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1. INTRODUCTION

The concentration of atmospheric carbon dioxide (CO₂) has increased from about 280 ppm, the pre-Industrial Revolution level (Leuenberger et al., 1992), to over 370 ppm (Bhattacharya, 2004). This increase has been caused mainly by CO2 emission from burning of fossil fuels, such as coal and petroleum. Since the first carbon dioxide measuring stations were started up in 1957/1958 (Geophysical Year) at Mauna Loa, Hawaii and at Antarctica (Pales and Keeling, 1965; Brown and Keeling, 1965), a global network was founded, called "Carbon Cycle Greenhouse Group" (CCGG). The network consists of CO₂-stations on- and offshore, also maintained by aircraft. Solely in urban spaces, which can potentially be expected as the largest anthropogenic CO2 sources (Takahashi et al., 2001), measurements were started up later (Offerle et al., 2001; Nemitz et al., 2002; Vogt et al., 2003).

2. PURPOSES

The aim of this highly frequented spatial and temporal investigation was to determine the allocation between carbon dioxide concentration within the urban canopy layer. It should be proven how the urban carbon dioxide is influenced by spatial variations of different types of land utilization and in the course of the seasonal change of meteorological conditions. Up to now, the main focus of measuring CO₂ in urban spaces was predominantly monitoring carbon dioxide within the urban boundary layer (so called tall tower measurements), above rooftop-level of the particular measuring location (Woodwell et al., 1972; Aikawa et al., 1993; Nasrallah et al.; 2003). Less was done within the urban canopy layer. Monitoring CO2 at one site makes a highly frequented temporal solution possible, but only for one homogeneous field of emission (Soegaard and Moller-Jensen, 2003). But in the urban area there are also inhomogeneous fields of emission, which can be determined by mobile measurements. So far there were less mobile measurements with short measuring periods (Shorter et al., 1998; Idso et al., 2000), even though it is possible to solve the disadvantage of low temporal solution by a high quantity of mobile measurements.

3. MEASURING SITE

The analyses were conducted in the City of Essen (51°28'N, 7°0'E; North Rhine-Westphalia, Germany). Since it is part of the German conurbation called "Ruhrgebiet" with about six million inhabitants

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altogether, Essen (587.000 inhabitants (2003), 210 $\rm km^2$) is considered as a typical conurbation city concerning its structure of carbon dioxide emissions (energy production 39%, transport sector 21%, industrial sector 19%, private sector 15%, others 4%).

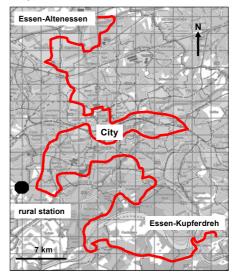


Fig.1: Street map of Essen (North Rhine-Westphalia, Germany) showing the location of the CO_2 transect route

The route of the taken measurements started in the southern part of the city and ended after 65 kilometers (s. Fig. 1) in the north of Essen, considering all kinds of its land utilization.

4. MEASURING PERIOD

Highly frequented spatial and temporal mobile measurements of carbon dioxide were taken during winter 2002/03 (December-February) and summer 2003 (June-August) regarding different conditions:

- during anticyclonic and cyclonic weather situations,
- on weekdays and weekends,
- at different times of the day (4 a.m.- 7 a.m.; 10 a.m.- 1 p.m.; 1 p.m.- 4 p.m.; 7 p.m.- 10 p.m.; 11 p.m.- 2 a.m.),
- during different seasons to have a look on the influence of the phases of vegetation, mainly in summer, or the contribution of domestic fuel in winter to the urban CO₂ in the urban canopy layer of Essen.

Primarily, the decision for the times of mobile measurements was influenced by the daily rush-hour in Essen. So the transect was driven respectively before (4 a.m.-7 a.m. resp. 1 p.m.-4 p.m.) and after (10 a.m.-1 p.m. resp. 7 p.m.-10 p.m.) the most vehicular traffic. There was also the time from 11 p.m.-2 a.m., the changeover from first to second part of the night. This five measuring times represent the

natural diurnal variations in CO_2 concentration of the air, aroused by the natural gas-exchange cycle of the biosphere. Likewise it was possible to have a look about the atmospheric boundary conditions close to the times of the day and its influence to the urban CO_2 .

5. METHODS

Measurement trips were made using the mobile laboratory of the Dept. of Applied Climatology and Landscape Ecology, University of Duisburg-Essen, Campus Essen. In addition to CO_2 , the air quality indicators CO, O_3 , NO and NO_2 were measured 1.5 m above ground level at the same time. The meteorological values air temperature, relative humidity (2 m a.g.l.) and global radiation (3.5 m a.g.l.) were also recorded. Analyzing carbon dioxide and other air quality indicators at the same time enables a reconstruction of the quantitative influence at CO_2 by anthropogenic sources. The different measurement methods are summarized in table 1.

Trace elements	Measurement methods		
CO ₂ , CO	IR absorption		
NO, NO _X	Chemoluminescence		
O ₃	UV absorption		

Table 1: Physical and chemical methods of measuring trace elements

The mobile laboratory traveled at a maximum speed of 30 km h⁻¹ (8 m s⁻¹) and with a measurement frequency of the analyzers of 1 Hz. So every 8 m one measured value was recorded. In spite of a very low delay time of the different analyzers (e.g. the delay time of $CO_2 = 13$ s), it was possible to determine the trace elements nearing real time.

It is necessary to keep a "safety distance" of more than two meters to have low influences by the exhaust plume of automobiles in front of the mobile laboratory.

In view of the rapid fluctuations of trace element concentration, provoked e.g. by the change of land utilization or the structure of housing along the transect, average values of homogeneous road sections were calculated.

Considering the results of each mobile measurement trip to average values of homogeneous route sections facilitated a comparison of the urban CO₂ concentration to the CO₂-data of a rural measuring station maintained by the Dept. of Applied Climatology and Landscape Ecology (s. black item, Fig.1). Differences between urban and rural carbon dioxide mixing ratio could be verified and the percentage diverge was being indicated. In cause of low roughness $(z_0 = 0.11 \text{ m})$ wind could flow unaffected against the rural measuring station from all directions. So it was possible to calculate CO2 concentration depended by wind-direction and it could be reconstructed if the flux of CO2 has its origin by the urban plume or above the agricultural fields near the station (s. 7.1).

6. REPRODUCIBILITY OF DATA

With assistance to different statistical methods (correlation- and regression analysis, cluster analysis, test of significance) it should be testified if the determined CO₂-data are representative for the situation of air quality in the city of Essen or if the measured concentration of each trip is only a snap-shot. Primarily, the cluster analysis should give information about similarities of the behavior of carbon dioxide along the transect between the accomplished measurement trips. Exemplarily for summer, Fig. 2 offers five separate clusters altogether identical with the five times of measuring, mentioned in part 4. A comparison of the measurement trips, which were connected in one cluster, presents a uniform allocation of CO₂ along the transect (s. Fig. 3)

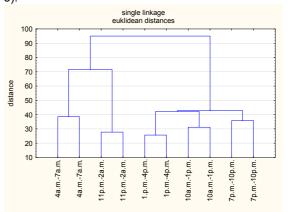


Fig.2: Cluster diagram of all mobile CO₂ measurements in Essen, North Rhine-Westphalia, Germany (summer 2003)

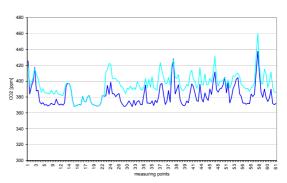


Fig.3: Example for similar CO₂ courses at one measuring time (1p.m.- 4p.m.; summer 2003) for two different days with two different weather situations

Significance tests presented a validation: measurements driven at the same time of the day display no significant differences ($\alpha > 0.5$), whereas trips by diverse times display a significance of $\alpha < 0.05$ resp. a highly significance of $\alpha < 0.01$. These results could be proven for summer as well as for winter, which demonstrates that there is, dependent on the time of the day, a recurrent CO₂-pattern along the transect. That is why a reproducibility of the behavior of carbon dioxide is necessarily given.

7. RESULTS

7.1 Comparison between urban and rural CO₂

One of the main questions was, whether there is a discrepancy of the CO_2 mixing ratio between the urban area of Essen and its surroundings or not.

The comparison of mobile determined urban carbon dioxide and simultaneous measured CO2 of the rural monitoring station at the city limit indicates for several measurement trips up to 25% higher CO2 concentration within the urban area in contrast to the surroundings. Beneath the time of the day and the stability of the atmospheric boundary conditions, one dominant factor of influence is the wind direction. During calms ($v \le 0.5 \text{ m s}^{-1}$) resp. a wind direction from S to SE, the CO2 difference between urban to rural concentration achieve more than 20%. whereas there are minor differences for NE to E (≤ 5%). Anytime the meteorological conditions arouse such a situation (wind from NE to E; by 15% of the time of the measuring period), the wind was influenced by the trace elements of the urban plume of Essen, which were taken along by passing the city. Finally the rural station recorded an increasing carbon dioxide concentration above normal.

Nevertheless, if the periods of influencing the rural carbon dioxide by the urban plume were neglected, the CO_2 concentration of this monitoring station could be accounted as representative. An additional analysis of CO_2 -data determined by a base line monitoring station maintained by the Federal Environmental Agency (UBA) also showed that there is solely a difference up to 30%. Consequently, the city of Essen did not obtain differences between the urban and rural areas by far as it has been proven for other cities, e.g. Copenhagen/Denmark (> 50%, Soegaard and Moller-Jensen, 2003) or Phoenix/USA (70%, Idso et al., 1998).

7.2 Seasonal variations of urban CO₂

It should be proven whether there is a difference between the urban CO_2 mixing ratio of the warm and cold season (Idso et al., 1998; Nasrallah et al., 2003), because of little fluctuations caused by the anthropogenic CO_2 emission which is permanently available in urban areas (Takahashi et al., 2001).

Fig. 4 displays the course of CO_2 along the transect for the winter months (blue bend) as well as for the summer months (red bend). Additionally, there are the average values for both seasons (solid line =

winter, χ Winter = 415 ppm; σ = 21,33 ppm; dashed

line = summer; $x_{\text{Summer}} = 393 \text{ ppm}$; $\sigma = 17,55 \text{ ppm}$). The high spatial variability of carbon dioxide, which is shown in Fig. 4, is a justification for determination of CO₂ within the urban canopy layer by mobile measurements.

The result of high CO_2 concentration in winter and lower ones in summer is absolutely not surprisingly. The city of Essen is an example for CO_2 mixing ratio of an urban agglomeration in the middle latitudes where differences in seasons appear. This is not

opposing against other mobile measurements in cities where no seasonal course is detectable (Idso et al., 1998) in fact of an other clime.

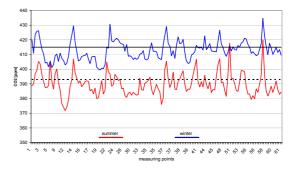


Fig.4: CO₂ courses through the city of Essen, North Rhine-Westphalia, Germany (winter 2002/03 and summer 2003)

The increase in CO₂ concentration in winter is due to several facts:

- additional CO₂ emissions caused by domestic fuel (up to 15%),
- a reduced plant activity which causes a lower photosynthesis,
- a higher share of CO₂ soil exchange, which is not affected by photosynthesis.

7.3 Day- and night time variations of urban CO2

The influence of the CO₂ course along the transect, e.g. by domestic fuel in winter or natural gasexchange by the vegetation in summer, could be displayed more exactly by differentiation of the measurements into day- and nighttime trips. Similar to Fig. 4 there is also a difference between the CO₂ concentration, indeed between day (s. Fig. 5, dashed bends) and nighttime measurements (s. Fig. 5, solid bends). Additionally, illustrated in Fig. 5 is the average value for day- (upper, dashed line; $\chi_{\text{day_winter}}$ 402 ppm; σ = 19,58 ppm) and nighttime (upper, solid line; $x_{\text{night_winter}}$ 427 ppm; σ = 23,17 ppm) in winter, also day- (lower, dashed line; $\chi_{\text{day_summer}}$ 369 ppm; σ = 15,57 ppm) and nighttime (lower, solid line; $x_{\text{night_summer}}$ 417 ppm; σ = 19,54 ppm) in summer.

One reason for higher concentration during nighttimes could be given by meteorological conditions in summer as well as in winter, which favor a CO2 accumulation. Stable conditions were built up within the second part of the night prior to sunrise, calculated by Polster (1969). Because of these conditions, additional CO2 emissions in winter and CO2 respiration by plants during summer nights increased the carbon dioxide concentration. After sunrise the stable conditions of the night started to break down, unstable conditions were built up. Due to increased wind speed, there is a better exchange of the urban atmosphere, which is responsible for decreasing CO₂ concentration. Likewise there is the increased activity by plants on summer days, which acted as potential CO2 sinks. According to these matters of fact the significant differences between the CO₂ concentration of night- (solid bends) and daytime (dashed bends) is explainable.

The CO₂ course for summer nights (red. solid bend) reflects the changing types of land utilization along the transect. Most of the displayed CO2 peaks (s. black arrows in Fig. 5) were similar to suburban and urban green spaces respectively spaces which show a high portion of vegetation. It can be noticed that CO₂ respiration dominates over anthropogenic sources in summer nights, because of e.g. low nighttime traffic density. In comparison to this, the CO₂ course of winter nights (blue, solid bend) indicates a relatively constant carbon dioxide level without additionally CO₂, due to the vegetation. For summer days (dashed, red line) as well as for winter days (dashed, blue line) there were no CO2 peaks provoked by green spaces in contrast to the nighttime measurements. At this time of the day, the dominating factor of anthropogenic sources, e.g. high traffic density, on account of cross-roads or traffic lights, was visible (see red arrows in Fig. 5).

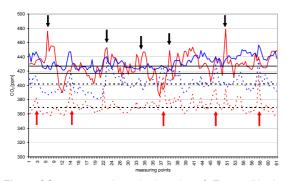


Fig.5: CO₂ courses through the city of Essen (North-Rhine-Westphalia, Germany), divided into day- and night-time measurements (winter 2002/03 and summer 2003) – for further information's see text (7.3)

7.4 CO₂ and other air quality indicators

By recording air quality indicators like CO, NO, NO $_2$ and O $_3$ it is possible to correlate them to carbon dioxide (Clarke and Faoro, 1966). Calculating the correlation coefficients may give information how two different air quality components have the same resp. a similar temporal and spatial pattern along the transect during clear and calm weather situations (s. Tab. 2).

	CO	NO	NO ₂	O ₃
day _{winter}	0,739	0,83	0,486	-0,658
nightwinter	0,399	0,469	0,272	-0,292
day _{summer}	0,628	0,668	0,478	-0,652
night _{summer}	0,256	0,266	0,169	-0,622

Table 2: Correlation analysis of air quality indicators with CO₂, divided into day- and nighttime measurements (winter 2002/03 and summer 2003)

Noticeably, the highest coefficients were reached during the day in winter as well was in summer, according to a higher rate of anthropogenic sources; e.g. the percentage of CO_2 emission by motorcars is about 21% in the city of Essen. For nighttimes winter coefficients were a little higher than in summer. This might be indicating an increase of the trace elements concentration by domestic fuel (about

 $15\%\ CO_2$ emission in the city of Essen), which can generally be measured during winter days and nights.

8. CONCLUSION

The results of carbon dioxide measurements within the urban canopy layer of Essen for winter 2002/2003 as well as for summer 2003 pointed out the importance of mobile measurements for the determination of urban CO2. It is not enough to measure urban carbon dioxide at fixed monitoring stations (tall tower measurements) due to the highly frequented spatial and temporal variability of CO₂ within the urban canopy layer. It has also been shown that the often in literature mentioned "CO2" dome" with steadily increasing concentration from rural to urban areas is not generally true for any city. Many different kinds of facts influence the CO₂ mixing ratio. Primarily, diurnal and annual components decide over the CO₂ content in a city. These are being influenced by meteorological conditions, which are dependent on the heterogeneous structure of housing. All these different components and conditions create a complex image of variable CO₂ concentration within the urban canopy layer. This image may arouse lower CO2 data within some urban types of land utilization in comparison to the surroundings due to the weather situation and measuring periods.

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