

transport out of the volume) and fully turbulent conditions with negligible storage. In urban environments during stable atmospheric conditions the ΔC_S term will be non-negligible (Helfter et al., 2011); for example, ΔC_S was found to be five times the magnitude of the turbulent vertical flux term (F_{CO_2}) close to dawn and dusk in suburban Vancouver, Canada (Crawford and Christen, 2014). Other urban studies found ΔC_S to be smaller, but still significant, with maximum ΔC_S values 11% and 22% of the magnitude of F_{CO_2} in Edinburgh, Scotland (Nemitz et al., 2002) and Basel, Switzerland (Feigenwinter et al., 2012), respectively. Similarly, in rural environments horizontal advection may be non-negligible (e.g., Aubinet et al., 2003). This paper focuses on the methodological considerations when assessing ΔC_S from a vertical profile in an urban environment. Future manuscripts will address horizontal variation and advection.

Of three studies discussed above (Vancouver, Edinburgh, Basel) with reported urban CO₂ storage values, only one (Vancouver, Crawford and Christen, 2014) presented values derived from a dataset of longer than one month; however, both these values and those reported for Edinburgh by Nemitz et al. (2002) were calculated based on the assumption of a constant relation between carbon dioxide concentration ($[CO_2]$) measured above the blending height and the concentration in the street canyon. In contrast, for Basel, Feigenwinter et al. (2012) did not make this assumption and reported ΔC_S calculated from $[CO_2]$ at ten levels; however, the results are only for one month (15th June to 15th July 2002). There is therefore scope to improve not only the understanding of the processes affecting CO₂ storage over a greater range of meteorological and anthropogenic conditions, but also to develop recommendations for future measurement programmes.

The objective of this paper is to evaluate potential approaches for such studies, illustrated with examples from, and analysis of, high temporal resolution data collected at 10 locations from 6.5 to 46.4 m above ground level between 2011 and 2014 at King's College London, in Central London, UK. The paper is organized as follows. In the rest of this Section 1 we provide a brief background of how CO₂ storage is calculated and then (Section 2) a discussion of the methods used in this paper. This is followed by an exploration of the temporal variation of CO₂ storage (Section 3) and the relation between measured CO₂ storage and anthropogenic and natural factors in a highly urbanised environment (Section 4). The required number and placement of sample points for CO₂ storage measurements in a deep urban street canyon is addressed (Section 5) and the effect of sensor response and sampling interval on calculated CO₂ storage is tested (Section 6). At the processing stage, three different temporal and spatial interpolation methods are evaluated against measured data (Section 7). Finally, the impact of CO₂ storage calculated by two different methods on the turbulent vertical CO₂ flux is assessed. The Supplementary material (noted by S.1 to S.9), includes the notation with corresponding units (S.1) used in the text, further information on CO₂ storage calculation (S.2), previous CO₂ storage studies (S.3), equipment (S.4), meteorological characteristics (S.5), example time series (S.6), variations of CO₂ with friction velocity, wind direction and height above ground level (S.7, S.8) and further references (S.9). The online version of this paper provides the figures in colour.

1.1. Calculation of CO₂ storage

There are two main approaches to calculating CO₂ storage flux density, i.e., the rate of change of CO₂ per unit area below the Eddy Covariance (EC) measurement height. Here they are referred to as the 'single height' and the 'profile' approaches. For a brief discussion of the theory and some reported results, see Supplementary material S.2 and S.3, respectively. For a more in depth discussion

of the theoretical considerations regarding CO₂ storage the reader is referred to Finnigan (2006) and subsequent discussion (Kowalksi, 2008; Finnigan, 2009).

The approach to calculate CO₂ storage depends upon the number of vertical locations at which CO₂ concentration ($[CO_2]$, the symbol $[]$ is used to indicate concentration) data are collected. In the first approach, 'single height' CO₂ storage (ΔC_{SS}) is calculated from $[CO_2]$ data at one location, usually by eddy covariance equipment in the inertial sub-layer (Nemitz et al., 2002; Crawford and Christen, 2014). In the second approach, the 'profile' method, ΔC_S is calculated from data collected at multiple heights (ΔC_{SP}). The profile method uses a vertical $[CO_2]$ profile at heights z_i , which is generally measured by cycling through all the sample locations within a set time period with a data-logger controlled valve array (Xu et al., 1999; Mölder et al., 2000; Vogt et al., 2006; Hutyra et al., 2008). This cycle period may not be the same as the averaging period used in the ΔC_{SP} calculation. For example, measurements collected with a sampling interval, t_s , of 2 Hz for 75 s at 8 heights, giving a full profile cycle every 10 min, may be used to calculate ΔC_{SP} with an averaging period (T) of 30 min. The storage is calculated as the sum of the changes in time averaged concentration ($\overline{[CO_2]}_i$) between time $t = -T/2$ and $t = T/2$ for each location (i) in the profile, weighted by the vertical span, Δz_i , over which each profile measurement is considered to be representative and divided by the averaging period (T), which can be expressed as (modified from Aubinet et al., 2005):

$$\Delta C_{SP} = \frac{1}{T} \sum_i \left(\overline{[CO_2]}_i, t=\frac{T}{2} - \overline{[CO_2]}_i, t=-\frac{T}{2} \right) \Delta z_i \quad (1)$$

If the measurements at each height are not made concurrently, $[CO_2]$ at each height may first be interpolated in time to generate instantaneous profiles from which ΔC_{SP} can be calculated, though this is neglected in some cases (Iwata et al., 2005). The impact of interpolation on calculated ΔC_{SP} is discussed further in Section 7.

The single height method is a simplification of the profile method to one height, which is usually the height of the eddy covariance equipment. The change in $[CO_2]$ with time at z_h ($\Delta [CO_2]/\Delta t$) is weighted by the vertical distance from the ground to the measurement point (z_h). The single height CO₂ storage (ΔC_{SS}) is given by (modified from Nemitz et al., 2002):

$$\Delta C_{SS} = \frac{\Delta [CO_2]}{\Delta t} z_h \quad (2)$$

As the data are continuous, the change in the instantaneous CO₂ concentration with time ($\Delta [CO_2]/\Delta t$) can be used instead of the change in the time averaged CO₂ concentration with time ($\overline{[CO_2]}/\Delta t$), though it may still be advisable to average in time to reduce measurement noise (Finnigan, 2006).

The ΔC_{SS} calculation assumes any change in $[CO_2]$ below the measurement height results in a change of equivalent magnitude at the measurement height. This assumption appears not to be supported by any evidence in the literature; reported diurnal cycles of CO₂ mixing ratios in the roughness sub-layer over both rural (e.g., Xu et al., 1999) and urban (e.g., Lietzke and Vogt, 2013) surfaces are known to vary with height. This problem is particularly acute during periods of low turbulence, such as at night or during cold weather, where measurements above the surface layer may become decoupled from processes near ground level (Helfter et al., 2011).

If temporal variability is large compared to the spatial variability, the single height method may provide a more accurate measure of storage than the profile method as the maximum data availability at each sample location for the latter may be $1/k$ of the total time