetation not only results in a substantial overall reduction of in-canyon pollutant concentrations, but it also forms a natural buffer against high-pollution episodes (which are often associated with low wind speeds), and associated acute impacts on human health[4].

Like green walls, street trees increase deposition, but in addition they reduce mixing, M, between street canyon air and the UBL[24, 56]. Because of this potential to alter M, it remains difficult to quantify the effect of street trees on in-canyon deposition fluxes. In order to assess whether trees have a beneficial or negative effect on in-canyon pollutant concentrations, the sensitivity of CiTTy-Street to deposition velocity and to canyon residence time was explored using a bi-variate sensitivity study (Figs. 3 and S5). In-canyon pollutant concentrations increased with residence time when deposition velocity was low. As deposition velocity increased, a compensation deposition velocity, $V_{d,i}(P)$, was reached for each pollutant species, *i*. Above $V_{d,i}(P)$, in-canyon concentrations decreased as residence times increased at a given deposition velocity. Therefore, if trees increase in-canyon deposition velocity sufficiently, they will improve, rather than worsen, in-canyon air pollution. The position of $V_{d,i}(P)$ for each pollutant depends on the in-canyon emission rate of that pollutant. Higher emission rates require a higher canyon-average deposition velocity to prevent concentration build-up. This could be achieved through using different or greater amounts of street tree vegetation. For the high emission scenario used here (central London), $V_{d,PM10}(P)$ corresponded to a LAI of 1.3 averaged across the canyon width, whereas $V_{d,NO2}(P)$ was beyond the maximum of the sensitivity study. Hence, it is expected that street trees will act to reduce street-level PM_{10} but increase NO_2 concentrations in highly polluted canyons in most circumstances. However, for streets with moderate or low emissions, trees will have an unambiguously beneficial effect. In this case the situation is analogous to air in the centre of a large wooded stand, where measurements have shown substantial concentration reductions[60].

Note that the effect of trees on deposition rates and residence time is unlikely to be constant. Residence time in street canyons will instead varying according to wind direction and speed. Deposition velocities will vary with aerodynamic factors, and tree species/size and health, and season. No sufficiently detailed dataset on urban tree health and net primary productivity exists to enable time-varying deposition velocities to be built into CiTTy-Street.

Discussion

These results show that in-canyon vegetation offers a method to improve urban air quality substantially. Urban greening can be effectively enacted on the local scale, providing a complement to top-down policy and regulation that encourages local ownership of pollution mitigation strategy, and helping to focus intervention on problem areas. Even if in-canyon pollutant sources are removed, in-canyon vegetation continues to offer substantial pollutant removal benefits (very close to the single canyon values in Table 1 and Fig. 2), with lower concentrations in the canyon than in the UBL above, in effect creating 'filtered avenues'. This effect is particularly important for pollutants with atmospheric lifetimes long enough to be transported long distances, such as PM_{10} and ozone. Hence, greened urban canyons may ultimately experience better air quality than in surrounding rural areas. The use of street trees must be considered on a case-by-case basis. In streets with low street-level emissions (i.e. light traffic), the filtered avenue effect will apply. Where street-level emissions are high, however, tree planting must be used with the utmost caution. The specific combination of tree species, canopy volume, canyon geometry and wind speed and direction must be modeled on a case-by-case basis.

Unlike tailpipe-based emission reduction strategies, greening also offers wider benefits, including reduced surface temperature and noise pollution and increased biodiversity and amenity value[45]. But it also offers challenges in ensuring vegetation health and minimizing damage to non-green infrastructure (e.g. underground water infrastructure). There are potential feedbacks between urban climate and tree health which cannot as yet be captured by the model. In reality, the existence of suitable plant species and the ongoing costs of maintenance will determine the viability of green infrastructure. The results presented here must be considered as part of the wide-ranging inter-disciplinary discussion on the merits and implementation of urban greening[50,51]. In particular, we expect there to be strong interdependencies between urban vegetation cover and urban water resources. It is not yet possible to treat such interdependencies in CiTTy-Street or, to the authors’ knowledge, in any other urban land-atmosphere model.

Many key uncertainties remain, which should be addressed as a matter of urgency. These are the residence times of pollutants under different canyon geometries and vegetation type/coverage (especially trees), the relationship between residence time and wind speed, deposition velocities of air pollutants to canyon walls and vegetation which take account of life-cycle and seasonality, and the behavior of vegetation in the street canyon environment. An alternative to green infrastructure for air quality benefits would be to increase deposition using e.g. titanium oxide or activated carbon surface coatings[54,62], although research suggests that these should also be applied with care as studies have indicated the re-volatisation of adsorbed NO_x as HONO[53, 55].

Of the green infrastructure options available in a densely-populated urban area, in-canyon vegetation offers by far the biggest benefits for street-level air quality, much greater than, for example, green roofs. The results of this analysis show that street-level reductions of as much as 40% for NO_2 and 60% for PM_{10} are achievable using green walls. This suggests that the potential benefits of green infrastructure for air quality have been substantially undervalued[11-15]. These results are consistent with field measurements of deposition to vegetation and point to the utility of innovative urban greening – e.g. increasing canyon aspect ratios with green billboards – for air quality control. Such changes may be retrofitted to existing developments or designed into new ones, with potential implications for how urban areas are structured. Green infrastructure in street canyons maximizes the ability of vegetation to remove pollutants, and offers the potential for large and sustained improvements in urban air quality in both single canyons, and across large areas of street canyons. It is therefore essential that the potential pollution mitigation effects of in-canyon greening inform the future development of urban areas.By not considering the adverse effects of tree planting on canyon ventilation, urban greening initiatives that concentrate on increasing the number of urban trees, without consideration of location risk actively worsening street-level air quality, whilst missing a considerable opportunity for air quality amelioration

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Supporting Information Available

Model description and further detail of results. Tables S1-S2. Figures S1-S7. This information is available free of charge via the Internet at http://pubs.acs.org.

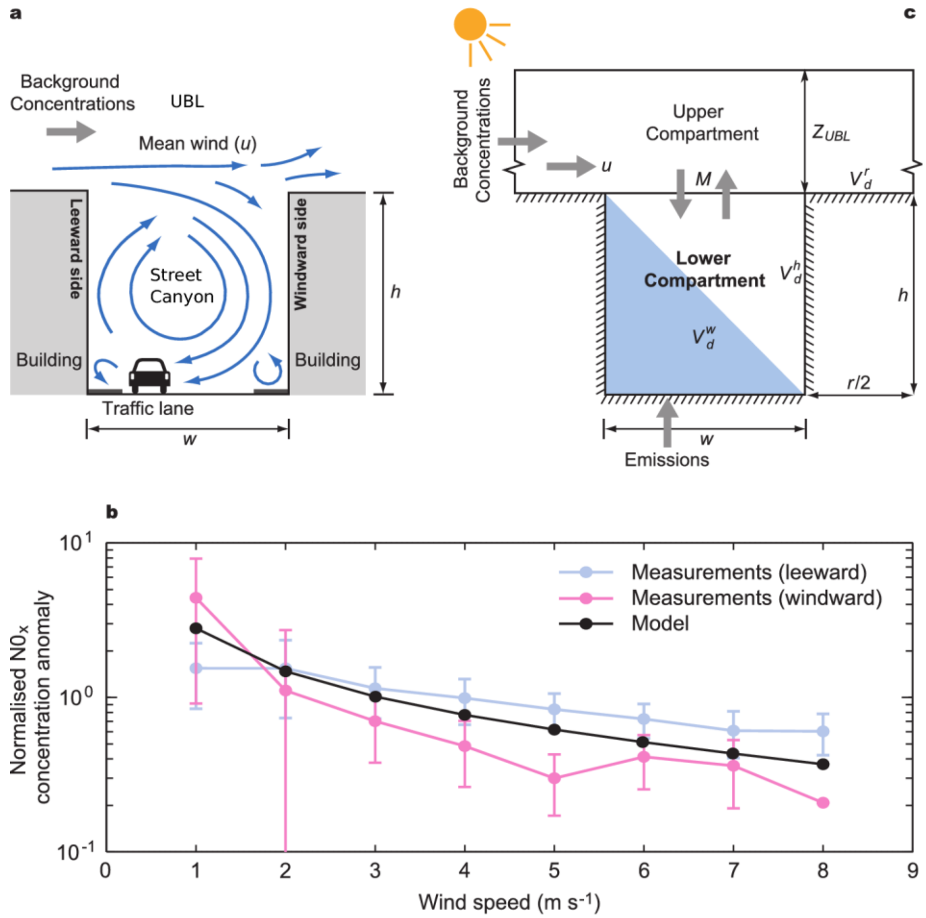

Figure 1. Interaction of street canyon and UBL air: (a) Conceptual view of circulation in street canyons redrawn from Vardoulakis et al.[52], (b) comparison of mean modeled street canyon NO_x (NO_x=NO+NO_2) concentration anomaly with measurements at varying wind speeds, (c) CiTTy-Street model formulation. Measurements are a year of data are from Göttinger Strasse, Hannover, which is an unvegetated canyon with h/w≈1 (http://www2.dmu.dk/atmosphericenvironment/Trapos/datadoc.htm). Anomalies are calculated by subtracting background concentrations from in-canyon concentrations for both model and measurements and normalizing against the mean concentration anomaly (see supporting information for details). Data are split according to whether the measurement is on the leeward or windward side of the canyon. Larger concentration anomalies are typically found at the leeward wall where pollutants tend to accumulate[52]. The error bars indicate plus/minus one standard deviation from the mean. The model results generally fall between those for the leeward and windward walls, consistent with that which would be expected for a street canyon average value.

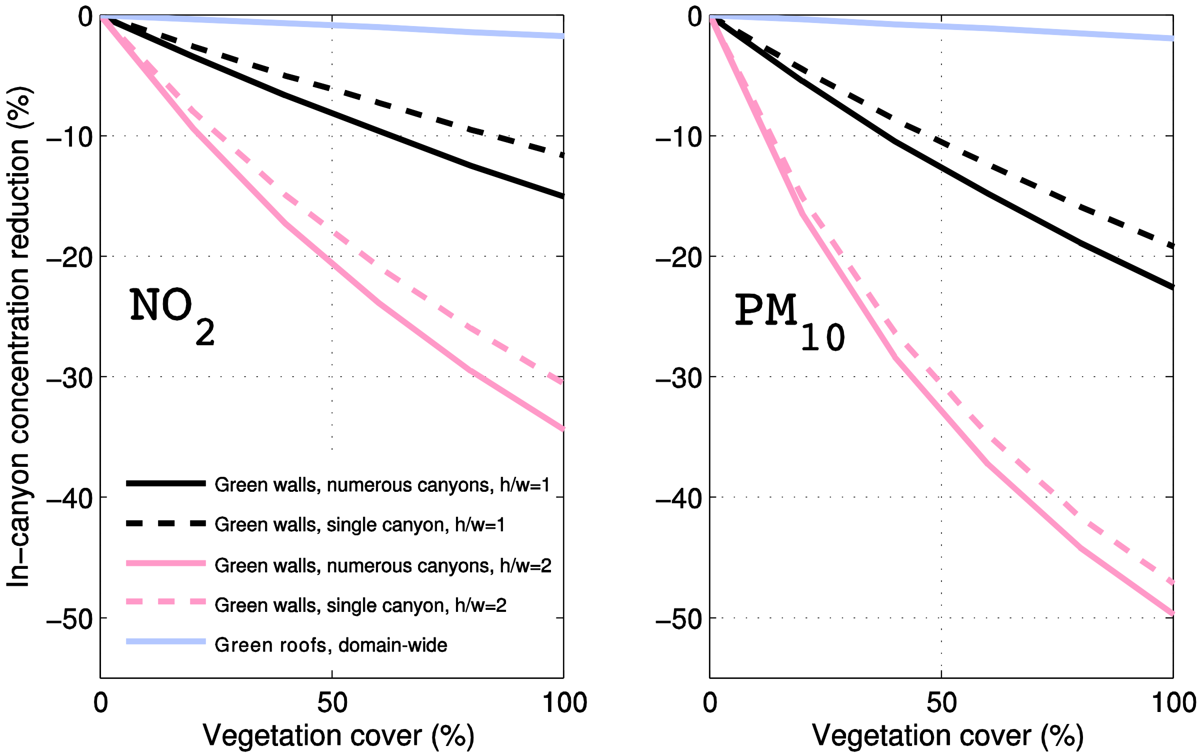

Figure 2. Modeled daytime average (0600-1800) in-canyon concentration reduction (relative to no vegetation cover) as a function of wall or roof vegetation coverage, when the above-roof wind speed is 1 m s^{-1}.

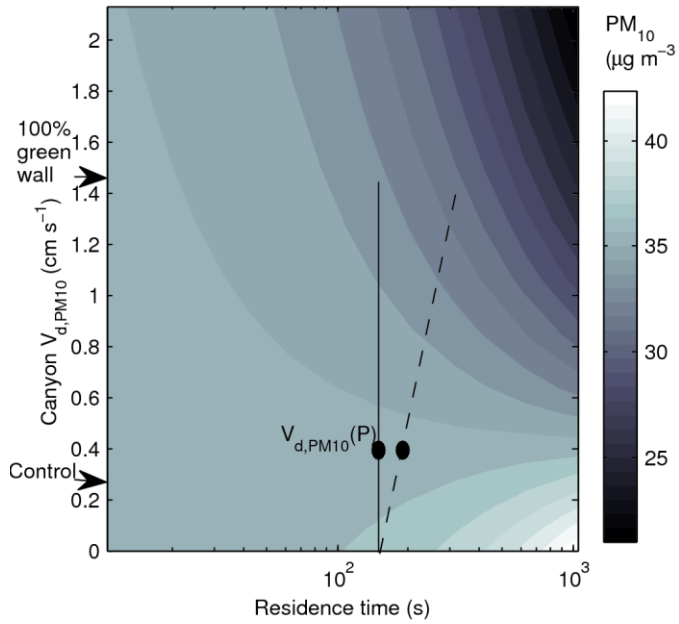

Figure 3. Effect of canyon residence time and canyon deposition velocity on modeled concentrations of PM_{10} for a single street in central London. Residence time is defined as the e-folding time for a pollutant initialized with a positive concentration in the lower compartment and a zero concentration in the upper compartment with no emissions. Total canyon $V_{d,PM10}$ is expressed relative to the width of the canyon to aid comparison of these results to future studies. The solid black line indicates the trajectory that may be followed as green walls are added, for a fixed canyon geometry and wind speed. Whereas the dashed black line shows how this trajectory may be altered by the addition of trees, which act to increase residence time as well as deposition velocity. Note that these lines are illustrative only. The compensation deposition velocity, $V_{d,PM10}(P)$, is that above which an increase in residence time yields a reduction in concentrations.

Table 1. Modeled vegetation scenarios and expected in-canyon concentration reductions under different canyon configurations and meteorological conditions.

Scenario	Deposition velocities ($cm\ s^{-1}$)[a]		Concentration change relative to control scenario (%)			
	NO_2	PM_{10}	U=2 $m\ s^{-1}$			U=0.5 $m\ s^{-1}$
			Aspect ratio=1		Aspect ratio=2	
			Numerous canyons	Single canyon		
Control (brick walls/roofs)	Walls: 0.05 Roof: 0.05	Walls: 0.02 Roof: 0.2				
Green walls (100% coverage)	Walls: 0.3 Roof: 0.05	Walls: 0.64 Roof: 0.2	NO_2: -8.9 PM_{10}: -13.1	NO_2: -6.4 PM_{10}: -10.8	NO_2: -19.9 PM_{10}: -32.0	NO_2: -42.9 PM_{10}: -61.9
Green roof	Walls: 0.05 Roof: 0.3	Walls: 0.02 Roof: 0.64	NO_2: -0.9 PM^{10}: -1.1			

[a] The choice of model deposition velocities is further discussed in the supporting information.

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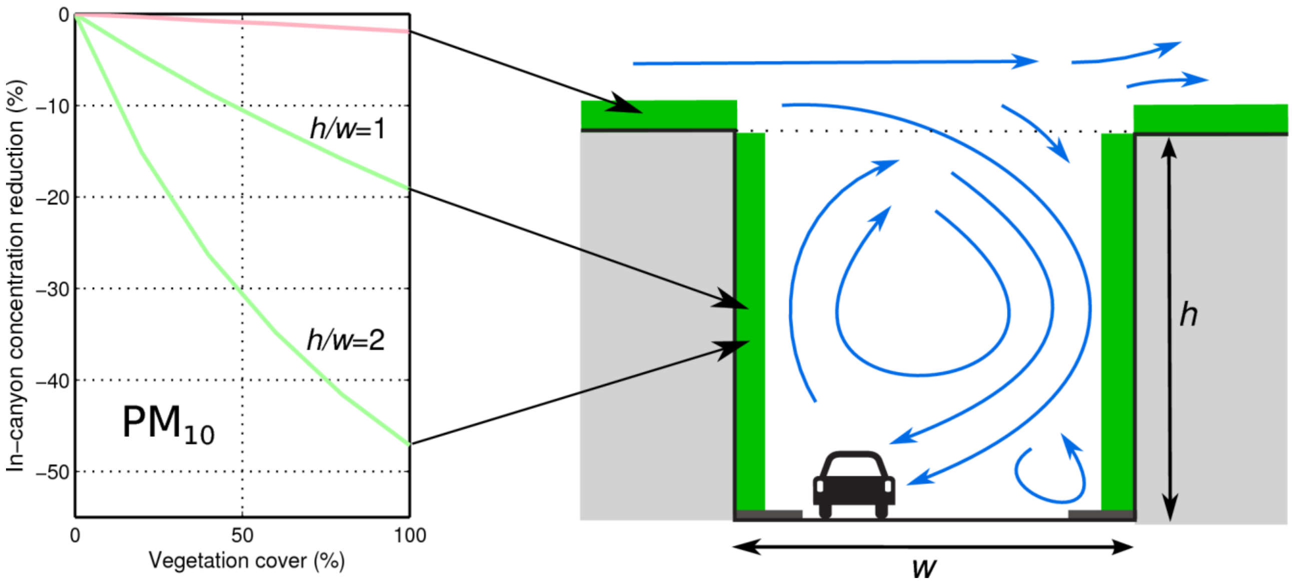

The effectiveness of green infrastructure to improve air quality in urban street canyons

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Table S1 – S2

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Model description

Previous studies of the effect of deposition to urban vegetation on air pollutant concentrations have used a zero-order method based upon average urban boundary layer (UBL) pollutant concentrations, the height of the UBL, and the deposition velocity at the surface[1-6, 43, 44]. Below, this method is referred to as the "constant boundary-layer concentration (CBLC) method". The CBLC method makes two assumptions that limit its utility for estimating the true deposition efficiency of urban surfaces. Firstly, the assumption of constant air concentration in the UBL implies that the depositional loss is too small to significantly impact the concentration; when that is not the case, the CBLC method will over-estimate the deposition. Secondly, as described in the main paper, the CBLC method assumes a well-mixed urban boundary layer (UBL), and so fails to account for the urban geometry which can inhibit mixing of air in street canyons with air in the overlying UBL.

The CiTTyCAT model of atmospheric chemistry[7] has been modified to represent an idealized urban area containing street canyons. The new model variant, CiTTy-Street, is run with two compartments (Fig. 1c of main text), the lower compartment represents a street canyon of height h and width w. Depending on the treatment of the upper compartment, the canyon compartment can be considered to represent a single street canyon or be representative of a large area of street canyons (in some cities this may be practically city-wide). In this work, unless otherwise stated, h=w=20 m, which are common street canyon dimensions (e.g. Table S1). The upper compartment represents the UBL, and was parameterized with a depth, $z_{UBL}=H(t_d)-h$, where $H(t_d)$ is the UBL depth and t_d is time-of-day. Although H is strictly a function of time of day, for the simulations here H was set to a typical daytime value of 1000 m. Mixing between the compartments was parameterized using the dimensionless air exchange rates (E) calculated by Liu et al.[9] for above-roof wind perpendicular to the along-canyon axis:

$$E=\frac{Q.T}{V}\,, \qquad \text{(S1)}$$

where Q is the air ventilation rate ($m^3\ s^{-1}$), V is the volume of the street canyon (m^3) and T is a characteristic timescale (s),

$$T=\frac{h}{u}\,, \qquad \text{(S2)}$$

where u is the above roof wind speed ($m\ s^{-1}$). In this work Q and V always appears as the ratio $Q/V=M$, where M is the fraction of canyon air replenished by mixing with the UBL per second, and therefore the length of the modeled canyon is arbitrary (The implications of finite street lengths are discussed below). Eqs. S1 and S2 are used to define the mixing parameter, M:

$$M = E \cdot \frac{u}{h}. \qquad \text{(S3)}$$

For a fixed canyon aspect (h/w) ratio, an increase in h will result in a decrease in M and hence an increase in the canyon air residence time. Conversely an increase in wind speed, u, will bring about a decrease in the canyon air residence time. Liu et al.[9] calculated E=0.05 for a canyon of h/w=1. The change in concentration, ΔC, of a species, i, in the lower compartment, due to mixing over model time step, Δt, is therefore

$$\Delta C_{i,L} = \left(C_{i,U} - C_{i,L}\right) \cdot M \cdot \Delta t, \qquad \text{(S4)}$$

and in the upper compartment,

$$\Delta C_{i,U} = \left(\left(C_{i,L} - C_{i,U}\right) \cdot M \cdot \frac{h \cdot w}{z_{UBL} \cdot (w + r)} + B_i \right) \cdot \Delta t\,, \qquad \text{(S5)}$$

where z_{UBL} is the depth of the upper compartment in meters, r is the width of the roof between two adjacent street canyons, and subscript U and L denote the upper and lower compartments respectively. The term $(h \cdot w)/(z_{UBL} \cdot (w+r))$ in Eq. S5 accounts for the different areas of the UCL and the UBL, including the fact that the upper compartment is wider than the lower compartment due to the space occupied by the buildings between street canyons (Fig. S1). In order to prevent the build-up of unrealistic concentrations, the upper compartment was ventilated by predefined background air with concentrations ($C_{i,B}$) at a rate determined by the above roof wind speed:

$$B_i = \left(C_{i,B} - C_{i,U}\right) \cdot \frac{u}{f}\,, \qquad \text{(S6)}$$

where f is the length scale (m) that the model is being used to represent, i.e. the model footprint. In this work f=10 000 m for modeling large areas of street canyons, and f=40 m for single canyon modeling

The modeled mixing rate out of the street canyon was based on a parameterization developed for wind flow perpendicular to the street canyon axis[9], this was a reasonable approximation for the purposes of this work as parallel flow is less effective at ventilating the street canyon vertically due to the lower roughness generated[10,11]. Under perpendicular or near-perpendicular flow, v_l, the along-canyon component of the in-canyon wind speed vector v, will be close to zero and horizontal mixing can be neglected[12]. Under parallel or near-parallel flow, horizontal along-canyon mixing becomes important, and a cumulative effect of emission in long streets has been observed[13]. The influence of dispersion at street intersections is uncertain. They can result in very limited canyon ventilation (for instance in the case of crossroads), in efficient mixing with neighboring canyons (when the in-canyon flow impinges on a building facet, creating a dividing streamline), or in increased ventilation to the UBL (for instance, in the case of in-canyon flow encountering a wall perpendicular to the flow direction, such as at a T-junction)[14], creating a very spatially heterogeneous response across an urban area. This effect is recognized but was not treated explicitly, as it has been shown that overall pollutant retention for an idealized grid of street canyons (an array of cubic obstacles in this case) is largely independent of wind direction for the range of possible oblique flows[15]. Further, pollutant retention for oblique flows was higher than for the average of parallel and perpendicular flows. Hence the parameterization of Liu et al.[9] is expected to be broadly representative of *M* under all wind directions across an urban area. When considering mixing within a single canyon, however, horizontal mixing rates will need to be considered for cases where the above-roof wind is not near-perpendicular. These cases are discussed further below.

Traffic-induced turbulence was not explicitly considered in this study. Traffic-induced turbulence may be expected to dominate over wind-induced turbulence when the above-roof wind speed is less than ~1.2 m s^{-1} [16]. Therefore for very low wind speeds in high-traffic canyons the Liu et al.[9] parameterization may underestimate *M*. However, the parameterizations of Liu et al.[9] were not modified here for these low wind speeds as the results presented in this study also apply to canyons with low amounts of, or no, traffic, in which cases traffic-induced turbulence will be absent or minimal. Under these conditions the air tends to stagnate in the canyon, as predicted by the model of Liu et al.[9].

The geometry of street canyons means that, in sunny conditions, a proportion of the canyon will be in shadow. This proportion will change according to the azimuth and zenith angles of the sun relative to the street, and according to the aspect ratio of the street canyon. In overcast conditions, nearly all solar radiation will be diffuse and the shadowing effect may be ignored. Koepke et al.[17] have calculated the reduction in photolysis rates of NO_2 within street canyons for a range of aspect ratios and solar zenith angles. For the conceptual modeling studies reported here, the simplifying assumption of Koepke et al.[17] was adopted, i.e. that street orientation within the urban area is random, and therefore the reduction in photolysis rate is averaged across all possible street orientations. Koepke et al.[17] show that the principal control on the average photolysis rate reduction is the aspect ratio, rather than the solar zenith angle, for those solar zenith angles found in the middle-latitudes. As a result, they suggest an average NO_2 photolysis rate reduction of 60% for a canyon of h/w=1. This reduction was applied in CiTTy-Street for all photolysis rates in the lower compartment. Differences in the spectral albedo of the canyon surface may result in some variation of the reduction for different wavelengths. However, Koepke et al.[17] determined the surface albedo to have a relatively minor effect compared to h/w and solar zenith angle. All runs described in the study described herein were carried out under clear sky conditions, unless stated otherwise, because these are conditions under which stomatal deposition to vegetation is expected to be greatest. The implications of this are discussed in Section S5.

Emission fluxes of NO, NO_2, volatile organic compounds (VOCs) and PM_{10} were made into the lower (street canyon) compartment. Aerosol particle concentration was treated as a passive scalar, in common with other approaches[18], implying that coagulation and growth/evaporation do not significantly affect the overall particle deposition mass flux on the time and space scales characteristic of the canyon. No emissions were made into the upper compartment. Liu et al.[9] calculate that for a canyon of h/w=1, the timescale of the primary circulation is about one quarter of the pollutant retention time within the street canyon. Therefore the air within a street canyon may be considered well-mixed relative to the timescale for exchange with the UBL; the assumption of instantaneous mixing is discussed further below. For the sensitivity runs, emissions were supplied by the National Atmospheric Emissions Inventory (NAEI)[19], for central London (51.522ºN, 0.157ºE) for the year 2008. Nitrogen oxide (NO_x = $NO + NO_2$) emissions into the modeled canyon were 8.2 mg m^{-2} hr^{-1} and PM_{10} emissions were 0.58 mg m^{-2} hr^{-1}. NAEI emissions are categorized by source type, and only those from road transport were emitted into the canyon. The speciation of NO_x emissions was specified as 18% as NO_2 and 82% as NO following the Air Quality Expert Group[20]. Biogenic VOC emissions (see, e.g., Donovan et al.[4]) were not considered in this study, although the model is capable of treating their emission and chemistry.

In the lower compartment, deposition was assumed to occur to both canyon walls and floor. It is assumed that horizontal and vertical mixing rates are equal, which is consistent with the formation of the rotational circulation typically seen in computational fluid dynamic (CFD) modeling studies[21] and shown schematically in Fig. 1a of the main text. Deposition velocities in CiTTy-Street were prescribed separately for the wall ($V^h_{d,i}$) and floor ($V^w_{d,i}$) surfaces, according to measurements made over the material making up those surfaces for species *i*. The overall rate of change of species *i* due to deposition is then calculated by

$$\frac{dC_{i,L}}{dt} = C_{i,L}\left(\frac{2V^h_{d,i}}{w} + \frac{V^w_{d,i}}{h}\right). \qquad \text{(S7)}$$

where length scales *w* and *h* are as defined in Fig 1(c) of the main text. In the upper compartment deposition occurs to roofs only, and was parameterized as

$$\frac{dC_{i,U}}{dt} = C_{i,U}\,\frac{V^r_{d,i}}{z}\left(\frac{r}{r+w}\right), \qquad \text{(S8)}$$

where $V^r_{d,i}$ is the deposition velocity to that roof. All roofs are assumed to be similar. Fractional coverage of green roofs, can be accommodated by scaling the deposition velocity accordingly. In principle, $V_{d,i}$ is also a function of the type and health of plant used to provide the green wall or roof, and the density of planting. Since in this study no particular kind of green infrastructure was being modeled, constant values of $V_{d,i}$ were chosen from the literature that are characteristic of gas and particle deposition to urban plant canopies (see Deposition Velocities section below). Unless otherwise stated, *r*=20 m. Studies have shown that there is variation in pollutant concentration within a street canyon due to the circulation driven by the above-roof wind, and the existence of point emissions sources[22,23]. In particular pollutant concentrations have been shown to be relatively higher at the base of the leeward wall when the above-roof wind is perpendicular to the canyon, and to show a generally negative gradient with height (assuming a traffic emission source at the canyon base)[22]. CiTTy-Street cannot capture these inhomogeneities but, as deposition rates vary linearly with concentration, the average deposition rate within the canyon is unaffected as long as the timescale for mixing within the canyon is shorter than the timescale for a pollutant concentration to be depleted via deposition. For an in-canyon NO_2 deposition rate equal to the 100% green wall scenario described in Table 1 of the main paper, a 10% depletion of in-canyon NO_2 occurs on a timescale of 340 s. Liu et al.[9] found that the rotation timescale for in-canyon air is ~15T. Therefore, for the longest canyon residence time investigated here, T=40 s (equivalent to u=0.5 m s^{-1} when h=20 m), the rotation timescale is ~600 s. The error in deposition rate introduced by the well-mixed approximation is therefore less than ~12% and decreases with residence time (~3% when u=2.0 m s^{-1} and h=20 m).

PM_{10} particles are substantially larger than trace gas molecules and therefore their distribution within the canyon will be affected to a greater extent by gravitational settling. However, the terminal settling velocity of a 10μm particle in air at 293K and 1013 hPa is 3 mm s^{-1}; significantly smaller than likely vertical velocities generated by turbulence and recirculation within the canyon.

To summarize, the model is characterized by five length scales (z_{UBL}, r, w, h and f), one dimensionless exchange scale (E) and four velocity scales (u, V_{di}^{r} , V_{di}^{w} , V_{di}^{h}). In this study the model was run for periods of 18 hours commencing at 0000Z on the 21st June, with the first 6 hours (mostly under night-time conditions) being discarded as spin-up. The residence time of air in the lower (street canyon, *h/w*=1) compartment was calculated as 21T, where residence time is the e-folding time for a pollutant initialized with a positive concentration in the lower compartment and a zero concentration in the upper compartment, and no emissions are allowed.

Deposition velocities

The following details are given in addition to those in the “Deposition velocities” section in the main text. For PM_{10} deposition no differentiation was made between horizontal and vertical vegetation surfaces since leaf angle varies considerably relative to the surface, and thus is implicitly incorporated in the deposition velocity used.

PM_{10} deposition velocities to horizontal and vertical brick and concrete surfaces were calculated following the model for rough surfaces described by Piskunov[24]. Median particle size was assumed to be 3 μm. Roughness lengths for the particle calculations were taken to be 3 mm for brick and 1 mm for concrete, and the friction velocity was set to 0.2 m s^{-1}. The mean particle size was selected for consistency with particle volume distributions measured from traffic emissions[25], and to avoid the sub-micrometer size range for which deposition is particularly uncertain. Theoretical models of dry deposition (e.g. Petroff and Zhang[26]) predict that deposition velocity continues to reduce for particles below 1 μm in aerodynamic diameter, before increasing again for particles less than ~100 nm in aerodynamic diameter. Yet field measurements suggest that deposition velocities may be relatively constant in the range 0.3 – 10 μm[27], with one study predicting deposition velocities that increase with decreasing particle diameter, yielding very large sub-micron deposition velocities (~10-30 cm s^{-1})[28]. Thus, based on measurements, assuming a particle diameter of 3 μm appears representative of deposition velocities for most of the sub 10 μm particle mass, and may even underestimate sub-micron deposition. Note that these assumptions are less likely to hold for the ultra-fine size fraction, of ~100 nm or less in diameter. There has been some discussion of a possible "saturation effect" which leads to reduced PM deposition on leaves as deposited material accumulates[27]. However the authors know of no systematic study which tests this hypothesis. In this work leaf surfaces were assumed to be washed clean by rainfall with sufficient regularity that any saturation effect could be disregarded.

Nitric acid was assigned a deposition velocity of 8.0 cm s^{-1} following measurements by Aikawa et al.[29] above a concrete roof in Kobe, Japan. Although this value is high, the modeled scenarios in this paper were not sensitive to the nitric acid deposition velocity. Brick and vegetation surfaces were used for the walls and/or roofs as specified in Table 1 of the main paper. The canyon floor was approximated as a coarse concrete surface in lieu of published deposition velocities to tarmac. In this work, CiTTy-Street was run for a single day. Over longer time periods, accumulations of pollutants on canyon surfaces are expected to be washed away by rainfall. This assumption may have to be reassessed if the results of this study are applied in a region subject to prolonged dry periods.

The dependence of model results on the overall in-canyon deposition velocity (green wall + hard surfaces) is discussed below and given by vertical sections through Figure S5 (i.e., model results for a given residence time).

Model mixing evaluation

The authors are aware of no available dataset against which to compare the modeled concentrations in vegetated canyons. This is probably because, until now, a measurable effect was not expected. Some field measurements were available, however, to compare the mixing performance of the model, upon which the results of this study are dependent. The CFD model of Liu et al.[9], from which the canyon mixing parameterization is taken, has also been evaluated against wind tunnel studies.

From Eq. 2 in the main text, a decrease in above-roof wind speed is expected to bring about an increase in canyon retention time, and hence an increase in pollutant concentration is expected. However a decrease in above-roof wind speed will also tend to lessen dispersion of pollutants from the urban area as a whole, leading to higher boundary layer pollutant concentrations, and therefore higher canyon concentrations. In order to control for this effect it is necessary to have simultaneous measurements both within and above the street canyon. Measurement data meeting this criterion recorded at three different street canyon sites was used (Table S1) to control for the effect of above-roof concentrations and hence illustrate the wind speed effect on pollutant retention. The street canyon model was then compared against this measurement data.

At each of these sites NO_x concentration measurements were made at street level on one side of the street canyon, and at a nearby rooftop measurement site. Wind speed and direction measurements were collected from a mast 10 m above the rooftop level. For the following analysis only measurements recorded when the wind direction was within a 12.5° arc of being perpendicular to the canyon axis were used. These measurements were sorted into windward and leeward groups, according to the wind direction relative to the position of the street-level measurement site. Larger concentration anomalies are typically found at the leeward wall where pollutants tend to accumulate[30]. Both rooftop and street-level measurements showed a correlation with wind speed, although this correlation was more noisy at street-level due to the wide variation in traffic emissions with time. In order to separate the street canyon effect from other effects, the difference between rooftop $\left(NO_x^r\right)$ and street-level $\left(NO_x^s\right)$ concentrations was found:

$$\Delta NO_x = NO_x^s - NO_x^r. \qquad \text{(S9)}$$

In order to correct for the effect of varying traffic emissions within the street canyon, ΔNO_x was divided by a correction factor C_E following Ketzel et al.[31],

$$\Delta NO_x^c = \frac{\Delta NO_x}{C_E}, \qquad \text{(S10)}$$

where

$$C_E = \frac{E}{\overline{\overline{E}}}, \qquad \text{(S11)}$$

in which,

$$E = \left(e_L \cdot N_l\right) + \left(e_H \cdot N_H\right), \qquad \text{(S12)}$$

where e_L and e_H are the emission factors for light vehicles (e.g. cars, vans) and heavy vehicles (e.g. trucks, buses) respectively, and N_L and N_H are the number of light and heavy vehicles. Emission factors were taken from Schädler et al.[32]. $\overline{E}$ was the mean emission rate over the entire dataset. Following this correction ΔNO_x^c was binned according to wind speed to aid comparison between the normalised measurements and the model. Finally a normalised concentration anomaly for the street canyon (A_{NOx}) was calculated by

$$A_{NOx}(u) = \frac{\Delta NO_x^c(u)}{\overline{\Delta NO_x^c}}. \qquad \text{(S13)}$$

Using A_{NOx} allowed the mixing response of the model to changes in wind speed to be evaluated independent of other factors. Figure S1 shows A_{NOx} as a function of wind speed for the three different canyons observed in the TRAPOS experiment (http://www2.dmu.dk/atmosphericenvironment/Trapos/datadoc.htm). More concentration variation with wind speed were seen on the windward side of the canyon, as concentrations here tended to be suppressed under all but very low (less than ~2 m s^{-1}) wind speeds.

The model output plotted in these runs was produced by running the model for each wind speed bin using the same setup as described in Section S1, with *f*=40 m. It was then processed according to Eqs. S9 and S13 (the model uses a constant emission and therefore has no need for emissions normalization). The model output fell between the normalized concentration anomaly for the windward and leeward walls, as would be expected for a canyon-average statistic, for all three street canyons. This indicates that the CiTTy-Street model is able to represent well the change in the canyon pollutant retention effect with changes in above-roof wind speed.

Evaluation against absolute measurements

The model setup was adjusted for an explicit comparison with measurements from Göttinger Strasse (Table S2) for 21/06/94. Initial conditions for NO, NO_2 and O_3 were taken from measurement data, and the measured temperature data was used. Photolysis was set for clear sky conditions, consistent with the net radiation recorded on this date. NAEI emission speciation was used, but NO_x and VOC emissions were scaled according to traffic counts and the emission factors of Schädler et al.[32]. The model footprint was set as *f*=40 m. Background concentrations and the above roof wind speed were set to match daytime average UBL measurements (32 ppbv O_3, 14 ppbv NO_2, 8 ppbv NO). Figure S2 shows good agreement between the model and mean street-level measurements for NO_2, indicating that this model is able to simulate well the concentration differential between street canyon and UBL.

Setup for sensitivity runs.

Initial and background concentrations for the model sensitivity runs are summarized in Table S2. For the numerous canyon runs background concentrations are taken from measurements made at Writtle (51.52ºN, 0.13ºE) during the TORCH measurement campaign (25/07/03-31/08/03). These measurements were chosen to give as wide a range of background species as possible. PM_{10}

concentrations were taken from an urban background site in London Bloomsbury (51.73ºN, 0.41ºE). For single canyon runs, upwind NO, NO_2, O_3 and CO concentrations were also specified using London Bloomsbury measurements.

Sensitivity of results to canyon volume

The absolute reductions in modeled street canyon concentrations were virtually insensitive to the size of a canyon of a given aspect ratio. Increasing *h* and *w* decreased the deposition rate per unit volume in the canyon. However, following Eq. S2, as *h* is increased, *T* must also increase proportionally, for a constant wind speed. Therefore, for larger *h* and *w*, the deposition flux now acts for a proportionally longer time due to the increased canyon residence time. As a result, the integrated loss per unit volume of a pollutant in the street canyon is invariant with canyon size (assuming *h/w*=1). When *h*=*w* and $V_{d,i}^{h}$ = $V_{d,i}^{w}$, Eq. S7 becomes

$$\frac{dC_{i,L}}{dt} = C_{i,L}\left(\frac{3\mathrm{V}_{d,i}}{h}\right). \qquad \text{(S14)}$$

For a species X, which is not emitted (e.g. O_3),

$$\frac{d[X]}{dT} = \frac{-3\mathrm{V}_{d,X}[X]}{h} + P_X - L_X. \qquad \text{(S15)}$$

Assuming $P_X \approx L_X$ and integrating over time until the characteristic timescale, *T*,

$$\int_{[X]_0}^{[X]_T} \frac{d[X]}{[X]} = \frac{-V_{d,X}}{h}\int_{t=0}^{T} dt, \qquad \text{(S16)}$$

gives

$$\ln\frac{[X]_T}{[X]_0} = \frac{-V_{d,X}T}{h} \equiv \frac{-V_{d,X}}{u} \qquad \text{(S17)}$$

or

$$\Delta[X] = e^{\left(\frac{-V_{d,X}T}{h}\right)} \equiv e^{\left(\frac{-V_{d,X}}{u}\right)}. \qquad \text{(S18)}$$

That is, for a constant wind speed $\Delta[X]$ is independent of canyon size.

Sensitivity to cloud cover

The runs described in this work were carried out under clear sky conditions. The reduced photolysis rate of NO_2, J(NO_2), under cloudy skies would be expected to lead to higher ambient NO_2

concentrations. Note, however, that the 50% reduction of peak $J(NO_2)$ calculated by CiTTy-Street for 100% cloud cover is similar to the 60% reduction of all photolysis rates applied inside the canyon during clear skies to account for shading. This canyon shading reduction was not applied under cloudy skies where all incident radiation is diffuse. Hence, the modeled reductions in NO_2 due to addition of in-canyon vegetation under cloudy skies were virtually identical to those under clear skies.

The reduction in direct radiation due to increased cloud cover may also reduce stomatal opening[33], and consequently the NO_2 and O_3 deposition velocities. The treatment of deposition in CiTTy-Street does not directly calculate this effect; however, the deposition velocities employed (Table S1) were collected under a variety of conditions and are therefore believed to be broadly representative of a wide variety of conditions. To assess the importance of stomatal closure due to reduced solar irradiance the bulk canopy stomatal resistance equation, r_s, of Wesely[34] was used,

$$r_s = r_i \cdot F_G \cdot F_T \ , \qquad \text{(S19)}$$

where r_i is the minimum bulk canopy resistance for water vapor, and F_G and F_T are modification factors for solar irradiance and surface air temperature respectively.

$$F_G = 1 + \left(\frac{200}{G + 0.1} \right)^2 , \qquad \text{(S20)}$$

where G is the solar irradiance (W m^{-2}). At a solar irradiance of 1000 W m^{-2}, broadly equivalent to a solar zenith angle of 0° under clear skies (25), F_G=1.04. In comparison, a solar irradiance of 400 W m^{-2}, broadly equivalent to a solar zenith angle of 0° under cloudy skies[17], yields F_G=1.25. Suggesting that the variability of NO_2 deposition velocity due to changes in irradiance is well within the variability of the measurements listed in the Deposition Velocities section

This study focuses on daytime deposition, as most street-level population exposure is likely to occur during the daytime. The stomatal component of deposition for NO_2 will tend towards zero at night-time, when solar irradiance is zero. As a result the deposition rate of NO_2 to vegetation is likely to decrease at night. Therefore the reductions in ambient NO_2 concentrations yielded by canyon vegetation may be smaller at night-time; however, such extrapolations are not straightforward due to (a) the diminished height of the night-time UBL which will tend to increase street-level pollutant concentrations and hence deposition rates, and (b) reduced traffic emissions during the night. Such a decrease is not expected for PM_{10} deposition rates, for which non-stomatal deposition to vegetation surfaces is dominant.

Sensitivity to emission magnitude

The modeled relative reductions in street canyon mixing ratios of NO_2 were not strongly sensitive to a doubling or halving of pollutant emissions. For instance a halving of NO_x, VOC and PM emissions led to a change in the NO_2 reduction caused by moving from the control scenario to the 100% green wall scenario from -11.6% to -11.9% (for the single canyon run). Hence the modeled percentage NO_2 reductions are likely to be valid for the concentrations of NO_2 found in most urban areas. The changes in O_3 were also quite robust. Halving the NO_x and VOC emissions changed the O_3 reduction caused by moving from the control scenario to the 100% green wall scenario from -14.9% to -16.9 %. The slightly larger variation for O_3 was due to the smaller NO titration effect caused by the lower NO_x concentrations. This led to higher overall in-canyon O_3 concentrations, and hence higher deposition fluxes. PM_{10} concentrations are not affected by chemical feedbacks in CiTTy-Street, and hence percentage PM_{10} reductions remained constant with a change in emission flux. These studies also indicated that biogenic VOC emissions, which might increase with canyon greening depending on the species used, do not make a significant difference to the canyon concentrations. Assessing the effect of canyon greening on regional-scale photochemistry would require biogenic VOC emissions to be included.

Sensitivity to canyon residence time

The sensitivity of pollutant concentrations to canyon residence time was tested by varying *u* from 0.5 m s^{-1} to 20 m s^{-1}, equivalent to residence times of 840 s and 21 s respectively for the modeled canyon. Figure S3 illustrates that the street canyon NO and NO_2 mixing ratios increased with residence time, as the reduced mixing rate out of the street canyon caused a greater build-up of these emitted species. The NO/NO_2 ratio increased with residence time, as the capacity of the canyon atmosphere to oxidize NO to NO_2 was overwhelmed. The effect of this change in NO/NO_2 ratio is seen in the street canyon ozone mixing ratios which decreased with increasing residence time. This was due to a combination of increased NO titration of O_3 and a greater influence of deposition on O_3 mixing ratios as residence time increased. Replacement of brick walls with green walls led to reductions in NO_2 and O_3 in both canyon and UBL, and the reduction became more marked as residence time increased. A modest increase in NO mixing ratio was observed in the 100% green wall scenario due to the reduction in its O_3 sink. Street canyon PM_{10} concentrations showed a limited increase with residence time in the control run, but addition of a substantial deposition velocity in the green wall run yielded a decrease in concentration with increasing residence time. The tendency for UBL NO_x mixing ratios to increase with residence time was a result of decreased dilution of the UBL by background concentrations as the longer residence times implied a lower wind speed. The same effect is seen in the UBL PM_{10} concentrations, although the effect is much more modest due to the lower PM_{10} emissions.

Figure S1 shows that the greatest anomaly in canyon pollutant concentrations compared to those in the UBL was found at low above-roof wind speed, when the canyon residence times were greatest. In addition, low wind speeds were effective in dispersing pollution in the UBL, increasing both UBL and canyon pollutant concentrations. Therefore, exceedences of limit values for pollutant concentrations are more likely to occur at low wind speeds. These calculations show that the efficacy of canyon vegetation for pollutant removal is greatest at low wind speeds (i.e. long canyon residence times). Figure S4 illustrates how the modeled in-canyon pollutant concentration varied with wind speed in the control run and the 100% green wall run for a canyon of h/w=1. The pollutant removal properties of the canyon vegetation were emphasized under the conditions of highest pollution. Therefore, street canyon vegetation not only results in a substantial overall reduction of in-canyon pollutants, it also forms a natural buffer against very high concentrations. Furthermore, the potential pollutant reductions due to vegetation are substantially larger in a canyon with h/w=2. The magnitude of these increased reductions is sufficient to more than cancel out the increased pollutant concentration in canyons of higher aspect ratio under the control run.

Along-canyon mixing

The importance of along-canyon ventilation can be estimated using the horizontal mixing parameter,

$$M_H = \beta \cdot \frac{v_l}{l}, \qquad \text{(S21)}$$

where l is the length of the canyon, v_l is the along-canyon component of the in-canyon wind speed vector, v, and β is a dimensionless factor accounting for aerodynamic resistance to mixing at the intersection. If $M_H \geq M$ then along-canyon ventilation is important. In this case, the general conclusions of this study remain valid but the canyon residence times calculated in the main text will not be suitable, and mixing rates should be recalculated by including an M_H term in Equations S4 and S5.

Consider an extreme case where all the air reaching the end of a canyon is ventilated to the UBL, l is short (50m), h=w=20 m, v_l=v and β=1. Following the average wind speeds between Marylebone Road (canyon) and Kew Gardens (UBL) in 2008 [35], v=0.3u. In this case M=0.0025 and M_H=0.006. Combining S3 and S21, and substituting u for v_l,

$$M_H = \frac{0.3\mathrm{h} \cdot \beta}{E \cdot l} \cdot M\,, \qquad \text{(S22)}$$

thus in this case M_H=2.4M. Therefore, the total mixing rate out of the canyon can be defined as M_{TOT}=M+M_H=3.4M. As $M \alpha u$ (Equation S3), the value of u required to generate M_{TOT} through the vertical mixing scheme of CiTTy-Street alone is 3.4 times that required to generate M. Thus, Fig. S4 can be used to examine the effect of along-canyon ventilation. For instance, in this extreme case, u=1 m s^{-1}

would produce the same results as generated for u=3.4 m s^{-1} using the vertical mixing scheme alone. The predicted reductions in pollutant concentration due to the use of green walls are still substantial, but are significantly reduced compared to the base case of an infinitely long canyon and perpendicular winds. It should be emphasized, however, that such large modifications to the results of this study are unlikely in reality as (a) the street canyon considered in the extreme example is short, (b) the along-canyon wind speed component only forms part of the overall in-canyon wind speed, and (c) β is dependent on intersection type and is currently unknown, but expected to be less than one. In the case of an intersection between two greened canyons (e.g. large-scale greening), only the component of β relevant to mixing with the UBL is important, as the greened canyons form a continuum for the purposes of air retention within a greened street.

A more realistic case might be for a street canyon within a dense urban area (i), with l=100m, v_l=0.5v, and β=0.75. In this scenario M_H=0.45M, giving M_{TOT}=1.45M. In this case, pollutant concentration reductions due to urban greening would be smaller, but still close to those for a perpendicular wind (Fig. S4). However, the maximum single canyon pollutant concentration reductions reported in the main text will only be realized under the case of a near-perpendicular wind. It is expected that v_l will decrease with increasing aspect ratio, and thus M_H will reduce along with M as aspect ratio increases. More work is required to deduce the form of this relationship.

Street Trees

Trees represent an obvious way of increasing in-canyon deposition rates, as they may have a very high leaf area index (defined as m^2 leaf per m^2 ground). Two rows of large trees can have a leaf area equal to or exceeding that of a green wall[27]. However, because of their potential to alter very substantially the exchange efficiency, E, of a canyon (see Eq. 2 of the main text), in addition to deposition velocities, it remains difficult to quantify the effect of street trees on in-canyon pollutant concentrations. The exchange efficiency will, among other variables, be sensitive to number of trees, tree height, crown dimensions, crown density and exact positioning and layout of trees within the canyon. Many of these variables will change dynamically as the trees grow or respond to seasonal changes or environmental stresses. Thus it is likely that a generalized exchange efficiency for trees in street canyons does not exist, and it must be calculated individually for each case. Several wind tunnel and computational fluid dynamical studies have demonstrated a reduction in E (i.e. increase in canyon residence time) with street tree planting, showing the general sign of the modification[37-42]. Only one of these studies however, has included a consideration of dry deposition[42]. This study suggested a small role for deposition in reduction pollutant concentrations, but importantly only investigated a very small portion of the parameter space.

Although CiTTy-Street is unable to simulate the complex fluid-dynamical flows needed to calculate the exchange efficiency for a particular canyon with trees, it can be used to map the parameter space due to changes in exchange efficiency (or residence time) and deposition velocity. Using the model setup for a single canyon, as described above, a bi-variate sensitivity study was carried out, varying the canyon residence time and the deposition velocity of the canyon surfaces, to probe the likely response of a single urban canyon to the addition of street trees. The results of this study are shown in Figs. 3 and S5. Deposition velocities are expressed relative to the floor area of the canyon to aid comparison of our results to other works, i.e.

$$V_{d,i}^{c} = \frac{(w\,V_{d,i}^{w}) + 2(h\,V_{d,i}^{h})}{w}, \quad \text{(S23)}$$

where, $V_{d,i}^{c}$is the canyon deposition velocity for pollutant i. For NO_2 in this scenario, an increase in canyon residence time always led to an increased NO_2 mixing ratio, although the mixing ratio increase became less marked as V_d increased. $V_{d,NO2}^{c}$= 1.0 cm s^{-1} is a factor of 1.5 greater than that estimated for 100% green walls. Note, however, that the model response was strongly dependent upon the scenario, specifically the in-canyon emission flux of NO_x. The emission fluxes used here are typical of central London. At lower NO_x emission fluxes a compensation deposition velocity could be reached at which the canyon deposition velocity effect balanced the residence time effect, leading to a decrease, rather than an increase, in in-canyon NO_2 concentrations. An equivalent compensation deposition velocity is clearly seen for PM_{10} at $V_{d,PM10}^{c}$=0.4 cm s^{-1} in the lower panel of Figure S5. This canyon deposition velocity for PM_{10} is only 27% of that for the 100% green wall scenario.

Top-of-canyon fluxes

Figure S6 (left) shows the reductions in NO_x flux at the top of the canyon caused by the different in-canyon surfaces for several values of canyon residence time. Compared to the NO_x emission flux of 2.12 x 10^{12} molecules cm^{-2} s^{-1}, deposition to a standard canyon with brick walls and concrete road (control scenario), along with chemical losses of NO_x, led to a NO_x flux reduction of 8.6% at the top of the canyon, for u=1 m s^{-1}. Inclusion of a green wall with 50% coverage increased this to a 12.6% reduction, and a green wall with 100% coverage gave a 16.1% reduction. Hence the inclusion of in-canyon vegetation can also make non-negligible reductions in the net pollutant fluxes emitted from an urban area.

The efficacy of in-canyon vegetation as opposed to green roofs for air pollutant removal is particularly demonstrated by Figure S6 (right), where the NO_2 deposition fluxes to a vegetated canyon were several times larger than those to green roofs. Indeed, under long residence times, the brick walled canyon was more effective that the green roof at NO_2 removal, owing to higher NO_2 concentrations within the canyon.

The recent UK National Ecosystem Assessment assumes that urbanization of vegetated land has reduced the potential sinks for pollutants[36]. To investigate this hypothesis a single-box CiTTyCAT run was carried out for a 100%-vegetated planar land surface and compared the calculated NO_2 deposition fluxes with those for our CiTTy-Street runs (Figure S7). A street canyon with 100% green walls was a more efficient NO_2 sink than a planar vegetated surface at all wind speeds. Therefore it may be concluded that 100% greening is not required in order for urban areas to provide a pollutant sink that is as efficient as those green spaces they replace. For the central London wind speed scenario used in this work, the level of wall greening required was ~50%.

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Table S1. Characteristics of the street canyon measurement sites. Data was gathered as part of the TRAPOS campaign. See http://www2.dmu.dk/atmosphericenvironment/Trapos/datadoc.htm for more details.

Site	Height (m)	Width (m)	Measurement year	Measurement institution
Göttinger Strasse, Hannover	20	25	1994	Niedersächsisches Landesamt für Ökologie, Hannover
Schildhornstrasse, Berlin	19 (NE), 22 (SW)	26	1995	Senatsverwaltung für Stadtentwicklung, Berlin
Jagtvej, Copenhagen	18	25	1994	National Environmental Research Institute, Denmark

Table S2. Initial/background concentrations for the numerous canyon and single canyon runs.

Species	Numerous canyons (ppbv)	Single canyon (ppbv)
NO	2.8	16.5
NO_2	10.6	30
O_3	34	18
PAN	0.27	0.27
HCHO	1.8	1.8
H_2O_2	0.15	0.15
C_6H_6	0.11	0.11
C_7H_8	0.24	0.24
CH_3COCH_3	2	2
CO	190	400
CH_4	1745	1745
PM_{10}	36 μg m^{-3}	36 μg m^{-3}

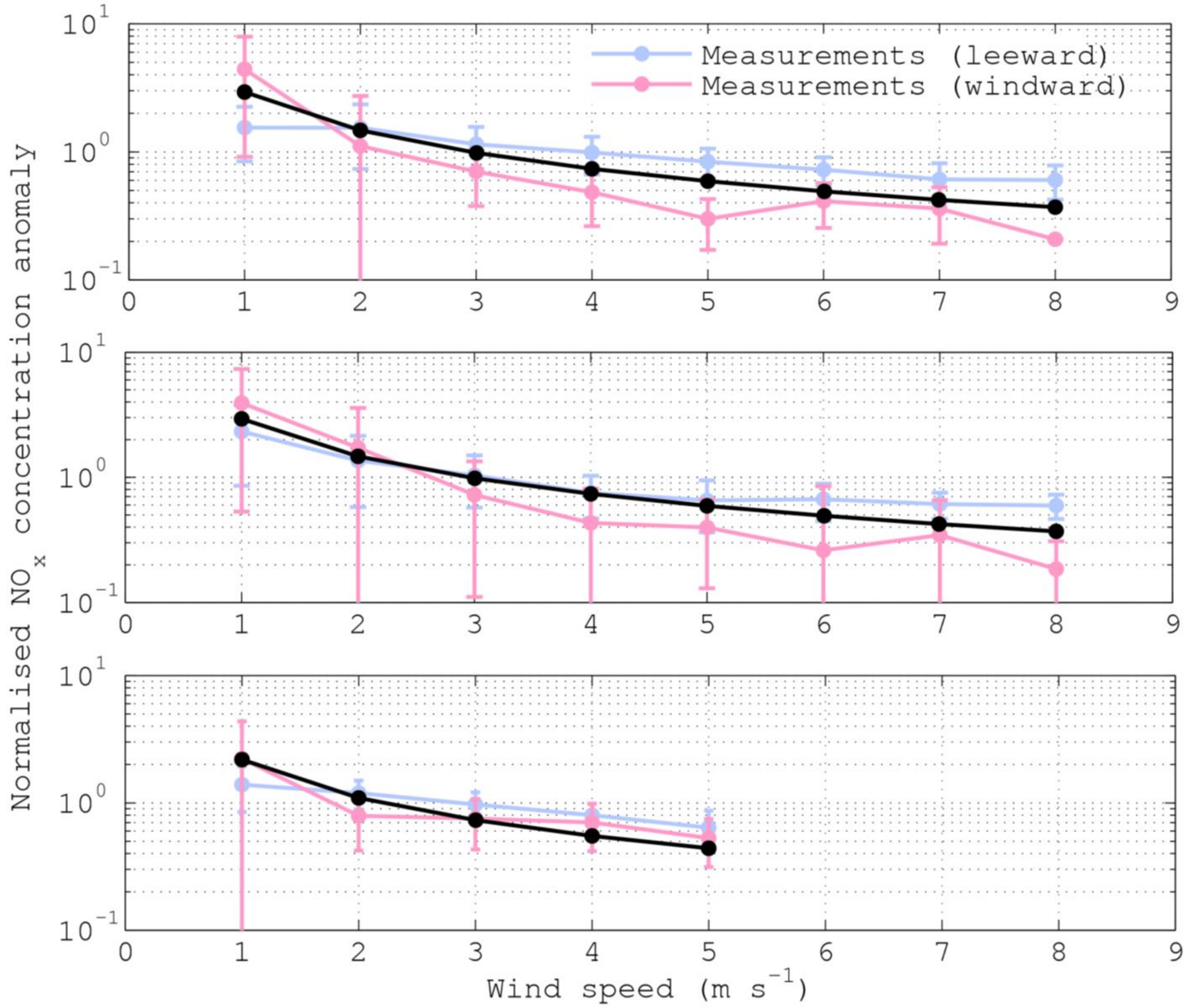

Figure S1. Variation of street canyon NO_x concentration with wind speed using a year of hourly data from three different street canyon measurement sites: Göttinger Strasse, Hannover (top); Jagtvej, Copenhagen (middle); Schildhornstrasse, Berlin (bottom). Anomalies were calculated by subtracting background measurements from in-canyon measurements and normalizing against traffic emissions and the mean concentration anomaly. Data is split according to whether the measurement is on the leeward (blue line) or windward (red line) side of the canyon. Output from the CiTTy-Street model is shown by the black line.

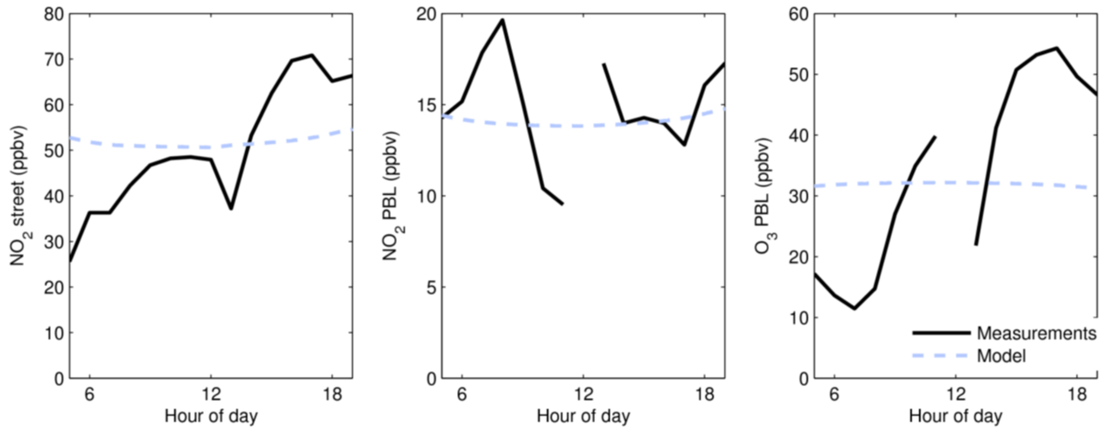

Figure S2. Comparison of modeled (dashed blue lines) NO_2 and O_3 with measurements (solid black lines) for Göttinger Strasse, Hanover, Germany on 21/06/94.

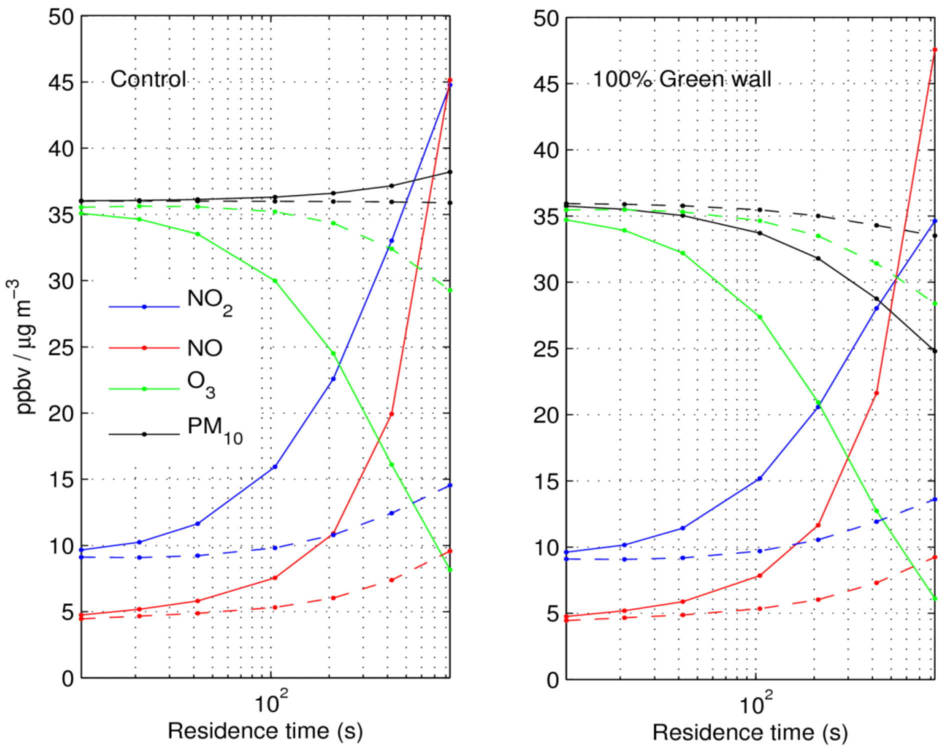

Figure S3. Change in modeled mixing ratios (concentration for PM_{10}) with increasing residence time for the control scenario (left) and the 100% green wall scenario (right) for the numerous canyons setup. The solid lines show street canyon mixing ratios and the dashed lines show UBL mixing ratios.

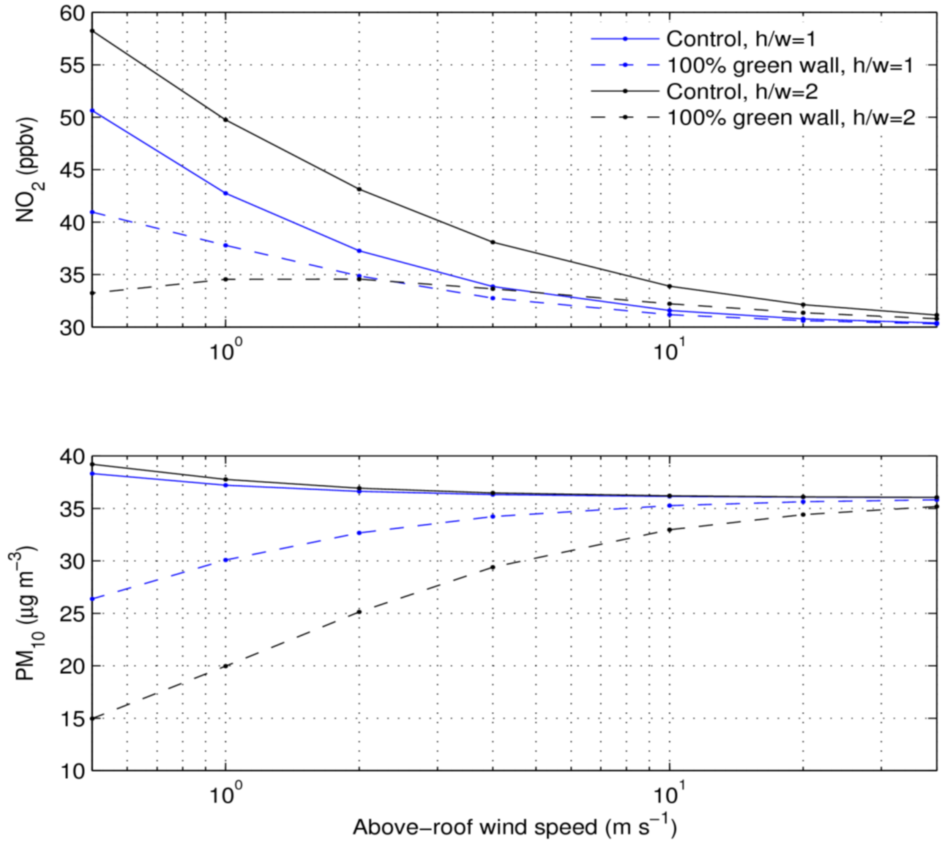

Figure S4. The variation of modeled in-canyon concentrations of NO_2 (top) and PM_{10} (bottom) with above-roof wind speed for a Central London canyon of *h/w*=1 (blue) and of *h/w*=2 (black). Solid lines show control runs and dashed lines show 100% green wall runs. The greatest pollutant concentrations reductions by vegetation are coincident with the conditions of highest pollution (see text).

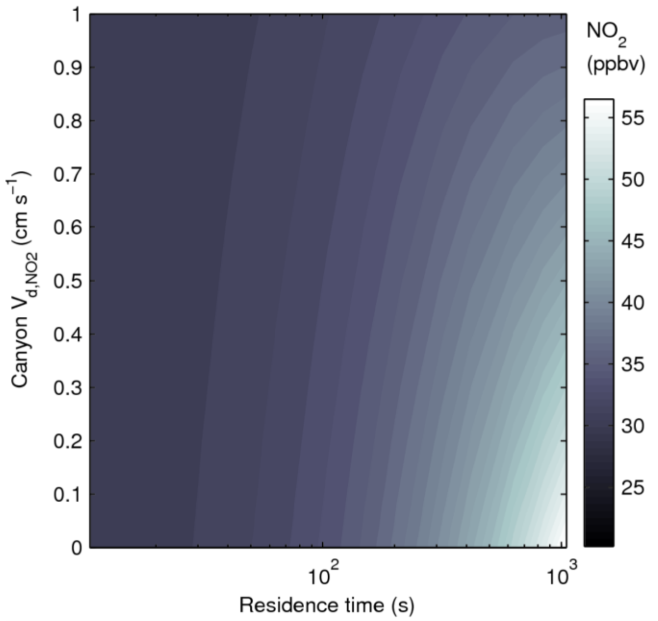

Figure S5. Effect of canyon residence time and canyon deposition velocity on modeled mixing ratios of NO_2 for a single canyon in central London. Total canyon $V_{d,NO2}$ is expressed relative to the width of the canyon to aid comparison of these results to future studies. Note that unlike $V_{d,PM10}(P)$, $V_{d,NO2}(P)$ (beyond the bounds of this plot) is not constant with residence time due to the effect of chemical transformations.

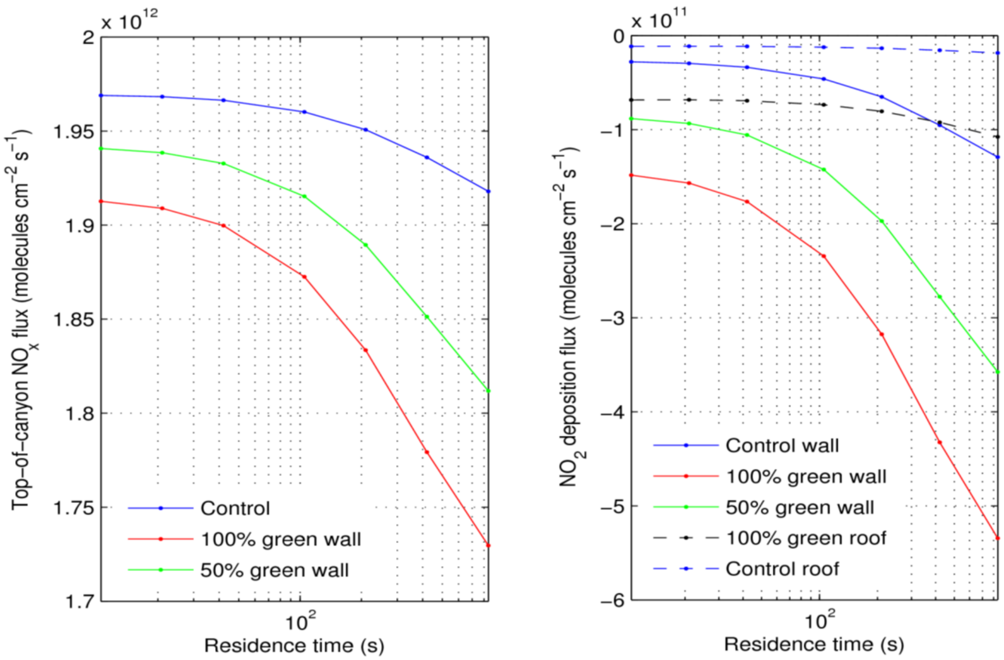

Figure S6. Left: Variation of top-of-canyon NO_x fluxes with canyon residence time with and without green walls. Right: Variation of NO_2 deposition fluxes. Solid lines show fluxes in the street canyon (relative to canyon width, *w*), and dashed lines show fluxes in the UBL (relative to building width, *r*). In these simulations 50% wall greening has the same area of vegetation as a 100% greened roof.

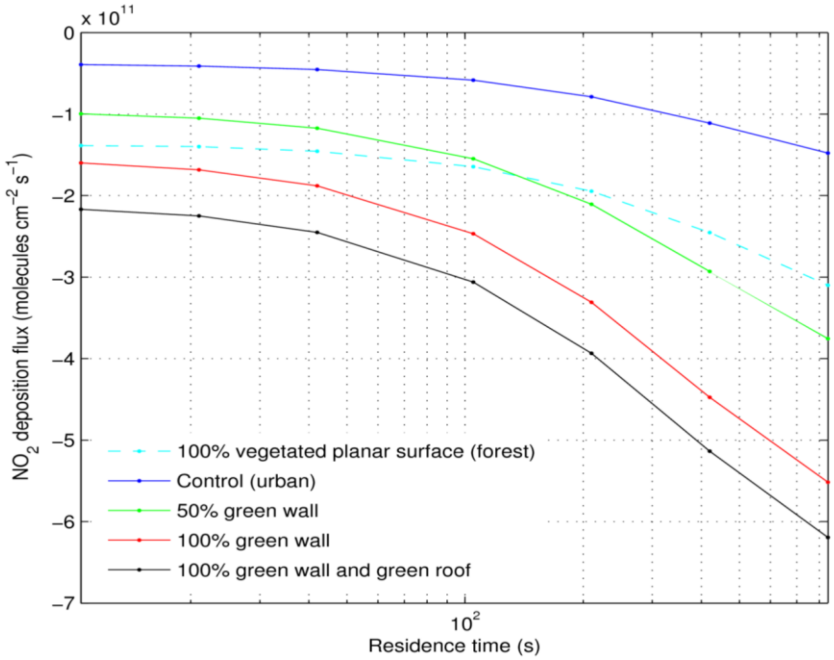

Figure S7. Comparison of NO_2 deposition fluxes to an urban surface with a 100% vegetated planar surface (i.e. pre-urbanization).