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A Mobile Measuring Methodology to Determine Near Surface Carbon Dioxide within Urban Areas

Henninger, Sascha

*Technical University of Kaiserslautern
Germany*

1. Introduction

Atmospheric carbon dioxide is one of the infra-red active trace gases responsible for the anthropogenic global warming. Due to the increasing use of fossil fuels within the lower atmosphere, but also within the urban boundary layer of urban agglomerations, an increase of the CO₂ concentration must be expected. Less is known about the temporal and spatial behavior of this trace gas, especially in cities and their surrounding areas. Between 2002 and 2004 first investigations were made about the distribution of the CO₂ concentration within the urban canopy layer of the city of Essen, Germany (51°28'N, 7°0'E). These first measurements should develop and verify a mobile measuring methodology to determine the air quality indicators, first of all CO₂, but also CO, NO, SO₂, O₃, in dependence of the urban types of land use, the topographical circumstances and the meteorological conditions and how to transfer this methodology to other cities. For this implementation there were additional mobile measurements done in different cities within different climatic zones from 2006 till 2010.

The structure of emission within an urban area is mainly characterized by traffic and the private domestic heating (especially in winter). The proportion of power plant and industrial facilities is less, because of the plume height of the stacks. Most of this emission is blown away from the urban sites. On the basis of the predominantly low source heights and the invariable and variable factors, which determine the distribution of the trace substances and define their chemical transformation, the question was how the emission is dependent on the local urban types of land use and how these were affiliated with each other. Because of the different sources of emission the urban air quality is spatially as well as temporarily extremely volatile. Some reasons for this inhomogeneous field of emission are the transportation infrastructure, different heights of the emission sources and the limited exchange of the urban canopy layer within the street canyons. Therefore, it is hardly possible to use results of air quality measurements from fixed urban measuring stations. An adequate transferability of these could not be guaranteed for more than the immediate proximity of the station. One way of analyzing the fine structure of the different fields of emission is creating a numerical analysis model which enables a prediction of the traffic-related exposure. However, this modeling requires a corresponding number of input values and a suitable validation.

Another possibility detecting the inhomogeneous urban fields of emission is using mobile air quality measurements. The advantage of this type of methodology is the high density of measurements, which could be mapped spatially. Although especially in the applied urban climatology the methodology of mobile measurements to detect data of air temperature and air humidity has been practiced for a long time, mobile air quality measurements do not have quite a long tradition. Already in the 1920's mobile air temperature measurements were made (Schmidt, 1927; Peppler, 1929). The first ones were semi-mobile, but in the course of the time the technological development allowed to measure continuously from the beginning to the end of the transect. Due to the high quality demands on the measurement equipment the number of mobile air quality measurements is low, mainly with a bulk on the air pollutants CO, NO and O₃, also for particulate matters. Up to now, there is no adequate single methodology for mobile air quality measurements, which ultimately ensures a comparability of the results of different publications. Thus all publications vary on the subject of travelling speed, length of the measuring route, the sampling rate of the analyzers, the measuring time and period and the types of detected trace elements (e. g. Heussner, 1988; Luria et al., 1990; Shorter et al., 1998; Kuttler & Straßburger, 1999; Idso et al., 2001; Bukowiecki et al., 2002; Kuttler & Weber, 2006; Henninger, 2008a).

2. Urban carbon dioxide

Attention on the urban CO₂ concentration was already paid in the 19th century. Probably one of the oldest analysis of continuously measured carbon dioxide within an urban area was from 1877 till 1910 in the outskirts of Paris, France (Stanhill, 1982). During the measuring period the annual average of the carbon dioxide varied between 284 ppm and 325 ppm. After the mid-20th century investigations considering the urban CO₂ started in its entirety. One of the first was a two-year measurement campaign in Vienna (Austria). Already at this time Steinhauser et al. (1959) were able to point out that an increase of the CO₂ concentration is dependent on the wind direction, which blows gently from the urban sectors and that domestic fuel combustion caused a significant difference of trace gas concentration between summer and winter month.

Traffic, domestic fuel combustion, industrial facilities, and power stations are verifiably the most important sources of CO₂ emission within urban conurbations. But in the case of carbon dioxide, the urban vegetation must also be mentioned, in fact the plant respiration has an undeniable amount on the total urban CO₂ concentration. But of course urban green areas have the function of natural CO₂ sinks of the anthropogenic carbon dioxide (Nowak & Crane, 2001; Yang et al., 2005; Henninger, 2005a; 2008; Henninger & Kuttler, 2007; 2010). Down to the present day the available literature shows a continuously increasing number of publications dealing with the arise and allocation of urban carbon dioxide. A simple classification offers five types of detecting CO₂ within the urban boundary layer:

1. Investigations of the turbulent vertical flux of carbon dioxide, especially within urban street canyons (e. g. Nemitz et al., 2002; Grimmond et al., 2004; Moriwaki & Kanda, 2004; Salmond et al., 2005; Velasco et al., 2005; Vogt et al., 2005; Coutts et al., 2007).
2. Analyzing the stable carbon isotopes to determine CO₂ sources (e. g. Clarke-Thorne & Yapp, 2003; Pataki et al., 2003; Carmi et al., 2005; Pataki et al., 2006).
3. Stationary CO₂ measurements to determine the diurnal or seasonal course of the concentration within a given type of land-use (e. g. Ghauri et al., 1994; Derwent et al., 1995; Inoue & Matseuda, 2001; Manuel et al., 2002; Sikar & La Skala, 2004; Salmond et al., 2005).

4. Measuring the gradient of carbon dioxide between urban and rural locations (e. g. Berry & Colls, 1990a/b; Ziska et al., 2004; George et al., 2007).

All of these studies were carried out by stationary measurements. These investigations require a lot of time, work, and equipment to ensure the transferability from the measurement location to its nearby vicinity. Measuring vertical turbulent fluxes and long time-series of CO₂ present representative concentration and fluxes, which can be very heterogeneous over small spatial scales.

An opportunity to solve this problem made it necessary to create a measurement methodology, which is applicable for different types of land usage and of trace elements, but also representative, so that an ultimately statistical reproducibility of the results can be guaranteed. This enables to classify a fifth type to determine urban carbon dioxide:

5. Mobile measurements with the aid of mobile air quality laboratories (e. g. Idso et al., 1998; 2001; Henninger, 2005a; 2008; Henninger & Kuttler, 2007; 2010).

Although mobile measurements promise a high spatial and temporal density of area-covering information, still only few publications deal with mobile measurements of CO₂ within urban environments. Especially, there is a gap between considering various influencing factors within the urban canopy layer, which could affect the pattern of the CO₂ concentration permanently. Publications about mobile measurements were based on a definite measuring route to determine typical inhomogeneous fields of air pollutants within urban spaces (e. g. Luria et al., 1990; Shorter et al., 1998; Idso et al., 1998; 2001; Bukowiecki et al., 2002). All these exemplarily shown investigations were only made over short time periods of few days up to several weeks. Due to this it is impossible to consider different seasons and different times of the day, which affect the variability of the CO₂ concentration within the urban boundary layer. Accordingly it is also impossible to get representative and reliable statements about the atmospheric CO₂ concentration within the urban canopy layer. Particularly with regard to the current discussion about reducing the emission of CO₂, analyzing urban trace elements becomes a specific relevance because today's urban agglomerations must be considered as one of the major carbon dioxide sources with an increasing tendency in the future. An accurate impression of the exhaust of the greenhouse gas is only possible if multifarious patterns of the different urban land uses are considered because not every urban land use is coevally a CO₂ source. So this is one of the major uncertainties, precisely because it is very difficult to relate CO₂ concentration to a specific type of land use by 100 %. Advective processes may have more or less influence, which could not be completely eliminated. However, it is very important to differ between urban green areas, industrial, commercial and residential areas. Mobile measurements have the ability to assure this because all different types of land use could be achieved, so that there is not only a differentiation between the land use, but also a diverse structure within one land use. For example residential areas can be classified by the variation of the structure of housing (Henninger, 2008a).

Due to a heterogeneous structure of different types of land use within urban areas we must expect a great number of diverse fields of emission of different atmospheric trace gases. Therefore these could poorly be recorded by conventional stationary measurements. Stationary measurements are particularly suitable for long-range homogeneous areas, however, their temporally highly resolved results could hardly be transferred to other types of land use. Hence, there is the opportunity of mobile measurements to solve this problem within such a heterogeneous structure of an urban area. An important point of discussion regarding mobile air quality measurements is the temporal and spatial representation in contrast to standardized stationary measurements. With the aid of highly frequented spatial

air quality measurement trips it is possible to have numerous measuring points along the measuring route. Due to this highly frequented spatial detection of different trace substances a mobile measuring route is well suited for recording the non-homogeneous urban area with its diverse fields of emission based on their different types of urban land use. Generally, the urban field of emission is mainly dependent from the emissions of traffic and the domestic fuel combustion, less from the emission of power plants and industrial areas. Especially, because of the uneven distribution of these different types of emission sources, mobile measurements are inevitable and the only possibility of obtaining spatially high resolutions of the pattern of different air quality substances. In addition, a high quantity of mobile survey tests solves the disadvantage of a low temporal resolution (Henninger, 2005a; 2008; Henninger & Kuttler, 2007; 2010).

Due to the fact that it is not possible to fade out the weather conditions and other influencing factor it must be the aim to analyze the dependence of urban CO₂ concentration by temporal variable (e. g. air temperature, atmospheric stability) as well as invariable (e. g. surface configuration) influencing factors within the urban canopy layer. It should prove how the urban CO₂ concentration is influenced by spatial variations as well as diurnal and seasonal meteorological conditions (Henninger, 2005a; 2008).

3. Measurement methodology

3.1 Mobile measurements

Even though, there exist many different investigations of mobile air quality measurements, there are lots of significant differences in spite of the used methodology. So it was necessary to create a general measuring method, which has the ability to determine the urban air quality in a representative way so that an ultimate statistical demonstrable reproducibility of results can be guaranteed.

The mobile measurements were made by a mobile laboratory. The analytical equipment allowed, in addition to CO₂, a continuous determination of the air quality indicators carbon monoxide (CO), nitrogen monoxide (NO), nitrogen oxides (NO_x), ozone (O₃) and particulate matter (PM₁₀) during the measuring trips at a height of 1.50 m above ground level. The air sampling was done on the right-hand side of the mobile laboratory to reduce the influence of passing motor vehicles. In addition to the trace elements the meteorological values air temperature and air humidity were measured in the front of the mobile lab at 2 m above ground level, also barometric pressure, solar radiation and UV radiation at 3.50 m above ground level on the roof top of the vehicle.

In consequence that the different air quality indicators were based on diverse analytical methods the equipment had to be calibrated before every measuring trip. Due to the fact that carbon dioxide is not classified as a classical air pollutant there is no engaging guideline how CO₂ should be measured in ambient air. So the CO₂ analyzer was calibrated according to the official guideline of the German VDI (VDI guideline 3950, sheet 1, 1994). The analyzers of the other air pollutants were also verified according to the VDI guidelines 2459, sheet 6, 1980 (CO), 2453, sheet 2, 2002 (NO, NO_x) and 2468, sheet 6, 1979 (O₃). Carbon dioxide and carbon monoxide were analyzed using IR absorption, ozone by UV absorption. In contrast, the nitrogen oxides were determined by chemiluminescence. Air quality analyzers as well as the equipment for meteorology were calibrated with a measuring frequency of 1 Hz, which made temporal corrections of all data less complicated.

The maximum driving speed was 30 km h⁻¹ along streets (8 m s⁻¹) and 60 km h⁻¹ (about 16 m s⁻¹) on freeways. In spite of the known delay times of the analyzers (e. g. CO₂ = 13 sec.) and a measuring frequency of 1 Hz the spatial resolution of the measurement was 8 m and 16 m respectively. With regard to the delay times of the different instruments and the low driving speed of the mobile lab measurements could be made approximately in real time. At the end of each measuring trip the analyzers were still kept on running for another of 30 seconds. Due to this the delay times of all analyzers were considered. This subsequent temporal correction of the measured values for CO₂, CO, NO, NO_x, O₃ and PM₁₀, but also for the meteorological parameters enabled most accurate and representative results of the air quality and meteorology along the transect. In addition to the measured values also GPS coordinates (measurement frequency of 1 Hz) allowed to relate every recorded value of the air quality indicators to its GPS-point along the measuring route.

Looking for a representative and an almost unaffected measuring method for air quality indicators within streets canyons to determine the pollutants without a direct influence of diverse vehicles standing or waiting in front of the mobile laboratory or beside it, was a great afford. Due to traffic jams or red lights there could be a lot of interruptions of the analysis of the data. Such a situation causes an accumulation of the air borne pollutants and accordingly ensures an increase of the concentration. A similar problem for measuring more or less representative values could be the exhaust plume of the vehicles, which are driving directly in front of the mobile lab and thus leads to a distortion of the results. Every second logged data were marked manually using GPS to solve this problem. For that each traffic stop and traffic jam could be mapped along the transect and was filtered out before the analysis of the raw data. It is of great importance that the suction unit of the air quality indicators of the mobile laboratory is placed on the opposite side of the road traffic and thus is already protected against the direct impact of vehicle emissions. Additionally a safety distance of > 2 m from the directly vehicles in front of the mobile lab was adhered to reduce the influence of others. This safety distance is based on Clifford et al. (1997). They could prove by different simulations that the influence on the concentration of the exhaust plume of vehicles in front of another is significantly decreasing and is nearly negligible up to 1.50 m or more meters. Nevertheless, the raw data must be checked for plausibility despite marking the data. So individual values of the data set, which deviate significantly from the others, should be removed manually before the subsequent analysis.

However a comparison of the concentration CO₂ concentration pattern along the transect indicates that there are no significant differences between the carbon dioxide courses with and without filtering out the stops ($n = 150$, $\alpha > 0.5$). A correlation between the corrected and the uncorrected results for the diverse measuring routes offers a correlation coefficient $R^2 = 0.94$ ($n = 150$; $\alpha > 0.5$) for all measuring times, day and night. This correlation coefficient is shown exemplarily for the whole measuring period in figure 1. Divided into day and nighttime measurements, the nighttime survey test indicates a plainly higher $R^2 = 0.98$ ($n = 60$; $\alpha > 0.5$) in comparison to the measuring trips during the day ($R^2 = 0.90$; $n = 90$; $\alpha > 0.5$). Due to a lower probability of traffic-related interruptions and verifiable more stable atmospheric conditions overnight the effect of different sources of CO₂ emissions is vanishingly low. The atmospheric conditions are based on the calculation of the stability index of Pasquill (1961) and Polster (1969) by using the data of meteorological stations, which were installed along the measuring route. Anyhow it was not abandoned filtering out the obviously influenced data because ultimately, even if there is a correlation coefficient of $R^2 > 0.90$ for all measuring trips, the determined values were still influenced.

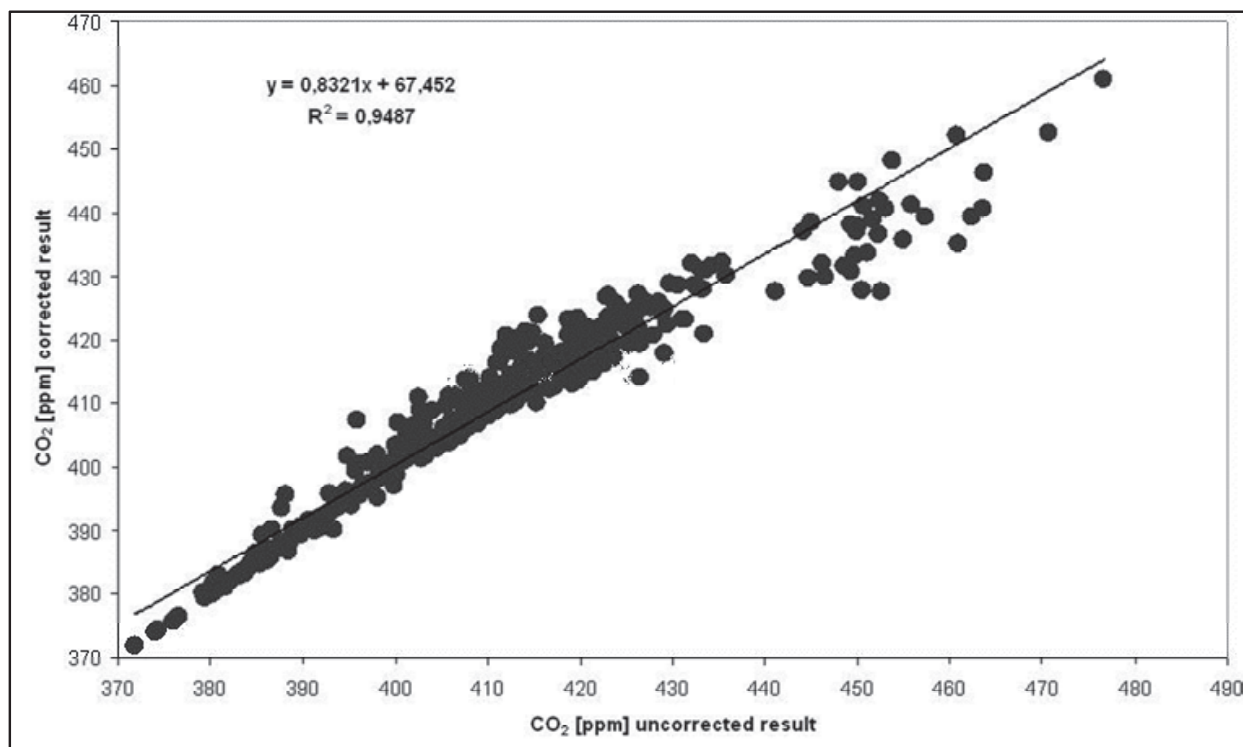


Fig. 1. Scattergram for the correlation between the uncorrected und corrected results of the CO₂ measurements made within different urban areas (n = 150)

Because of a relatively high spatial fluctuation of the trace gas concentration along the measuring route it was necessary to calculate the arithmetic mean values of the so-called homogeneous road sections (Kuttler & Wacker, 2001; Henninger, 2005a; 2008; Henninger & Kuttler, 2007; 2010). Spatial fluctuations could be caused by the change of the structure of housing along the streets, varying density of traffic or the change of land use and different climatopes. By this way, creating different route sections along the transect enables a direct comparison of single measuring trips with each other and a better interpretation for the data processing. Though every road section is characterized by a type of land usage, the length of a section could vary from time to time. So it is unavoidable that a continuous transition from one type of land usage to another could not always be guaranteed. Exemplarily, due to a length of 63 kilometers the measuring route could be subdivided into 61 road sections with a length of nearly 1000 meters each (Henninger, 2008a). In order to reduce the influence of the transition from one area to the neighboring road section it was ensured that these five seconds of travelling (~ 40 m) were not taken into account.

3.2 Measuring site

Generally all urban areas present a heterogeneous structure due to the different types of land use. As it is reflected in the local emission structure of the different trace elements within the urban site. For this reason, the measuring route has to take all urban types land of use into account in order to obtain a representative pattern of the appropriate carbon dioxide situation.

First measurements determined the near surface urban carbon dioxide by a mobile laboratory in the city of Essen, Germany (51°28'N, 7°0'E) between 2002 and 2004 to verify the theoretical deliberations. Due to its location and structure within the conurbation area

“Ruhrgebiet“, Essen should be representative for its structure of anthropogenic carbon dioxide emissions. Regarding its structure of emission within the urban canopy layer of Essen, the most important impacts within the investigation area are determined to be the low emission heights of traffic and domestic fuel. The measurement route had a total length 63 kilometers and led the transect from the south to the north of the urban area. It displayed a serpentine route to ensure that the measuring transect included all varieties of urban land use. Additional mobile measurements have been made between 2003 and 2010 within different urban areas with diverse sizes and in different climatic zones to investigate the transferability of the measuring method (Tab. 1):

Location	Measuring time	Trace elements	References
Essen, Germany (51°28`N, 7°0`E); 580,000 inhabitants; A = 210 km²	2002 till 2004	CO ₂ , CO, NO, NO _x , O ₃	Henninger, 2005a/b; Henninger, 2008a; Henninger & Kuttler, 2007; Henninger & Kuttler, 2010
Krefeld, Germany (51 ° 20`N, 6° 35 `E); 238,000 inhabitants; A = 138 km²	2003 till 2004	CO ₂ , CO, NO, NO _x , O ₃	Henninger, 2005b
Bad Ems, Germany (50°25`N, 7°45`E); 10,000 inhabitants; A = 16 km²	2005	CO ₂ , CO, NO, NO _x , O ₃ , PM ₁₀	Henninger 2008b/c
Koblenz, Germany (50°21`N, 7°36`E); 106,500 inhabitants; A = 105 km²	2006	CO ₂ , CO, NO, NO _x , O ₃ , PM ₁₀	
Kigali, Rwanda (1°57`S, 30°4`E); 1,000,000 inhabitants; A = 738 km²	2008-2009	CO ₂ , CO, NO, NO _x , O ₃ , PM ₁₀	Henninger 2009a/b
Saarbrücken, Germany (49°14`N, 7°0`E); 176,000 inhabitants; A = 167 km²	2010	CO ₂ , CO, NO, NO _x , O ₃ , PM ₁₀	

Table 1. Schedule of mobile CO₂ measurements with the same measuring methodology

Based on the described measuring method further investigations were made by Ptak (2009). Between 2005 and 2007 she performed in two German cities (Münster; 51°57`N, 7°37`E and Lüdenscheid; 51°13`N, 7°37`E) mobile carbon dioxide measurements, confirmed the method and the following described representative status of it.

Generally, for the choice of a measuring route in dependence of the location and its characteristic and typical urban types of land use the following factors should be considered:

- a big variety of different types of land use because all types of urban usage within the urban area should be taken into account,
- the route should be planned along roads with not much traffic, to ensure that increased CO₂ concentration within the investigation area does not necessarily be attributable only to urban traffic and

- a comparable and a similar type of land use respectively should be at the beginning and end of the measuring route.

3.3 Measuring times

A total of 150 mobile measurements was made between 2002 and 2010 on weekdays and weekends regarding different conditions. Most of the mobile measurements were made during clear and calm weather conditions ($v \leq 1.5 \text{ m s}^{-1}$) and at different times of the day. The low wind speed guaranteed more pronounced local differences of the near surface urban carbon dioxide in relation to the respective types of land use. Thus enables a representation of the urban CO_2 situation for a so-called "worst-case" with low exchange ratios and a negligible influence on a long-distance transport.

The measurement times were primarily based on the daily occurring rush hour. Due to the fact that during the daily rush hours only a short-term situation of the daily air pollution is rendered, the measurements were made in each case before (4 a.m. - 7 a.m. respectively 1 p.m. - 4 p.m.) and after the traffic peak hours (10 a.m. - 1 p.m. respectively 7 p.m. - 10 p.m.) to enable inter alia a uniform traffic flow along the measuring route, but of course also a homogeneous structure of trace elements, especially for CO_2 , in order to show a representative carbon dioxide situation within the urban canopy layer.

The mobile measurements should be performed during both day- and nighttime hours. So the influence of e. g. urban green areas as potential sources of CO_2 (respiratory gas exchange at night) and CO_2 sinks (photosynthetic gas exchange during the day) can be considered. The natural diurnal variations in CO_2 concentration, aroused by the gas-exchange cycle of the biosphere could be represented. For this reason additional trips were taken between 11 p.m. and 2 a.m. to cover the transition time from the first to the second part of the night. This night-time measuring period ensures the determination of the second peak of natural CO_2 caused by the respiratory gas exchange around midnight (Allen, 1965). In addition it was also possible to have a look at the atmospheric boundary layer conditions in connection with the times of the day and its influence on the urban CO_2 . Regardless, the dependence of the time of the day measurements should be placed on weekdays (Monday till Friday) as well as on weekends (Sunday) and holidays (Henninger, 2005a; 2008).

3.4 Classification of variable and invariable influencing factors

Trace elements within the urban area are highly volatile components of the air. As a result of the heterogeneous urban structure the pattern of the CO_2 concentration along a measuring route is affected by a number of different temporal variable as well as invariable influencing factors (Henninger, 2008a). Therefore it is not possible to evaluate the urban carbon dioxide along a transect considering only different measuring times and different weather conditions like e. g. Idso et al. (1998; 2001) did in Phoenix, Arizona, USA, giving a representative statement about the behavior of near surface urban carbon dioxide. Instead, the multidimensional dependence of CO_2 was determined first by a correlation analysis (Pearson and Bravais) and a partial/multiple correlation analysis (Schönwiese, 2006). The different influencing factors were analyzed separately to identify the dominant one. Hence, it was necessary to differentiate between the following temporal variable and invariable factors (Tab. 2; Henninger, 2008a):

Temporal variable factors	Temporal invariable factors
Atmospheric stability of the urban canopy layer	Sky view factor (ψ_s)
Air temperature	Surface configuration
Air humidity	Traffic density
Urban vegetation	

Table 2. Schedule of the different influencing factors which could manipulate the CO₂ pattern within the urban canopy layer

The decision to interpret traffic density as a temporal invariable factor is based on the calculation of traffic data from the council, which is being published at the end of each month. Thus, there is a fixed number of vehicles for each hour.

4. Statistical proofs

Using various statistical methods like cluster analysis, test of significance (*t-test*) and correlation analysis the reproducibility of the mobile measuring trips should be verified. A statement should be given for the situation of air quality within its urban investigation area and whether this determined pattern of carbon dioxide concentration is not only a snap-shot, but rather a recurring incident. The statistical analysis should show whether the measured CO₂ data is in both temporal and spatial behavior representative and reproducible for the route sections or whether it is the result of a random acquired CO₂ pattern.

Primarily, the single linkage cluster analysis with an Euclidean distance (in ppm) should give information about similarities of the behavior of CO₂ concentration along the transect between all completed measuring trips for a definite investigation area. Exemplarily, this is shown in figure 3. It offers five separate clusters, which are identical with the five different times of measuring. This result was checked by a comparison between two measuring trips, being connected in one cluster but also for measuring trips being placed in different clusters by a big distance. Figure 4 presents a uniform allocation of CO₂ along the transect for the measurements made at the same time of the day which creates one similar cluster. An additional test of significance (t-test) confirmed this validation. Measurements taken at the same time of the day, but on different days display no significant differences ($\alpha > 0.5$, Fig. 4). In contrast, trips driven at diverse times show significant differences ($\alpha < 0.05$) respectively a high significant difference ($\alpha < 0.01$) and no similarities in respect of the pattern along the transect (Fig. 5).

These results could be proven for all survey tests of the first initial measurements which were taken between 2002 and 2004 ($n = 44$) as well as for the all additional ones driven between 2003 till 2010 ($n = 150$) to validate the measuring methodology being devised by Henninger (2005a). The preliminary statistical analysis demonstrates that there is, in dependence on the time of the day, a recurrent CO₂ pattern along the transect. That is why a reproducibility of the behavior of CO₂ concentration can be verified and enables an allocation of the different classified variable and invariable influencing factors along the transect (Henninger, 2008a).

5. Reproducibility of the data

At this stage the statistical analysis of the mobile measurements of near surface carbon dioxide between 2002 and 2010 has shown that it is possible to resolve the CO₂ mixing ratio spatially as well as temporarily in dependence of the structure of the urban types of land use. It could be demonstrated that the methodology of measuring carbon dioxide near the ground was not only feasible for one urban area, but it rather works for every urban settlement. Notwithstanding of the general achievements mentioned before, the reproducibility of the data should be offered for one detailed example reconstructing the conclusion of this disquisition. As a consequence the results of a measuring period of at least two years within the city of Essen could explain the applicability of the method the best way. First of all, with the aid of a cluster analysis the CO₂ data for the whole measuring period (n = 40) were divided into meaningful sub-collectives and groups respectively. This calculation based on the comparison of the temporal courses of the CO₂ concentration patterns during each measuring trip. As it is shown in figure 2 three defined clusters were composed of the respective measuring trips for the seasons autumn, winter and spring. Therefore it could be assumed that the temporal behavior of the involved measurements offer extensive similarities within each season. A solitary exception indicated the summer months. The splitting of the summer measuring trips into two clusters could be explained by the significant concentration differences, which occur between the day- and night-time situation during this season. Indeed, there are also detectable night and day concentration gradients for carbon dioxide during the other three seasons, but plainly smaller and less noticeable.

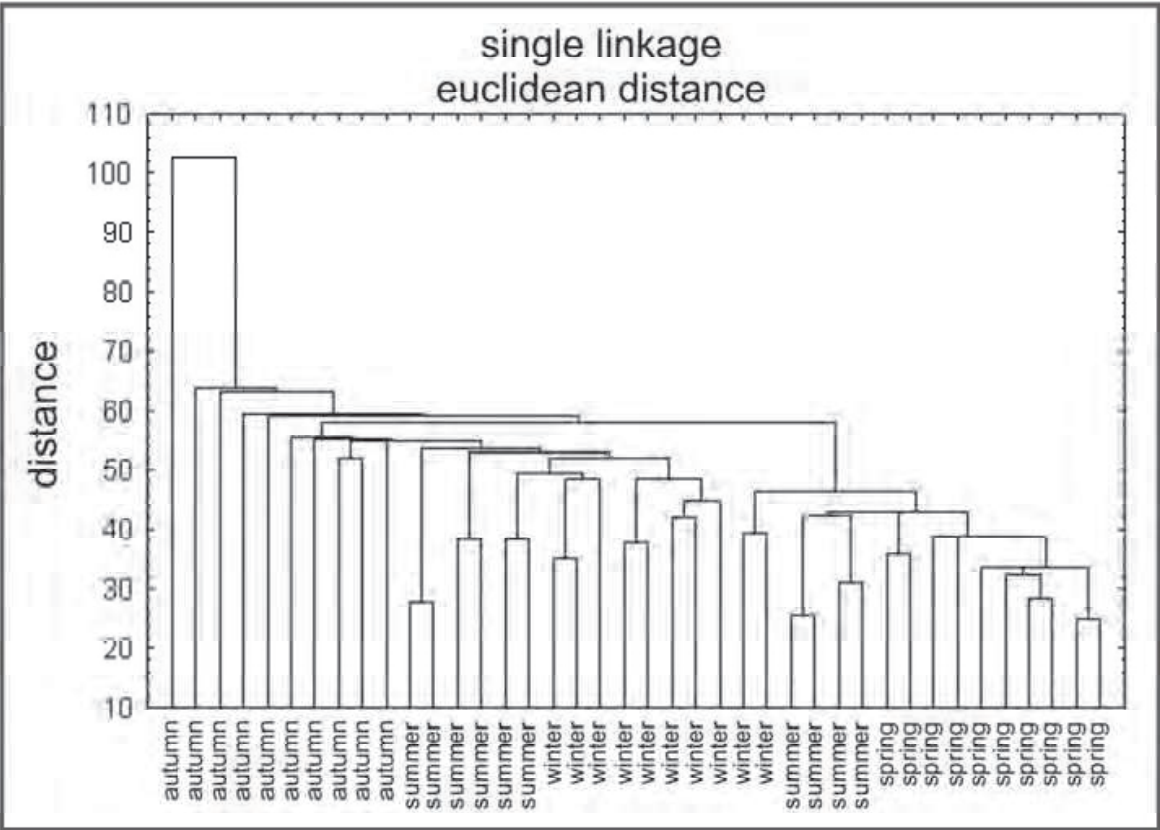


Fig. 2. Seasonal cluster analysis and cluster diagram of all CO₂ measuring trips taken in 2002 and 2003 within the urban area of Essen, Germany (n = 40)

This result was also analyzed by a test of significance (*t-test*), which showed that $\alpha < 0.05$ ($Si = 95\%$) indicates, however, that there is no direct correlation between the measuring trips in spring, summer, autumn and winter. Finally, this *t-test* confirmed the results of the cluster analysis displayed in figure 2.

For the next step the data of each “seasonal cluster” were treated separately. A secondary cluster analysis revealed that in the individual assessment of the seasons the groups were clearly distinguished from each other again. Five different clusters could be established within the four “seasonal clusters”, each identical with the five different times of measuring. As an example of this result the “summer cluster” is shown in figure 3. This one was not only specifically chosen to point out the similarities of the measuring period from June to August because it could not only be shown how the five clusters represent the different measuring times, but also the well-known splitting within the season, which was mentioned in figure 2. The day time measurements were reflected in one cluster group (10 a.m. – 1 p.m.; 1 p.m. – 4 p.m.), also the night-time measuring trips (11 p.m. – 2 a.m.; 4 a.m. – 7 a.m.; Fig. 3). The measurements from 7 p.m. till 10 p.m. can also be assigned to the day time hours because throughout this part of the day there was no sundown at all during the measurements.

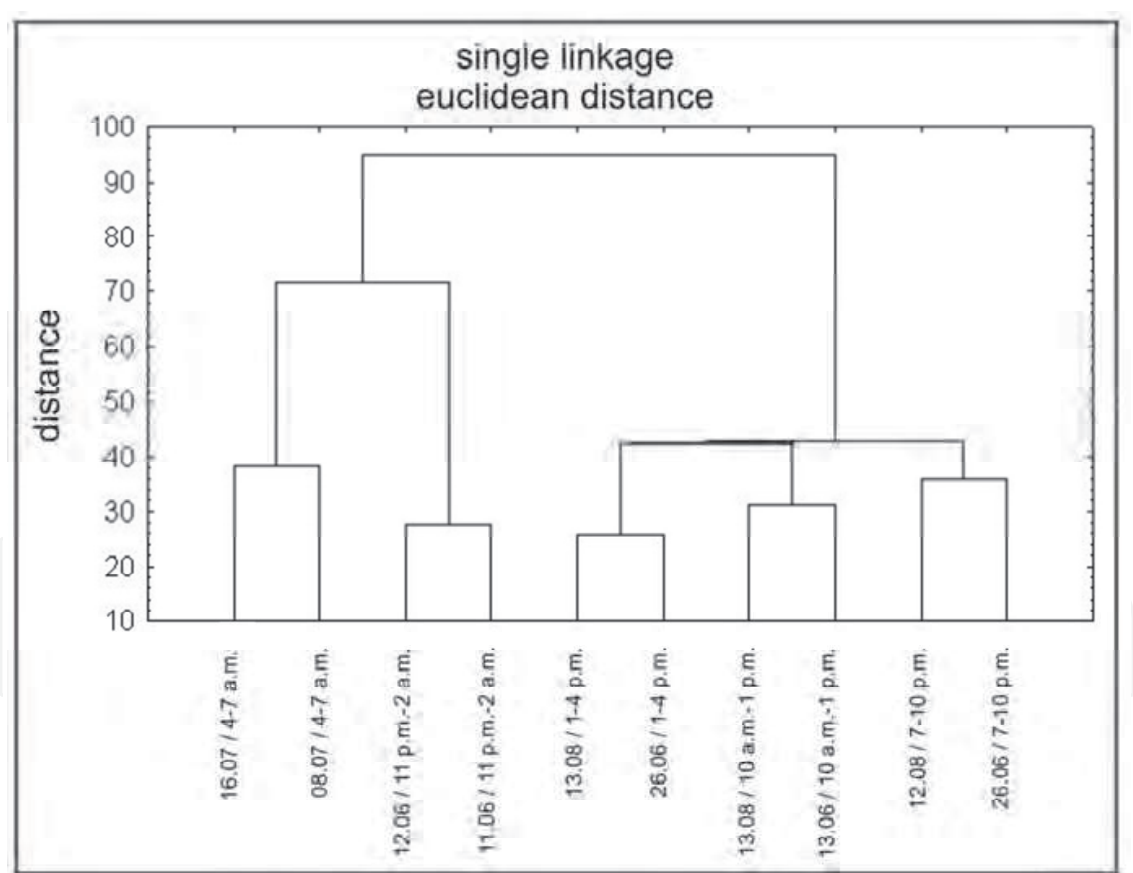


Fig. 3. Cluster diagram of the summer CO₂ measuring trips within the urban area of Essen, Germany (n = 10)

Nevertheless, there had to be similarities within the measurements at the same time to constitute a separate cluster for these trips. Therefore, measuring trips, which offered a common cluster (e. g. 16.06.03, 7 p.m. – 10 p.m. and 12.08.03, 7 p.m. – 10 p.m., Fig. 3), were

analyzed on their relationship between two characteristics (route sections and average values of the route sections) and ongoing calculating of the correlation coefficient after *Pearson* and *Bravais*. The result is, that the CO₂ patterns of the two measuring trips along the transect reveal a nearly identical profile (Fig. 4). This feature of figure 4 was confirmed by a high correlation coefficient of $R^2 = 0.91$. The variety in the concentration levels along the measuring route and the difference between the two curves respectively could be explained in virtue of wind speed (16.06.03 $v > 1.5 \text{ m s}^{-1}$ and 12.08.03 $v \leq 1.5 \text{ m s}^{-1}$) during the measurements. However, it is obvious that wind speed affects the height of the near surface urban CO₂ concentration, but not the spatial pattern and the occurrence of trace elements.

A comparison of two measuring trips, which were not related in a temporal cluster (e. g. 11.06.03, 11 p.m. – 2 a.m. and 08.07.03, 4 a.m. – 7 a.m., Fig. 5), confirmed the output of figure 3 as well as figure 4. There are almost no similarities shown in the CO₂ pattern of two survey tests ($R^2 = 0.17$), which had not been done at the same time of day. A crucial moment to this significant difference is the distinction of the atmospheric stability and the variation of the traffic density during these two times of measuring.

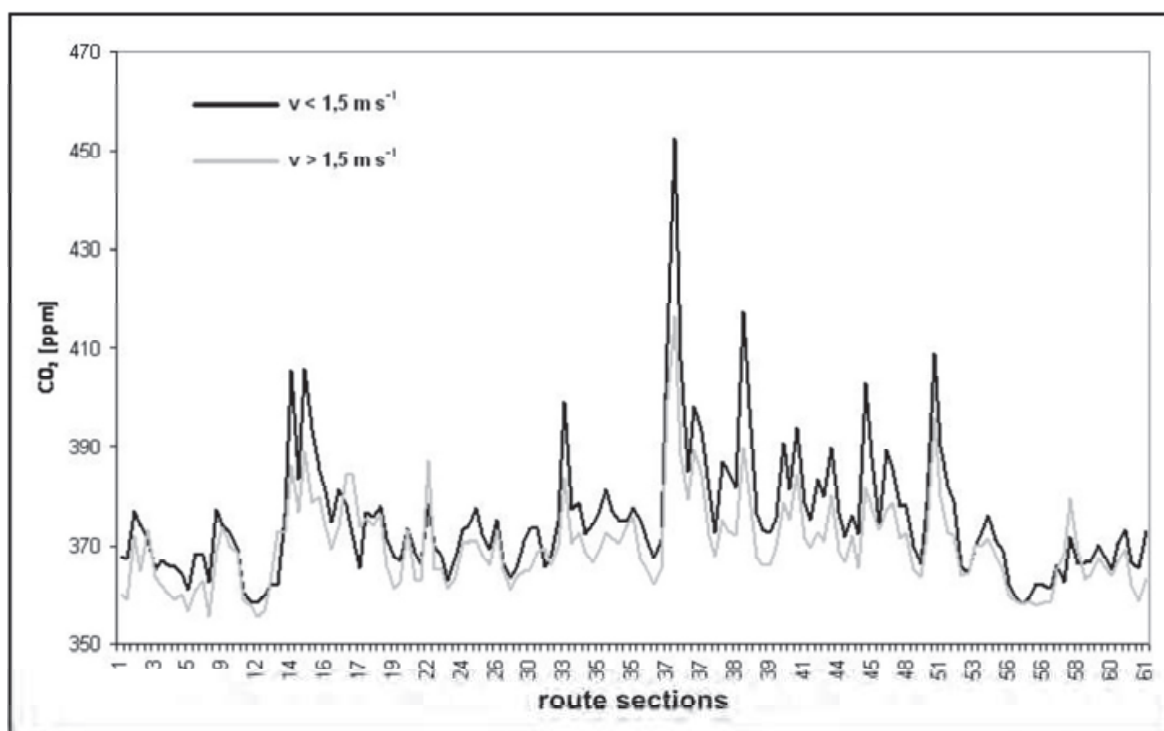


Fig. 4. CO₂ profiles ($R^2 = 0.91$) for two summer measuring trips with an identical measuring time (7 p.m. – 10 p.m.), but different measuring days within the urban area of Essen, Germany. Though both trips are part of one cluster (fig. 3) they showed up different wind speed, but no significant differences ($\alpha > 0.5$) for the carbon dioxide situation along the measuring route

An additionally implemented calculation of the product moment correlation coefficient by *Pearson* ratifies similarities to the results of the cluster analysis (Tab. 3). Thus the calculation showed high correlation coefficients for the same times of measuring, but only low positive to low negative correlations for the different times. Furthermore, using the *t-test*, it could be demonstrated that the measuring trips of the same season driven at the same measuring time, revealing a common cluster, offered no significant differences ($\alpha > 0.5$). Accordingly to this, it could be calculated that for measurements taken at different times of the day

indicated a significant ($\alpha < 0.05$) and a highly significant difference respectively from each other ($\alpha < 0.01$). These results could be illustrated for all seasons. That is why it could be postulated that in dependence of the time of day and the season a recurring pattern of near surface carbon dioxide along the measuring route is verifiable. So this could be regarded as an evidence for the conclusion that the reproducibility and thus the representativeness of the CO₂ data is given determined within the urban area.

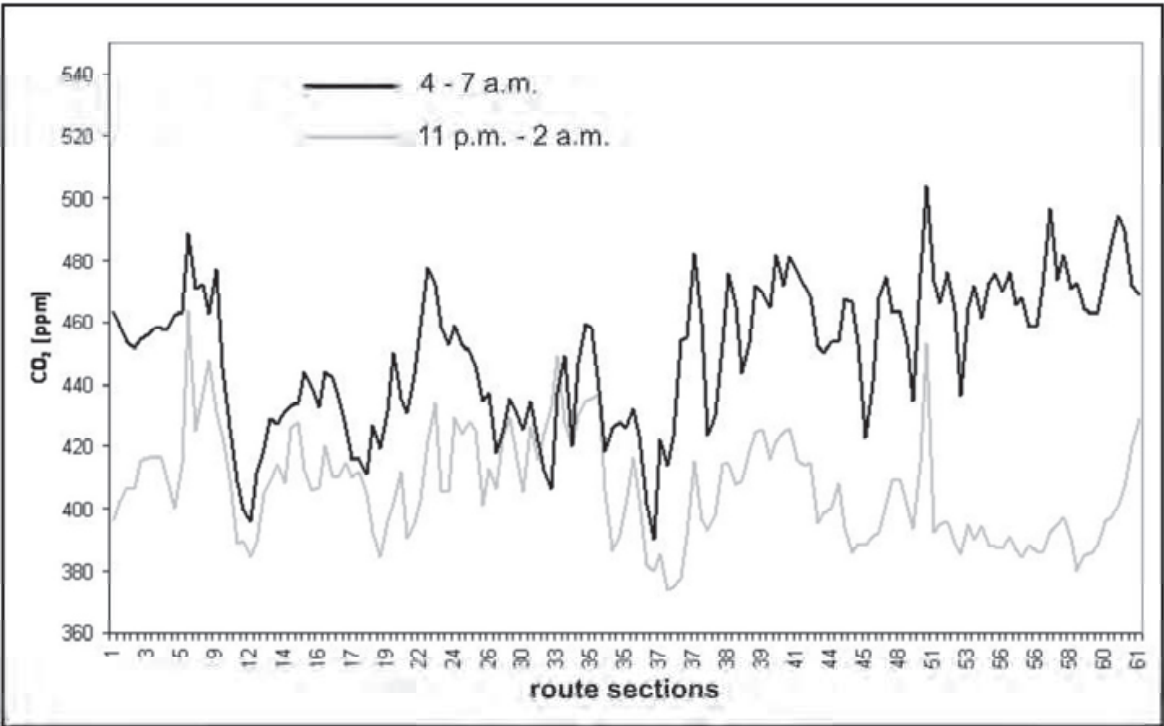


Fig. 5. CO₂ profiles ($R^2 = 0.17$) for two measuring trips with different measuring times (4 a.m. - 7 a.m. & 11 p.m. - 2 a.m.), but identical wind speed ($v < 1.5 \text{ m s}^{-1}$) within the urban area of Essen, Germany. Both trips are not part of the similar cluster (fig. 3), showing a significant difference of $\alpha < 0.05$ for the carbon dioxide situation along the measuring route

	Evening 1	Evening 2	Midnight 1	Midnight 2	Morning 1	Morning 2	Night 1	Night 2	Day 1	Day 2
Evening 1	1.00	0.89	0.28	-0.38	-0.06	0.31	-0.27	-0.44	0.12	-0.10
Evening 2	0.89	1.00	0.28	-0.39	-0.11	0.35	-0.25	-0.38	0.13	-0.05
Midnight 1	0.26	0.28	1.00	-0.85	-0.12	-0.09	-0.21	-0.20	0.22	-0.02
Midnight 2	0.38	0.39	-0.85	1.00	-0.09	-0.01	-0.34	-0.39	0.06	-0.16
Morning 1	0.06	0.11	-0.12	-0.09	1.00	0.76	0.07	0.08	0.02	0.08
Morning 2	0.31	0.35	-0.09	-0.01	0.76	1.00	0.12	0.01	0.27	0.38
Night 1	-0.27	-0.25	-0.21	-0.34	0.07	0.12	1.00	0.92	0.47	0.48
Night 2	-0.44	-0.38	-0.20	-0.39	0.06	0.01	0.92	1.00	0.42	0.47
Day 1	0.12	0.13	0.22	0.06	0.02	0.27	0.47	0.42	1.00	0.80
Day 2	-0.10	-0.05	-0.02	-0.16	0.08	0.36	0.48	0.47	0.80	1.00

Table 3. Product moment correlation coefficient exemplarily shown for CO₂ measuring trips in winter (evening = 7 p.m. - 10 p.m.; midnight = 11 p.m. - 2 a.m.; morning = 10 a.m. - 1 p.m.; night = 4 a.m. - 7 a.m.; day = 1 a.m. - 4 p.m.); evening 1 = 11.12.02, evening 2 = 05.02.03; midnight 1 = 06.01.03, midnight 2 = 19.02.03; morning 1 = 02.12.02, morning 2 = 12.02.03; night 1 = 19.12.02, night 1 = 12.02.03; day 1 = 05.02.03, day 2 = 18.02.02.

The statistical analysis of the CO₂ concentration in 2002 and 2003 was confirmed in the following years by comparing measurements along the same measuring route. Measuring trips throughout the different seasons of winter and summer 2004 as well as in spring 2005 have revealed that there is a roughly similar pattern of carbon dioxide near the ground ($R^2 > 0.78$; $\alpha > 0.5$). Exemplarily, this is shown with the aid of another cluster analysis (Fig. 6) and a CO₂ profile (Fig. 7) for measuring trips within Essen in summer 2004 compared to those from 2003.

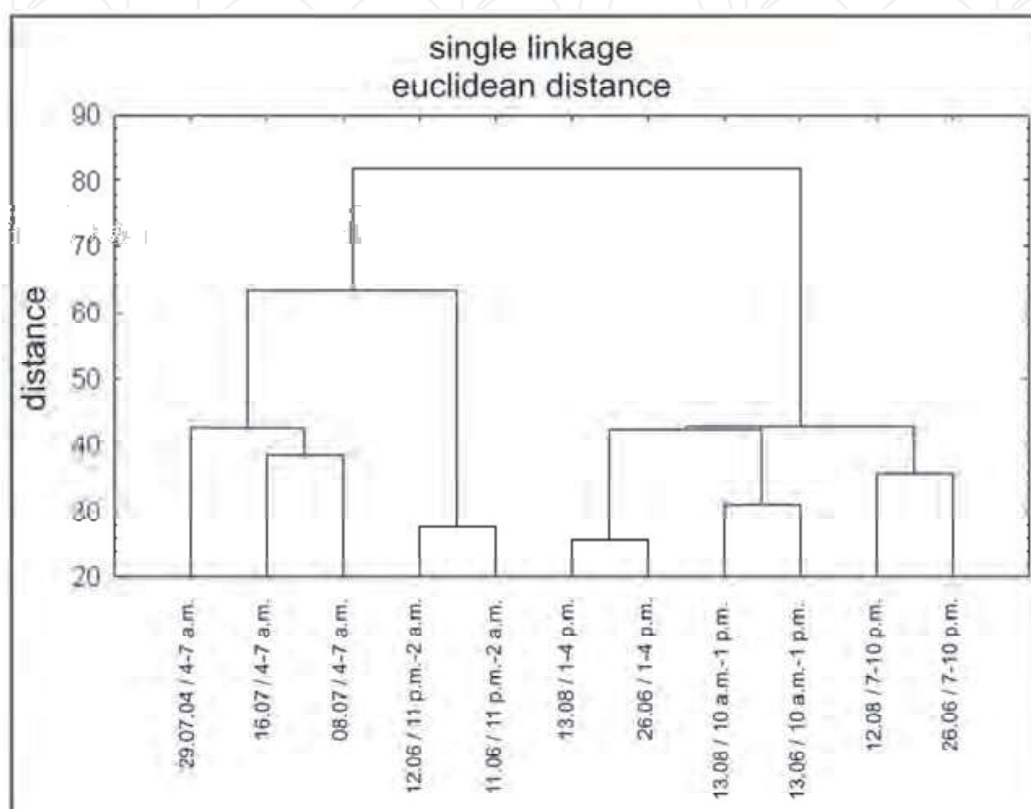


Fig. 6. Cluster diagram for CO₂ measuring trips within the urban area of Essen, Germany, for summer 2003 appended by an additional CO₂ measurement in summer 2004 at the same time of the day (4 a.m. – 7 a.m.), the same measuring route and comparable weather conditions

Figure 8 offers that the applied measuring methodology tested within the city of Essen is solely suitable for mobile measurements at this city structure. It could be proven that statistically representative, recurring patterns of CO₂ and other trace elements can also be determined within other urban areas, as it is shown for one route within the city of Krefeld. For day time as well as for the night-time measuring trips it is clearly obvious that there is no significant difference ($\alpha > 0.5$) between the CO₂ patterns along the transect. Particularly, the comparison of the night-time measurements of 17.02.04 and 20.02.04 showed a nearly congruent CO₂ profile ($R^2 = 0.98$; Fig. 7) due to a several days lasting clear and calm weather condition with $v \leq 1 \text{ m s}^{-1}$ and a negligible atmospheric exchange. Similar to the city of Essen a lower correlation coefficient ($R^2 = 0.70$), which is displayed in figure 6 for the day time measurements of 11.03.2004 and 13.03.2004, indicated a higher variability of potential CO₂ sources (primarily from motor vehicles).

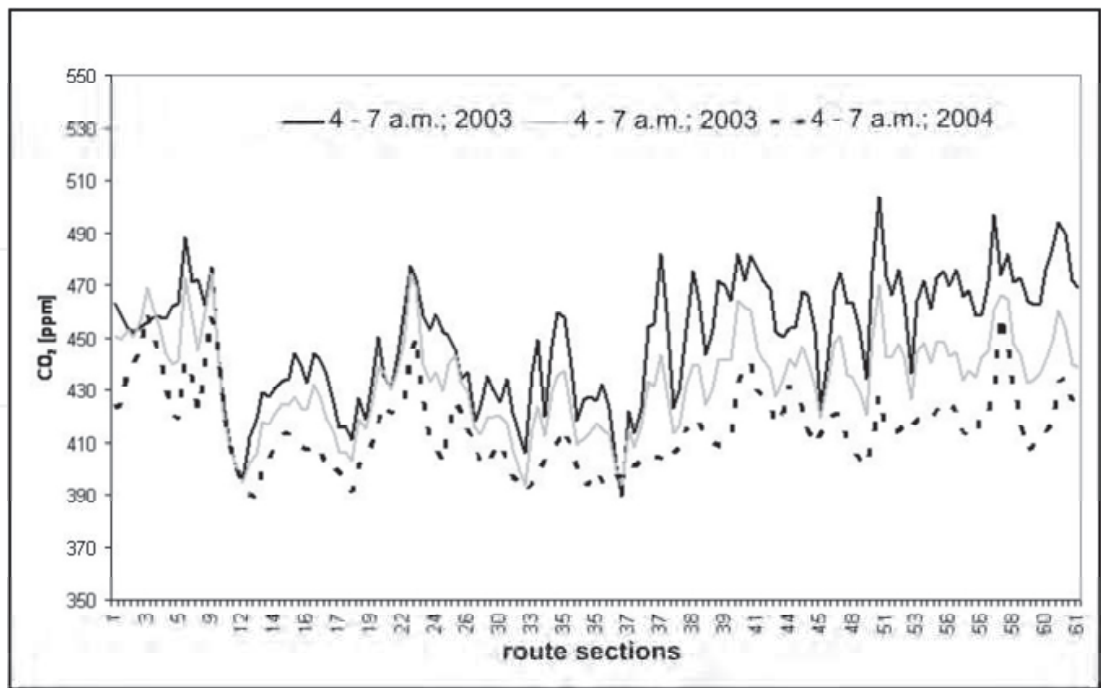


Fig. 7. CO₂ profiles ($R^2 = 0.79$) for three summer measuring trips with an identical measuring time (4 a.m. – 7 a.m.) within the urban area of Essen, Germany, different measuring days (black line = 2003; grey line = 2004), but comparable wind speed ($v < 1.5 \text{ m s}^{-1}$). The trips are part of one cluster (fig. 6) and showed up no significant differences ($\alpha > 0.5$) for the carbon dioxide situation along the measuring route

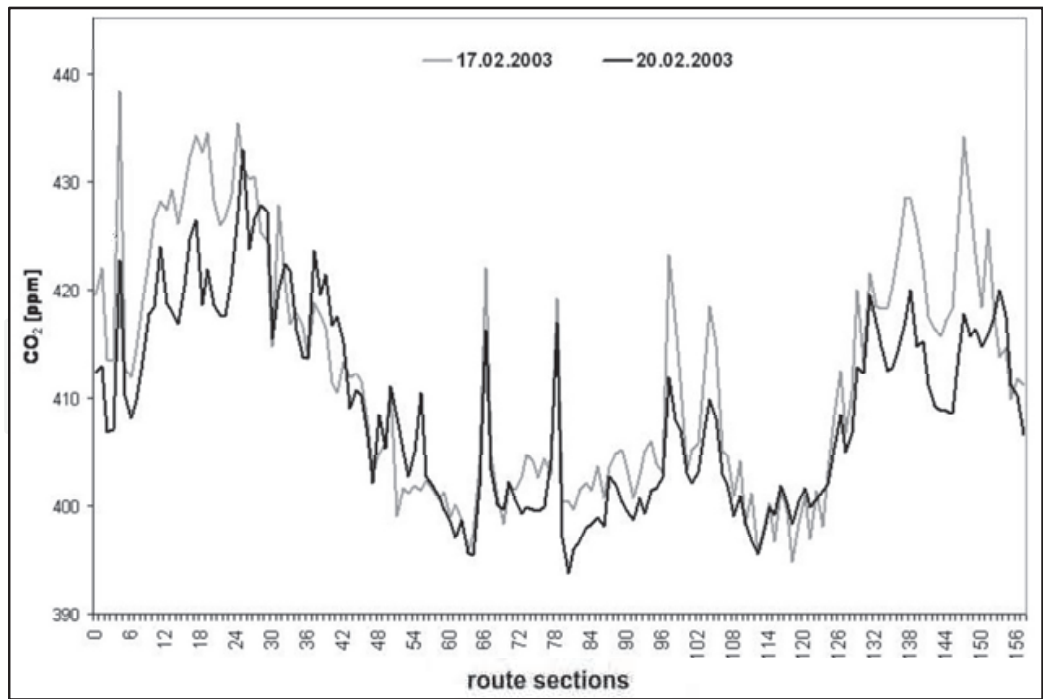


Fig. 8. CO₂ profiles ($R^2 = 0.90$) for two winter measuring trips with an identical measuring time (10.30 p.m. – 1.00 a.m.), but different measuring days within the urban area of Krefeld, Germany, $\alpha < 0.5$

The transferability of the measuring methodology was also checked for mobile measurements of near surface carbon dioxide and particulate matters (PM₁₀) in smaller towns, which do not have such an enormous emission of trace elements in comparison to urban agglomerations. Moreover, the method was used to determine different air quality indicators in the tropical city of Kigali, Rwanda. Exemplarily, based on figure 9 it is revealed for measuring trips within the city for Kigali, Rwanda, during the dry seasons of 2008 and 2009 for two different day time measuring periods.

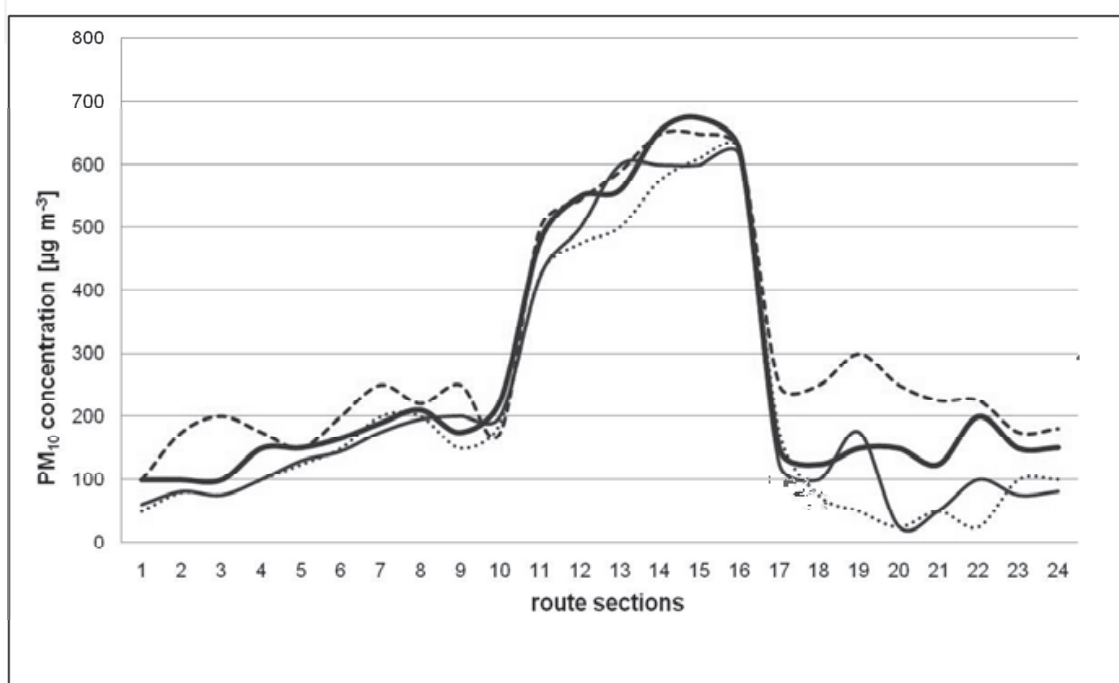


Fig. 9. PM₁₀ profiles ($R^2 = 0.89$) for measuring trips during the dry seasons of 2008 and 2009 with identical measuring times (9 a.m. – 10 a.m. = solid lines & 4 p.m. – 5 p.m. = dotted lines) within the urban area of Kigali, Rwanda, and different measuring days, but comparable wind speed ($v < 1.5 \text{ m s}^{-1}$). The trips showed up no significant differences ($\alpha > 0.5$) for the particulate matter situation along the measuring route

6. Discussion and concluding remarks

Carbon dioxide is one greenhouse gas, which is responsible for the anthropogenic induced climate change. Above all, urban agglomerations are a potential CO₂ source due to its usage of fossil energy sources. Less is known about the temporal and spatial behavior of this trace gas, especially in cities and their surrounding areas. Most studies were carried out by stationary measurements. But these investigations could hardly ensure the transferability from the measurement location to its nearby vicinity. An opportunity to solve this problem is using mobile air quality measurements, which ensure a highly frequented spatial as well as temporal density of area-covering information within an urban environment. Unfortunately, there are less investigations using the methodology of mobile measurements

along exactly coordinated transects. Furthermore the problem of existing methods is the significant difference within the methodologies of mobile air quality measurements. Thus it was necessary to create a methodology, which is applicable for different types of trace elements, but it also has to be representative, so that a ultimately statistical reproducibility of the results can be guaranteed.

Momentarily valid is the statistical analysis of the collected mobile measurements of near surface carbon dioxide between 2002 and 2010 has shown the possibility to resolve the CO₂ pattern within the urban canopy layer spatially as well as temporally in a high frequency in dependence of the structure of urban types of land use. It could be demonstrated that the methodology of measurements was not only feasible for one urban area, but it rather works for every urban settlement, because the transfer to other urban settlements is possible. Also it was obviously necessary to have a measuring period of more than one year and an exact consideration of the specific types of land usage because otherwise seasonal and spatial variations of the urban CO₂ mixing ratio could not be reproduced satisfactorily. So this investigation could be considered as a supplemental step in measuring urban CO₂ apart from fixed measurement locations using statistical proofs (test of significance, correlation analysis, product-moment analysis) to demonstrate which factors most strongly influence CO₂ within the urban canopy layer.

Based on these solid results of the diverse investigations within different urban areas (different sizes of the urban areas as well as varying climatic zones) three findings could be accentuated, which should be considered in the context of planning mobile air quality measurements, which need a minimum of necessary mobile measuring trips along the transect to determine the spatial and temporal behavior of near surface urban carbon dioxide:

1. The comparison of different measurement times throughout the day indicated that there is only one significant difference between day- and night-time measuring trips ($\alpha < 0.05$, Fig. 3). Therefore it remains to be noted that two day- and night-time measurements at a predefined time, however, showed only a weakly significance ($\alpha > 0.1$). It may be sufficient to get a first look and compare the time of day CO₂ profile of an urban space. The most important requirement for a comparison of measuring trips with one another is not measuring within the same year, but at the same time of day.
2. Two more additionally trips should be made at exactly the same day- or night-time and at similar atmospheric conditions (clear and calm weather conditions; low wind speed $v \leq 1.5 \text{ m s}^{-1}$) to confirm the area-use-dependent CO₂ pattern for the comparative trips and to ensure an adequate comparability of the determined data of the first two measuring trips (one day, one night-time trip). Following the analysis of two equal measuring times with a distinct comparable CO₂ profile ($\alpha > 0.5$), it must be assumed, based on the results of all measurements from 2002 to 2010, that also a third and fourth measuring trip for analog conditions constitutes a similar result, which ultimately reveals that more than four runs (two day and two night-time measurements) seem to be superfluous. A necessity of a third or perhaps fourth measuring trip is only given, when the first differs significantly from the second one (whether it is a day- or night-time trip). Also it is negligible, if it is on weekdays and on weekends respectively. The differences between the CO₂ patterns along the measuring route are undersized and not significant, as it is displayed for the cluster analysis in figure 10 and the CO₂ profiles in figure 11.

3. Furthermore it could be demonstrated in the course of the measurements from 2002 till 2010, that there are significant differences between the seasons (Fig. 2). So consequently, all four seasons must be considered to get an adequate impression of the spatial as well as temporal near surface pattern of the urban CO₂. At least it could be concluded that it is sufficient, being planned to measure urban carbon dioxide within the urban canopy layer over a minimum period of one year, calculating with at least sixteen mobile measurements (eight day- and eight night-time measurements), and assuming that the exit criteria mentioned in fact number 2 are fulfilled.

Based on the mentioned three-point plan Ptak (2009) used this handout for measuring carbon dioxide near the ground with the aid of a mobile laboratory within to urban areas. At least she planned a measuring period of one year. While it was great afford measuring CO₂ within the urban canopy layer of two cities which are far apart from each other, she calculated, as it was supposed, 16 measuring trips (four per season; two per night and day) for Münster as well as Lüdenscheid. Finally, she got a highly frequented spatial as well as temporal area-covering pattern of the CO₂ situation of both urban sites, which were also replicable and recurring for comparing trips one year later.

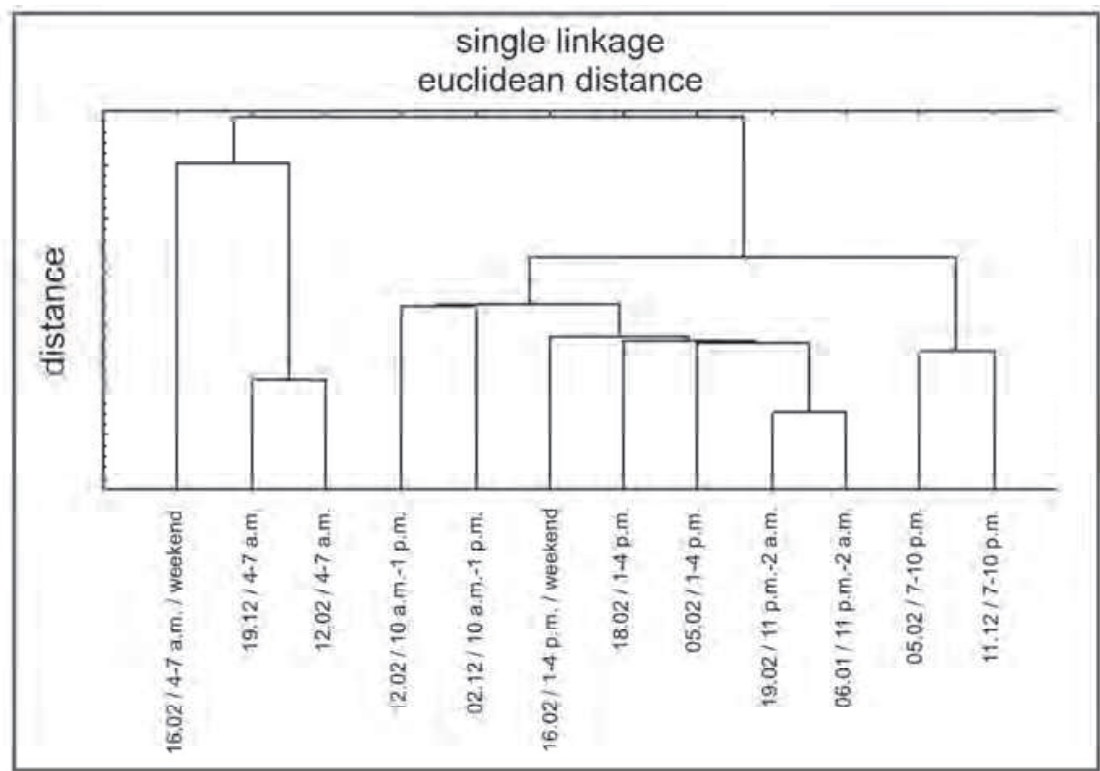


Fig. 10. Cluster diagram for CO₂ measuring trips within the urban area of Essen, Germany, for summer 2003 appended by an additional CO₂ measurement on a weekend at the same time of the day (4 a.m. – 7 a.m.), the same measuring route and comparable weather conditions

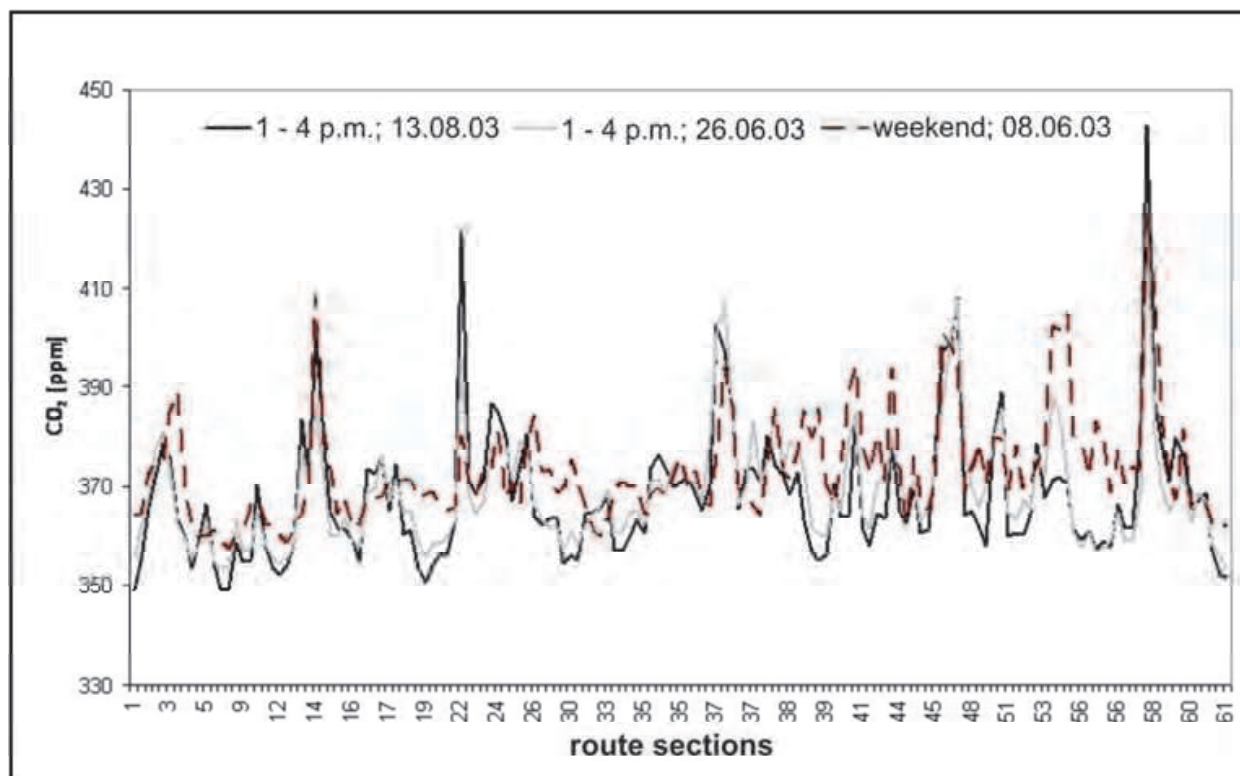


Fig. 11. CO₂ profiles ($R^2 = 0.89$) for three summer measuring trips with an identical measuring time (4 a.m. – 7 a.m.) within the urban area of Essen, Germany, and different measuring days (solid lines = weekdays; dotted line = weekend), but comparable wind speed ($v < 1.5 \text{ ms}^{-1}$). The trips are part of one cluster (fig. 10) and showed up no significant differences ($\alpha > 0.5$) for the carbon dioxide situation along the measuring route

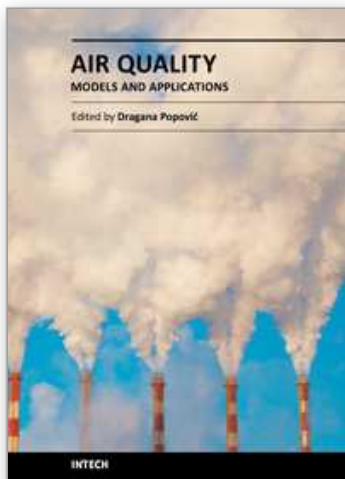
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Air pollution has been a major transboundary problem and a matter of global concern for decades. High concentrations of different air pollutants are particularly harmful to large cities residents, where numerous anthropogenic activities strongly influence the quality of air. Although there are many books on the subject, the one in front of you will hopefully fulfill some of the gaps in the area of air quality monitoring and modeling, and be of help to graduate students, professionals and researchers. The book is divided in five sections, dealing with mathematical models and computing techniques used in air pollution monitoring and forecasting; air pollution models and application; measuring methodologies in air pollution monitoring and control; experimental data on urban air pollution in China, Egypt, Northeastern U.S, Brazil and Romania; and finally, the health effects due to exposure to benzene, and on the influence of air pollutants on the acute respiratory diseases in children in Mexico.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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