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Variation of Greenhouse Gases in Urban Areas-Case Study: CO_2, CO and CH_4 in Three Romanian Cities

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1. Introduction

The natural equilibrium of atmospheric gases has been maintained for millions of years, but with the beginning of the industrial age, it became more fragile due to human activity. In the Intergovernmental Panel on Climate Change Report (IPCC) named "Climate Change 2007" (IPCC-AR4, 2007) it is specified that "*the keep going emissions of the greenhouse gases (GHG) at/over current rate, will cause in the future global warming and will induce more global climate changes in the 21st century than those of 20th century*". More than , in the coming IPCC Report named "Carbon cycle including ocean acidification (CCT)" (IPCC-AR5, 2010) is stipulated that ocean acidification will be a further critical and direct consequence of increasing atmospheric GHG concentrations.

In 1886, the chemist Svante Arrhenius (Nobel prize for Chemistry in 1903) calculated for the first time the CO_2 contribution (from fossil fuel combustion) to climatic changes and used for the first time the term of "greenhouse effect". Almost 100 years were necessary for the confirmation of Arrhenius predictions about the evolution of global climatic factors, and the fact that CO_2 is the main greenhouse gas, with a contribution of 55% to Global Warming Effect. The first IPCC Report (IPCC-FAR, 1990) draws the conclusion about the possible existence of a global warming phenomenon. The second IPCC Report (IPCC-SAR, 1995) shows the contribution of humans to global warming and predicts a major warming in the 21st century. The third IPCC Report (IPCC-TAR, 2001) affirms a very probable (60% - 90%) warming for the next century. In the IPCC-AR4 Report (IPCC-AR4, 2007) adds for the understanding of the impact of climate changes over the vulnerability and the adaptation of the environment, the most relevant scientific, technical and socio-economical information from more than 1500 scientific papers. This report accepts with a probability of over 90% that the emission of greenhouse gases and not the environmental conditions gives the global warming effect.

The IPCC Guide from 2006 makes an inventory of gases from atmosphere and distinguishes between:

a. gases with GWP (Global Warming Potential) listed in IPCC 2001: CO_2, CH_4, N_2O, hydro fluorocarbons, per fluorocarbons, SF_6, NF_3, SF_5CF_3, halogenated ether, $C_4F_9OC_2H_5$, $CHF_2OCF_2OC_2F_4OCHF_2$, $CHF_2OCF_2OCHF_2$ and other halocarbons CF_3I, CH_2Br2, $CHCl_3$, CH_3Cl, CH_2Cl_2.

b.   gases without GWP: $C_3F_7C(O)C_2F_5$, C_7F_{16}, C_4F_6, C_5F_8 and C_4F_8O.

As a follow-up of these reports, the scientific community had started a cycle of research programs having as scientific goal the complex study (emission sources, consumption sources, the balance of changes between the components of environment etc.) of these gases and the effect produced by them (Projects CARBOEUROPE, AEROCARD, CHIOTTO, Global Carbon Project, IGOS, NACP etc).

The CO_2 it is an important green-house gas and it level in the atmosphere has significantly increased from 280 ppm in the pre-industrial era to current 380 ppm. The first increase of 50 ppm occurred during a period of ca. 200 years, starting with the beginning of the industrial revolution until 1973. Between 1973 and 2006 the concentration of CO_2 increased with another 50 ppm.

The Global Warming Potential (GWP) for CO_2 is conventionally choose as 1, i.e. the atmospheric residence time between 50 and 200 years, and its contribution to the greenhouse effect is ca. 52 %.

According to IPCC Report (IPCC-AR4, 2007), the contribution of anthropic CO_2 is predominant, and the main anthropic sources are:
-    the energetic sector 30 %
-    industrial processes 20 %
-    fuels used in transportation 20 %
-    burning of biomass 9.1 %
-    processing and distribution of fossil fuels 8.4 %
-    other sources 12.5%

According to IPCC estimations, the increase of CO_2 concentration in the atmosphere leads to climate changes and will produce a global warming of the planet through the greenhouse effect.

The monitoring of the global levels of CO_2 is the concern of American government since about 30 years. The National Oceanic & Atmospheric Administration - Earth System Research Laboratory (NOAA-ESRL) performs measurements for main greenhouse gases in about 68 locations spread all over the world. According to NOAA data, the concentration of CO_2 has an ascending trend. Figure 1 shows the CO_2 variations in Mauna Loa for the period of 2003-2008 according to NOAA-ESRL source.
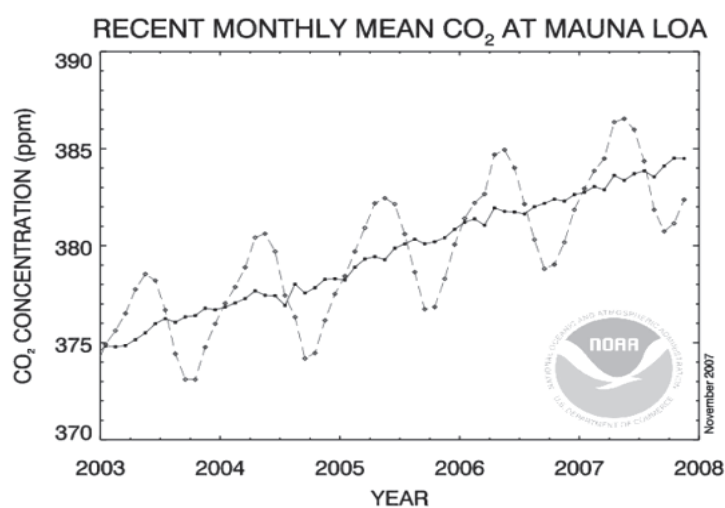

Fig. 1. Variation of the monthly average of CO_2 in Mauna Loa

At the European level, the Carboeurope-Clusters Program (CarboEurope) carries out measurements of atmospheric CO_2 concentrations in 61 locations in 17 countries. This program contains eight different projects working together to contribute to the understanding of the carbon cycle at the European level. The projects involved in this program are: AEROCARB, CAMELS, CARBOAGE, CARBODATA, CARBOEUROFLUX, CARBOEUROPE GHG; CARBOINVENT, CHIOTTO, CARBODATA, TACOS, EUROSIBERIAN CARBONFLUX, FORCAST, GREENGRASS, RECAB, TACOS-INFRASTRUCTURE, and TCOS SIBERIA. Two other projects, CARBOMONT and SILVISTRAT are associated to this program.

In 1998 Idso and co-workers (Idso et al., 2001) introduced the term ""urban DOME" for the persistence of CO_2 over the urban cities as a result of anthropogenic contribution to CO_2 budget. After that, several individual studies regarding to CO_2 variation in urban areas have been reported (Day et al., 2002; Idso et al., 2002). These studies showed that the concentration of CO_2 in urban area is higher that the CO_2 concentration in rural area and this fact is a consequence of human activities. A literature review about these results is presented in this chapter.

Methane (CH_4) is another important greenhouse gas, with GWP = 25 and a residence time of more than 100 years. It is produced both naturally and through human activities. The global mixing ratios of CH_4 in the atmosphere have more than doubled since the pre-industrial period, rising from around 750 ppb (parts per billion) in 1800 (Simpson et al., 2002; Dlugokencky et al., 2003) to the current level of around 1770 ppb (NOAA-ESRL). The global trend of the methane concentration in the air is ascending, with a rate of increase of 5–10 ppb/year, and for the period 1984-2004 this tendency is shown in Figure 2.
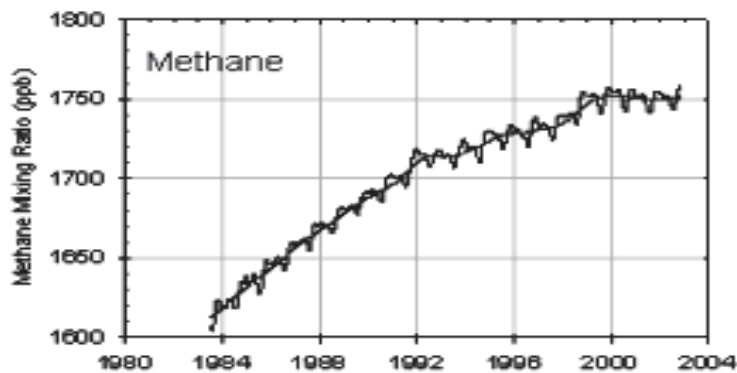

Fig. 2. The variation of the global average concentration of CH_4. (source NOAA-ESRL)

The main natural source of methane are dominated by wetlands. The primary way for CH_4 transformation is its destruction in the atmosphere by hydroxyl radicals (Prinn et al., 1995, 2001). Some CH_4 is also oxidized by microorganisms (called methanotrophs), which use CH_4 as a source of carbon and energy. Tropospheric CH_4 is eventually oxidized to carbon dioxide; its atmospheric lifetime is estimated to be 8–12 years (NOAA-ESRL; Cunnold et al., 2002; IPCC-AR4, 2007).

It is estimated that the contribution of methane to the greenhouse effect is 18%, and the most important sources are:

- Residual agricultural products 40%
- Processing and distribution of fossil fuels 29.6%

- Storage and processing of domestic waste 18.1%
- Burning of biomass and grazing 6.6%
- Other sources 4.8%

In the IPCC Report (IPCC-TAR, 2001) is suggested that the natural sources account for ca. 40% of total methane sources. Aikawa (Aikawa, 2006) indicates that the transportation contributes 1.1% of CH_4 emissions in Japan and suggests that there is a small influence of methane emissions from mobile sources on the concentrations in ambient air. The possible evolution of anthropogenic methane emissions at global level has been discussed by Cofala (Cofala et al., 2007) who predicts an increase of CH_4 emissions from 250 Tg/year in 1990 to 420 Tg/year in 2030.

Carbon monoxide (CO) is the most significant polutant. It has a short life time in the atmosphere due to its reaction with other atmospheric components, such as hydroxyl radicals. It has an indirect radiative effect by increasing the concentration of methane and trosperic ozone. In urban areas, CO reacts photochemically with aldehydes, to produce peroxy radicals. These radicals react with nitrogen oxide, to form nitrogen dioxide, which is the main responsible for the formation of the fotochemical smog.

Through natural processes, the CO can be oxidized to CO_2, thus contributing to the increase of the later in the atmosphere. Thus, through resulting products the anthropogenic CO can indirectly contribute to the greenhouse effect and to the global warming.

Anyway, even if CO_2 and CH_4 are the main greenhouse gases, with a contribution of more than 70% (CO_2 55%, CH_4 15%) on global warming (IPCC-AR4, 2007), for a good estimation of these two gases to the Global Warming Potential (GWP) in urban areas it is necessary to take into account the indirect contribution of CO which is not a greenhouse gas but changes the atmospheric chemistry and the abundance of other greenhouse gases. CO is a key air pollutant which can be utilized like tracer in the separation of CO_2 and CH_4 from biogenic and anthropogenic sources (Daniel & Solomon, 1998).

Different studies (Daniel & Solomon, 1998; Fuglesvedt et al., 1996; Prather, 1996 cited in IPCC-TAR, Chapter 4, 2001) estimate the indirect GWP of the CO due to O_3 production and to feedbacks on the CH_4. This approach was made using a box model and estimate the indirect GWP of CO for time horizons of 20, 100, and 500 years. The indirect GWP value due to CO is gave in table 1.

Authors/Models	Indirect Global Warming Potentials of CO, Time horizon		
	20 years	100 years	500 years
Daniel and Solomon (1998): box model considering CH_4 feedbacks only	2.8	1.0	0.3
Fuglestvedt et al. (1996): two-dimensional model including CH_4 feedbacks and tropospheric O_3 production by CO itself	10	3.0	1.0
Johnson and Derwent (1996): two-dimensional model including CH_4 feedbacks and tropospheric O_3 production by CO itself	-	2.1	-

Table 1. Estimated Indirect Global Warming Potentials of CO for time horizons of 20, 100, and 500 years, (source IPCC-TAR, 2001)

Regarding to long time measurement of CO_2 concentration in urban area as well as the variation of meteorological parameters allow to understanding the rule of the ecosystem functioning and meteorological parameters over inter-annual variation in carbon fluxes. The inter-annual variation of CO_2 fluxes has been typically studied either by modeling approaches (Higuchi et al., 2005; Ito et al., 2005; Bergeron & Strachan, 2011) or by correlation coefficient analyses together with meteorological parameters (Aubinet et al., 2002; Aurela et al., 2004; Wohlfahrt et al., 2008). These studies showed that, the CO_2 flux is strongly influenced by biological vegetation cycle and the variation of meteorological parameters. Thus the maximum value of CO_2 is registered during the cold season while the minimum value of CO_2 was registered during the summer. Another study (Sottocornola & Kiely, 2010), show that the wet conditions favored the CO_2 uptake by the ecosystem in autumn and in winter, while the warmer and dryer weather reduce the sequestration of CO_2 in the ecosystem. A study performed in urban and sub-urban area of Montreal (Bergeron & Strachan, 2011) showed that the CO_2 flux is also influenced by the anthropic activity. According to this study, "*Lower emissions at the suburban site are attributed to the large biological uptake in summer and to its relatively low population density inducing low anthropogenic emissions. Higher emissions at the urban site are partly associated with its greater population and building density, promoting higher emissions from vehicular traffic and heating fuel combustion. Vehicular traffic CO_2 emissions influenced the diurnal cycle of CO_2 fluxes throughout the year at the urban site. At the suburban site, summer CO_2 fluxes were dominated by vegetation sources and sinks as daytime CO_2 uptake occurred and CO_2 fluxes responded to incoming light levels and air temperature in a fashion similar to natural ecosystems. To a lesser extent, the vegetation component also helped offset CO_2 emissions from other sources in summer at the urban site.*"

This chapter will present the results of a case study of CO_2, CH_4 and CO variations during one year in three selected cities from Romania with different anthropic activity. In order to identify the influence of biogenic and anthropogenic sources to the budget of mentioned greenhouse gases the $^{13}CO_2$ and $^{13}CH_4$ isotopic composition have been determinate. Experimental results were finally correlated with meteorological parameters.

2. CO_2 in urban area

2.1 Trends of CO_2 variation in urban areas. A literature review

The problem of urban carbon dioxide came into the attention of scientists in the year 1998, with the discovery and characterization of the urban CO_2 dome of Phoenix, Arizona, USA by Idso and col. (Idso et al., 2001). Early work found that under certain meteorological conditions, urban CO_2 concentrations could be as high as 550-600 ppm (some 200 ppm higher than the surrounding countryside) (Idso et al., 2002). Soegaard and Moller-Jensen (Soegaard & Moller-Jensen, 2003) studied the urban CO_2 dome of Copenhagen and indicated that "traffic is the largest single CO_2 source in the city," and demonstrate that "emission rates range from less than 0.8 g CO_2 m^{-2} h^{-1} in the residential areas up to a maximum of 16 g CO_2 m^{-2} h^{-1} along the major entrance roads in the city center."

Following these studies, research regarding the urban CO_2 domes has been performed in many other parts of the world (Table 2). The results obtained from studies conducted in several cities from all over the world, show several commonalities. Thus, anthropogenic CO_2 emissions are the primary source of the urban CO_2 dome; the dome is generally stronger in city centers, in winter, on weekdays, at night, under conditions of heavy traffic, close to the ground, with little to no wind, and in the presence of strong temperature inversions. These

conclusions are in agreement with the data provided by Commonwealth Scientific and Industrial Research Organisation (CSIRO) which indicate that typical concentrations of CO_2 in urban areas is situated between 350 and 600 ppm and depend on meteorological parameters and urban agglomeration.

Authors	Place of measurements	Period of measurement	CO_2 range concentrations
Coutts A. M.	Melbourne, Australia	February - July, 2004	355 - 380 ppm (daily mean concentration).
Day T. A. et al.	Phoenix, USA	March - April, 2000	377 - 396 ppm (daily mean concentration)
George K. et al.	Baltimore, USA	2007	488 in urban area, 442 in sub-urban area, 422 in rural area
Ghauri B.	Six cities, Pakistan	2003 - 2004	270 - 325 ppm in Islamabad, 289 - 389 ppm in Quetta, 316.5 - 360 ppm in Karachi, 324.1 - 380 ppm in Lahore 295.2 - 356 ppm in Rawalpindi, 312 - 382 ppm in Peshawar.
Gratani L. et al.	Rome, Italy	1995 - 2004	367 ± 29 ppm in 1995 (montly mean variation) 477 ± 30 ppm in 2004 (montly mean variation) 414 ± 25 ppm green zone 505 ± 28 centrale zone
Grimmond et al.	Chicago, USA	July 11-August 14, 1995	338 - 370 ppm (diurnal variation) 405 - 441 ppm (nightly variation)
Idso S. B. et al.	Phoenix, USA	2000	390.2 ± 0.2 ppm (minimum daily concentration) 424.3 - 490.6 ppm (maximum daily concentration) 619.3 ppm (maximum daily concentration in cold season)
Kuc T. et al.	Kasprowy Wierch and Krakow, Poland	2000	370 ppm (monthly mean variation in Kasprowy Wierch) 370 - 430 ppm (monthly mean variation in Krakow)
Moriwaki R. et al.	Tokyo, Japan	October-Nov., 2005	380 - 580 ppm (daily mean concentration).
Nasrallah H.A. et al.	Kuwait City, Kuwait	1996 - 2001	368 - 371 ppm (daily mean concentration at 7 metter high).
Velasco E. et al.	Mexico city, USA	June 11-August 14, 1995	398 – 444 ppm (daily variation) 421 ppm (daily mean)

Table 2. Overview of urban CO_2 measurements

Taking in to account the concentration of CO_2 from the cities, some of researches were focused on the impact of local CO_2 emissions over local temperature. Thus, Balling et al. running the CO_2 concentration though a radiation model calculated that local CO_2 emissions modify the local temperature with more than one-tenth of one degree Celsius. In fact, Balling

et al. sugest that this increasing of temperature is insignificant by comparing it to the overall urban heat island in Phoenix which typically adds 5 to 10 degrees C. (Balling, Jr., et al., 2001).

Recently, Jacobson (Jacobson, 2010) found that domes form above cities more than a decade ago, cause local temperature increases that in turn increase the amounts of local air pollutants, raising concentrations of health-damaging ground-level ozone, as well as particles in urban air. Also, this study has shown that "CO_2 dome" that develops over urban areas is a local problem, which creates much more health problems than in rural areas.

The conclusions of Jacobson about the human health effects of CO_2 created many controversies; therefore, more research is necessary on the measurement of CO_2 variation over the urban areas.

2.2 CO_2 variation in three Romanian cities. Case study

The available literature contains no information about the variation of CO_2 concentrations in Romania in urban areas. However, the American system of global monitoring of CO_2 (NOAA-ESRL) has a station of continuous measurement of the main parameters of air quality placed in Constanta, which also measures CO_2 concentrations.

According to NOAA-ESRL data, the variation of CO_2 concentrations at the Constanţa measurement station has an ascending trend; the yearly average values are between 365 ppm in 1995 and 395 ppm in 2007. According to the same source the concentration of CO_2 has a seasonal variation with maxima in the cold season and minima in the warm season.

In order to study the influence of anthropic activity upon the CO_2 level the study was performed in three different Romanian cities from Cluj County, as follows:

a.   Cluj-Napoca city, 400 000 inhabitants,
b.   Turda city, 59 600 inhabitants
c.   Huedin town, 10 000 inhabitants

The case study has been carried out during one year (four seasons) from July 2008 to June 2009.

The measurements were performed monthly (during 8 hours from 8.30 am to 15.30 pm) in all the three selected locations using a NDIR CO_2 analyzer model EMG-4. The measurements of CO_2 levels were performed in a portable meteorological shelter.

For the estimation of the anthropogenic contribution over the CO_2 budget in all three studied areas a reference point situated outside of the cities has been chosen (Roba et all, 2009).

For the Cluj-Napoca city,three measurement points have been selected: one situated in a zone with intense traffic (Piaţa Mărăşti), one with moderate traffic (Cartier Grigorescu) and a reference point located in a periphery location (meteorological station in Cartier Gruia).

The results of the measurements recorded in the three locations in the city of Cluj-Napoca show that during the year the CO_2 level is strongly influenced by the amplitude of the anthropic activities. The highest levels were recorded in the location with intense anthropic activity (Piata Marasti) and the lowest levels in the reference point located outside of the city. The recorded values are comprised between 380 and 530 ppm (Mărăşti), 376-456 (Grigorescu) and 373-444 (reference point).

It was also found that the highest values were recorded during the months of October and November (during the final period of the biological cycle of plants) and during the winter. It was also found that starting with the months of March; the CO_2 concentrations decrease and become comparable with the summer values (Figure 3).

For the Turda city two measurement points have been selected: one in the city (Potaisa School) and another one located outside of the city (Meteo Station).

The results of the measurements in the two locations indicate a concentration difference between 15 and 20 ppm, depending of the period of measurements. The largest values of CO_2 concentration were obtained in the months of October and November, at the end of the biological cycle of plants and in the winter. The concentrations measured are in the range 380-502 ppm at Potaisa site and 371-450 ppm at the reference point.

In the town of Huedin the measurements were carried out simultaneously in two locations: one in the interior of the city (Liceul Octavian Goga) and a reference point in the peripheral area (Meteo Station). The results show a slight difference between the two locations. It was also observed again that the largest values are recorded in the months of October and November, i.e. at the end of the biological cycle of plants, and during the winter.

Starting with the month of March, the CO_2 concentrations decrease to normal values, comparable to those of the summer. The values recorded are in the range 355- 433 ppm (Octavian Goga site) and 350-411 ppm (reference point).

A comparison of the measured values carried out in different locations shows that the CO_2 concentrations depend on the size of the town, the highest values being recorded in Cluj-Napoca city, followed by Turda and Huedin (Figure 3).
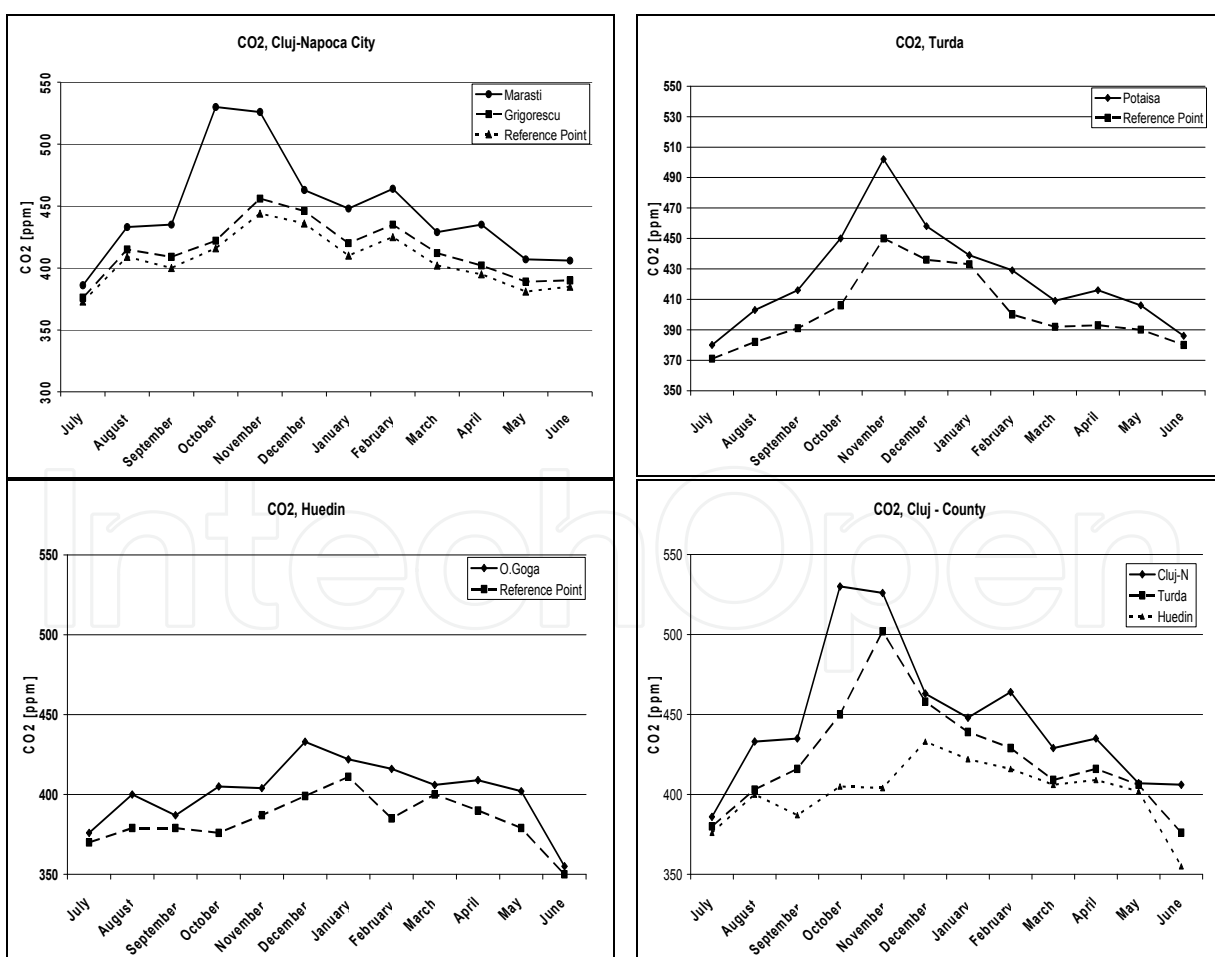

Fig. 3. Annual variation of CO_2 in urban studied areas

Diurnal variations were also observed; the highest values were measured in the morning and the lowest values at the astronomic midday, both in summer and in winter seasons (Figure 4).
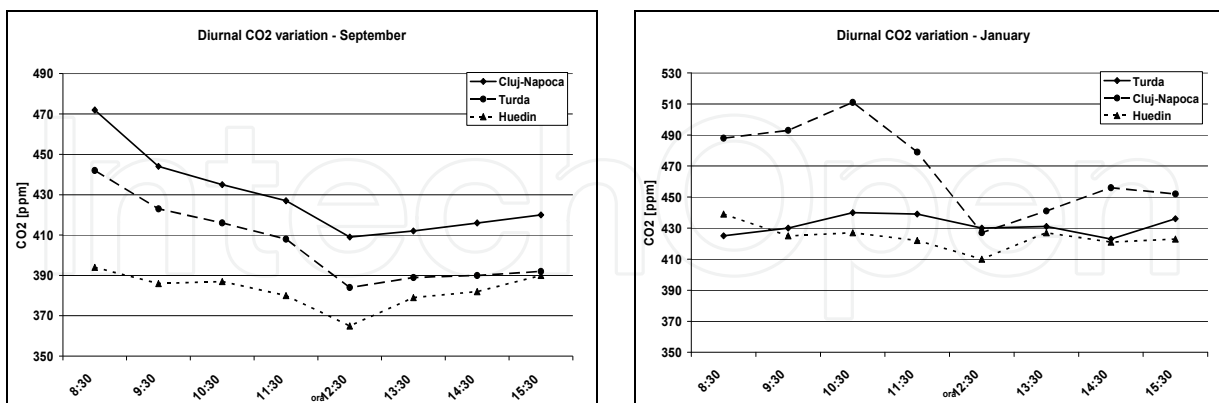

Fig. 4. Diurnal variation of CO_2 in urban studied areas

Taking into account the results of this case study we can conclude that the variation of CO_2 in studied urban areas is in agreement with other results reported in the scientific literature, which report that in urban areas the CO_2 levels are situated between 350 and 600 ppm, depending on meteorological parameters and urban agglomeration, with the observation that in the absence of rainfall the CO_2 level increases both in urban areas and outside.

3. CH₄ in urban area

3.1 Trends of CH₄ variation in urban areas. A literature review

Regarding to CH_4 variation in urban areas there are only a few studies about the level of methane in urban atmosphere, and these results are reported starting after the year 1980. For Romania such data are available only after 1995.

According to data from CSIRO the common concentrations of CH_4 in urban areas have values between 1700-2500 ppb and are influenced by meteorological parameters and urban agglomeration. Kuc and co-workers (Kuc et al., 2003) show that, the CH_4 level in urban areas is comprised between the natural level (1650 ppb) and 4200 ppb. Ito and co-workers (Ito et al. 2000) compared the atmospheric CH_4 concentrations recorded in Nagoya with the values measured at Mauna Loa Observatory in Hawaii (USA) and estimated that the excess concentration of CH_4 in the urban atmosphere of Nagoya was 170 ppb in 1988 and 150 ppb in 1997. A selective bibliography on the subject in presented in Table 3.

3.2 CH₄ variation in three Romanian cities. Case study

In Romania, the available literature provides no information about the variation of methane concentrations in urban areas and no such studies are reported. However, the American System of Global Monitoring of Air Quality (NOAA-ESRL), has a station of continuous measurements of atmospheric methane concentrations at Constanța. According to NOAA data, the concentration of CH_4 has an ascending trend, with average values comprised between 1880 ppb in 1995 and 1980 ppb in 2006. According to the same source, the methane concentration shows a seasonal variation, with maxima in the summer months and minima in the autumn and spring.

Authors	Place of measurements	Period of measurement	CH$_4$ range concentrations
Aikawa M. et al.	Urban,Sub-urban, Nagoya, Japan	2004	1.80 - 1.84ppm -urban area 1.78 - 1.80 ppm-suburban area
Derwent R.G. et al.	Island	1990 - 2003	1.75 - 2.00 ppm
Ghauri B. et al.	Pakistan	2003 - 2004	0.5 – 1.7 ppm
Hsu Y.K. et al.	California, USA	April 2007 - Feb. 2008	1.75 - 2.16 ppm
Ito A. et al.	Nagoya, Japan	1983 – 1997	1.85 ppm in 1998, 1.91 ppm in 1995, 1.90 ppm in 1997. 1983 - 1997 increese 13 ppb/year
Kuc T. et al	Kasprowy Wierch Krakow, Poland	2000	1650 ppb Kasprowy Wierch (monthly mean concentration) 2000 - 2800 ppb Krakow (monthly mean concentration)
Sikar E. & La Scala N.	Urban area, Brasil	1998 – 1999	1.80 ppm
Smith F.A. et al.	Mexico City	March, 1993	1.8 ppm during the night 7.971 ppm in the morning 2.001 - 2.999 midle of the day
Thi Nguyen H et al.	Seul, Korea	1996 - 2006	2.24 ± 0.42 ppm urban road-side 2.06 ± 0.31 ppm urban background
Veenhuysen D. et al	Amsterdam, Netherlands	1994	1.75 - 3.00 ppm
Wang J.L. et al.	Sub-urban area, Taiwan	1-27 April, 2000	1.9 - 3.7 ppm

Table 3. Overview of urban CH$_4$ measurements

Our case study has been focused on the measurement of the CH$_4$ variation in three urban areas from Cluj county as described in sub-chapter 2. The study was carried out during one year (four seasons) from July 2008 to June 2009. The measurements were performed monthly in all selected areas at the astronomic midday (in Romania at 12.30 h). In all three areas a measurement point located in the city and a reference point located outside has been selected.

The samples were collected in Cluj-Napoca, in Marasti location in the city and as reference point at Gruia location. In Turda the measurements in the city were made at Liceul Potaisa, and the reference point at the Meteo station. In Huedin the measurements were made at Liceul Octavian Goga in the town and the reference point was the meteo station.

For atmospheric CH$_4$ measurements, the air samples where collected by the flask sampling method and analysed by gas chromatography technique (GC) coupled with a flame ionisation detector (FID) (Cristea et all., 2009).

The results show a signficant variation of atmospheric methane, depending on the season and the urban aglomeration degree. Thus, the highest values were recorded in the city of Cluj-Napoca (11.5 ppm in April 2009) and the lowest values were recorded in the month of August 2008 (2.5 ppm).

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In Turda the concentrations of atmospheric methane were comprised between 2.2 and 8.6 ppm, with the lowest values measured in August 2008 (2.2 ppm) and the highest values recorded in April 2009 (8.6 ppm).

In Huedin the concentrations of methane were measured between 1.4 and 7 ppm, with the lowest values recorded in July 2008 (1.4 ppm) and the highest ones in April 2009 (7 ppm).

Significant differences are also bserved between te methane concentrations in the interior of the cities and the reference points located outside. These differences were recorded throughout the experiments, which leads to the conclusion that the anthropic activities, the automobil traffic in particular, are an important source of methane in the urban atmosphere.

The analysis of the methane concentrations in the three areas investigated indicates a similar profile for the measurements in the interior of the cities, with minima in the summer months and maxima during the spring. This may be attributed to the absence of rains in the spring (March-April). In May 2009, when the precipitations started, the concentration of atmospheric methane became closer to the values measured at the reference points.

For the reference points, the values of the atmospheric methane concentrations are in the range 2.1-4.2 ppm in Cluj-Napoca, 1.7-3.5 in Turda and 1.4-2.9 ppm in Huedin. As for the measurements in the city, a slight increase of the concentrations were observed in the spring period of 2009, due to the lack of precipitations.
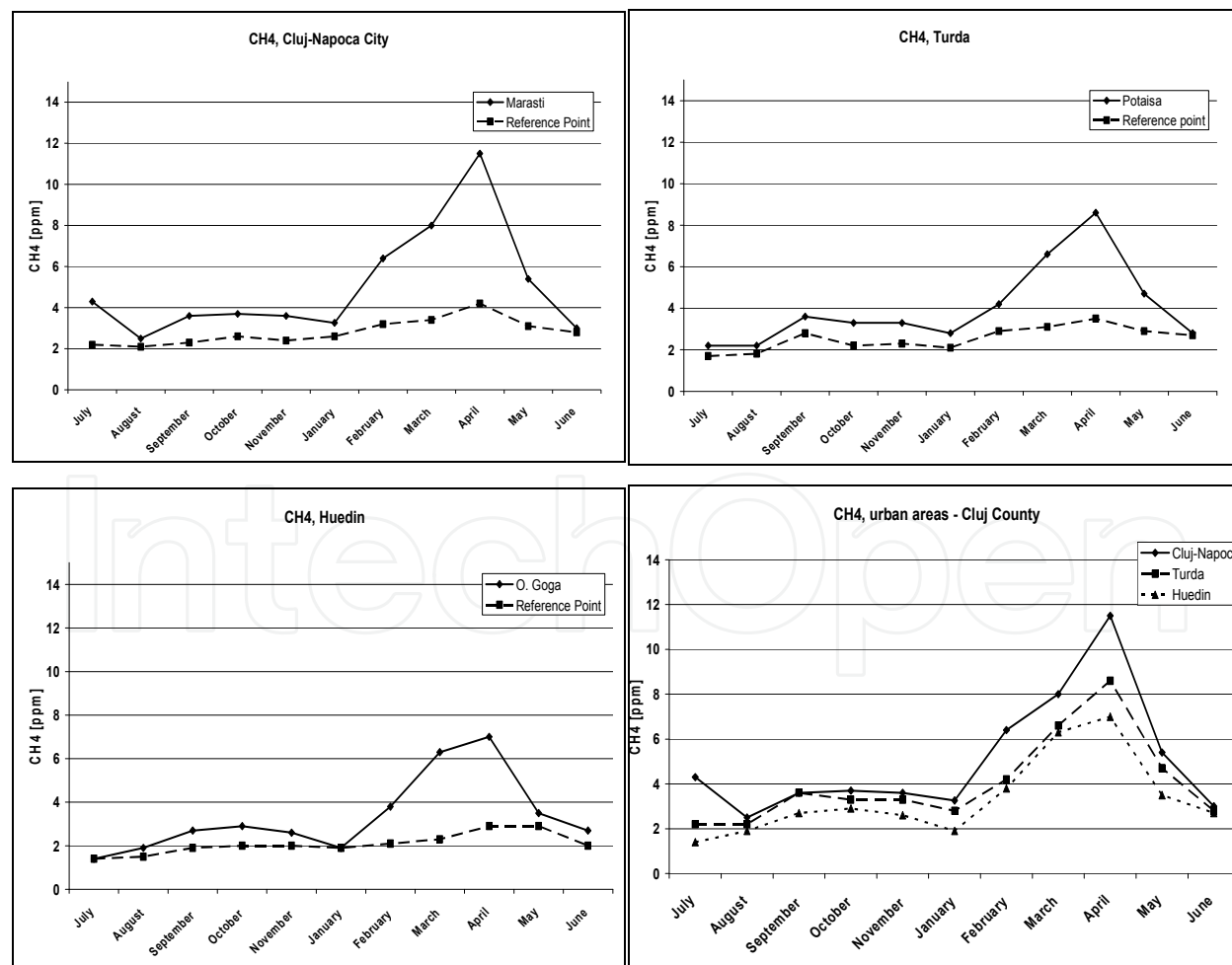

Fig. 5. The variation of methane concentration in the urban areas of Cluj county locations.

The results of our measurements indicate that the atmospheric CH_4 level in urban areas is strongly influenced by the size of the urban aglomeration as well as by the meteorological parameters. These results is in agreement with other results from scientific literatures.

4. CO in urban areas

4.1 Trends of CO variation in urban areas. A literature review

According to World Health Organization data (WHO, 2000), in the main European cities the average atmospheric CO concentration is situated under 2 mg/m^3 air, with a maximum concentration lower than 6.0 mg/m^3 air. At global level, the concentration of CO is composed between 0.05 and 0.12 ppm in the air. This concentration is an average between the values measured in urban and rural areas. In rural areas the CO concentration is due mainly to natural processes, but in urban areas it is strongly influenced by anthropic activities.

The CO concentration in the air of urban zones depends upon the density of combustion sources, the topography of the measurements location, the meteorological conditions and from the distance between the measurement point and the auto traffic routes.

The monitoring of CO in USA is carried out since 1980; currently, there are 243 measurement stations distributed all over the USA territory. According to EPA Reports (EPA, 2009), the concentration of CO decreased in the period 1980-2006 from 14 ppm to 3 ppm.

In Europe, the monitoring of CO in urban areas is 20 years old. Several European projects were in action, to evaluate the exposure of the population to CO, and the measurements were carried out both with fixed and mobile stations. According to WHO data (WHO, 2000) in large European cities the CO concentrations (during 8 hours measurements) are situated bellow 20 mg/m^3 in the air, and the maxima are not higher than 10 mg/m^3 in the air.

The first network for the measurement of pollutants resulted from anthropic activities was created in France in 1979 under the name AIRPARIF and measures the daily, monthly and annual concentrations of NOx, SO_2, O_3, PM, CO and of some organic compounds. According to this source, the CO concentration in the Paris region decreased from 4000 µg/m^3 air in 1994 to 1200 µg/m^3 air in 2006. In 2004 started measuring background measurements. The variation of annual average decreased from 500 de µg/m3 air in 2003 to 400 µg/m^3 air in 2006.

In Great Britain, the measurement of the concentrations of atmospheric pollutants dates from 1973; currently, there are more than 100 station in urban zones for continuous monitoring of the air quality parameters. In London, the quality of air is monitorised by as many as 30 stations. The network was created in 1993 under the name London Air Quality Network (LAQN), and since 1997 this network also measures the evolution of daily CO concentrations.

At the European level functions the European Environment Agency (EEA) with 32 members: all the 27 EU member countries, also Island, Liechtenstein, Norway, Switzerland and Turkey. Under the coordination of EEA was created the European Environment Information and Observation Network (EIONET), with the role of processing and validating the data from the stations of the member countries connected to this network. The information is available as Reports to interested users. Among the workstations connected to EIONET, 163 measure the concentrations of CO. According to EEA data, the concentration of CO at the European level decreased from 1 mg/m^3 air in 1995 to 0.5 mg/m^3 air in 2005.

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In addition to the data from the monitoring stations there are numerous studies about the determination of CO concentrations in urban zones all over the world. A synthesis of these results is given in Table 4.

Authors	Place of measurements	Period measurement	CO range concentrations [ppm]
Chatterton T.et al.	Norwich, UK	1997 - 1998	0.4 - 10.9
Chelani A.B. et al.	Delhi, India	2000 - 2003	1.66 - 8.4
Cheng C. S. et al.	Canada	1974 - 2000	Montreal: 0.5 - 2.1, Toronto: 0.7 - 3.7
Corti A. et al.	Salerno, Italy	Not specified	0.55 - 0.85
DEQ-Oregon	Portland-SUA	1980 - 1998	13.0 - 4.7
Emmerson K. et al.	Birmingham, UK	1999 - 2000	0.17 - 0.66
EPA	USA	1990 - 2006	Washington (decrease from 9 to 2), New-York (8.6 - 1.8), Los Angeles (14 – 4) ,
Ghauri B. et al.	Pakistan	2003 - 2004	Islamabad : 6 - 13; Quetta: 1.9 - 14 , Karachi: 1.6 - 8.0; Lahore: 1.3 - 12; Rawalpindi: 1.6 - 8
Ghose M. K. et al.	Calcutta, India	2003	2.6 - 5.1
Jones S. G. et al.	Paris, France	1997	0.38 - 1.45
Kim S.Y. et al.	Seoul , Koreea	2002	0.8 - 44.0
Kukkonen J. et al.	Helsinki, Sweden	1997	0.1 - 4.5
Lijteroff R. et al.	San Luis, Argentina	1994 - 1995	3.43 - 9.17
Linden J. et al.	Burkina Faso, Africa	2004 - 2005	Background: 1 - 9, Traffic: 6.5 - 6.0
Makra L. et al.	Szeged, Hungary	1997 - 2001	0.24 - 0.93
Manning A.J. et al.	Leek, UK	1997	0.25 - 4.0
Martín M.L. et al.	Bay of Algeciras	1999 - 2001	0.5 - 2.9
Milton R. et al.	Londra, UK	2004 - 2005	0.9 - 14.9
Muttamara S. et al.	Bangkok	1997	8.23 - 26.89
Ni-Bin Chang et al.	Kaohsiung, Taiwan	1995	0.1 - 2.0
Park S. S. et al.	Seoul, Koreea	1998 - 1999	1.74 - 2.81
Reich S. et al.	Buenos Aires	2001	0.60 - 2.44
Rubio M. A. et al.	Santiago City, Chile	2005 - 2006	0.31 - 3.06
Sanchez-Coyllo O. et al.	Sao-Paulo, Brazilia	1999	1.20 - 4.00
Sathitkunarat S. et al.	Chiang Mai, China	2002	0.9 - 1.5
Shiva Nagendra S.M.	Delhi, India	1997 - 1999	0.1 - 18
Turias I.J. et al.	Campo de Gibraltar	1999 - 2001	0.4 - 4.5
Venegas L.E. et al.	Buenos Aires	1994 - 1996	Autumn:10,0, Winter: 9.80, Spring :10,7

Table 4. Overview of urban CO measurements

4.2 Case study Cluj-Napoca city

In Romania, the monitoring of air quality is done by the Agencies for Environment Protection and follows the concentrations of nitrogen oxides, sulfur dioxide, ozone, BTEX, material particles, etc. Of these, 53 monitoring stations are connected to the European EIONET System and 12 stations also measure the concentrations of CO in urban zones.

In the city of Cluj-Napoca, there are four stations for continuous monitoring of air quality, and beginning with August 2005 the Agency measures the CO concentrations in two locations in the city of Cluj-Napoca and one in the city of Dej. The measurements in Cluj county show that the concentration of CO in the atmosphere is much below the admitted level (10 mg/m^3) and varies between 0.09 and 0.4 mg/m^3 air.

In this case study the measurements were performed daily in Cluj-Napoca at the astronomic midday (in Romania at 12.30 h) using a NDIR CO analyzer Horiba model APMA-360. The results showed that the CO level in Cluj-Napoca is less than 1 mg/m^3 with a tendency of accumulation during the winter season. It is also observed a trend of accumulation during the spring months, due to the lack of precipitations. Beginning with the end of May, when the rain regime becomes normal, the values of CO concentrations are around 0.1 mg/m^3 air (Figure 6).
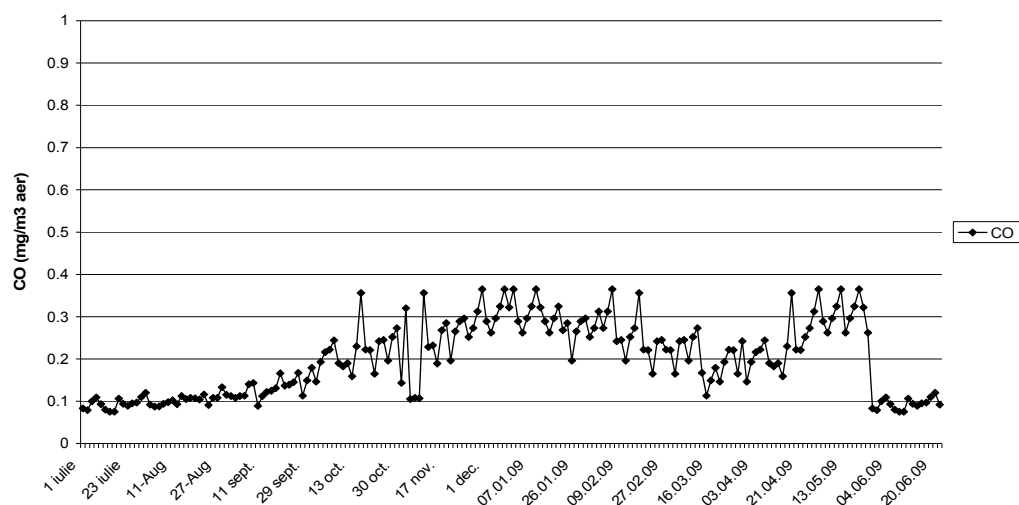

Fig. 6. Variation of CO concentrations in Cluj-Napoca in the period July 2008-June 2009

5. Anthropogenic contribution in CO$_2$ and CH$_4$ budgets

5.1 Isotopic ^{13}CO$_2$ measurements

Knowledge of the terrestrial CO$_2$ cycle will help to understand the climate change phenomena and to predicting the future atmospheric CO$_2$ concentrations and global temperatures. By estimating the terrestrial CO$_2$ cycle, including such factors as emissions, storages and fluxes and combining this with the isotope compositions of atmospheric CO$_2$ will help to identify the contribution of different factors to the atmospheric CO$_2$ budget. More than the observation of the CO$_2$ isotopic composition provides important information about sources such as fossil fuel combustion and biogenic respiration. The determination of isotopic concentrations of ^{13}C enforces the analyze of different species of atmospheric CO$_2$ and CH$_4$ collected in situ in glass recipients of different measures (flask sampling) by mass spectrometry. Thus, Takahashi et al. (2001, 2002) using CO$_2$ isotope compositions method

for investigating the sources of atmospheric CO_2 observed carbon isotope compositions of $\Delta^{14}C$ and $\delta^{13}C$ in atmospheric CO_2 and estimated the contributions of fossil fuels and biogenic respiration, while Pataki (Pataki et al., 2003, 2006a,b) observing $\delta^{13}C$ and $\delta^{18}O$ isotope compositions in atmospheric CO_2 has reported the contribution of natural gas combustion, gasoline combustion and biogenic respiration over the total atmospheric CO_2 budget.

To identify sources of carbon and to quantify these sources it is used the Keeling plot (Pataki et al., 2003). The equation used in the Keeling plot is derived from the basic assumption that the atmospheric concentration of a substance (CO_2, CH_4) in air reflects the combination of some background amount of the substance that is already present in the atmosphere and some amount of substance that is added or removed by sources or sinks:

$$C_T = C_A + C_S \qquad (1)$$

where C_T, C_A, and C_S are the concentrations of the substance in air, in the background of atmosphere, and that contributed by sources, respectively. Isotope ratios of these different components can be expressed by a simple mass balance equation:

$$C_T\delta_T = C_A\delta_A + C_S\delta_S \qquad (2)$$

where δ_T, δ_A, and δ_S represent the isotopic composition of the substance in the atmosphere, in the background, and of the sources, respectively. By combine Eqs. 1 and 2 it is obtained equation 3:

$$\delta_T = C_A (\delta_A - \delta_S)(1/C_T) + \delta_S \qquad (3)$$

This is a linear relationship with a slope of $C_A (\delta_A - \delta_S)$ and an intercept at the δ_S value of the net sources/sinks in the atmosphere.

According to Pataki (Pataki et al., 2006) the mixing ratios originating from local sources (C_S) is composed from the CO_2 mixing of natural gas combustion (C_N) and CO_2 mixing of gasoline combustion (C_G):

$$C_T = C_A + C_N + C_G \qquad (4)$$

Using the values of measured concentrations of CO_2 (C_T) in the same time and in the same air as the measurements of δ_T, and know the δ_N, δ_G and C_N it is possible to estimate C_G. The isotopic mass balance equation in this case is:

$$\delta_T C_T = \delta_B C_B + \delta_N C_N + \delta_G C_G \qquad (5)$$

where δ_T and δ_G represent the isotopic composition of the CO_2 results from natural gas combustion and δ_G is the isotopic composition of the CO_2 results from gasoline combustion.

In order to study the effects of the emission and diffusion of CO_2 from fossil fuel combustion most of the recent studies have focused on urban areas where CO_2 is mainly the product of power plants and transportation. The results of these measurements were correlated with variations in carbon isotopic composition and its show that while the natural level of $\delta^{13}C$ value is −8.02‰, in urban areas the $\delta^{13}C$ values is down to −12‰ for atmospheric CO_2. This difference is given by the increasing input of CO_2 derived from fossil fuel (Clark- Thorne and Yapp, 2003, Lichtfouse et al., 2003; Widory and Javoy, 2003, Newman S et al. 2008, Wada et al 2010).

5.2 Isotopic $^{13}CH_4$ measurements

The carbon isotopic composition (^{12}C, ^{13}C and ^{14}C) of atmospheric methane is used to estimate the local CH_4 sources contribution over the CH_4 budget in a local areas (Moriizumi et al., 1998)

According to (Miller et al., 2003 cited by Cuna et al. 2008) the methane mixing ratio in air, $[CH_4]$, and its isotopic ratio, $\delta^{13}C_{CH4}$, may be derived from three main sources: methane produced by microbial, $[CH_4]_{micr}$, fossil methane, $[CH_4]_{ff}$, and methane produced from biomass burning, $[CH_4]_{bmb}$

$$[CH_4]_T = [CH_4]_{micr,} + [CH_4]_{ff,} + [CH_4]_{bmb} + [CH_4]_{bg} \qquad (1)$$

In equation (1) $[CH_4]_{bg}$ is defined as the smoothed marine boundary layer (MBL) at the latitude of interest (Dlugokencky et al., 1994 cited by Cuna et al. 2008).

Each of these emissions has a more-or-less distinct isotopic signature with bacterial methane $\delta^{13}C_{micr} \approx 60‰$, thermogenic methane $\delta^{13}C_{ff} \approx 40‰$, and biomass burning methane $\delta^{13}C_{bmb} \approx 25‰$ (Quay et al., 1999 cited by Cuna et al. 2008).

$$\delta^{13}C[CH_4]_T = \delta^{13}C[CH_4]_{micr,} + \delta^{13}C[CH_4]_{ff,} + \delta^{13}C[CH_4]_{bmb} + \delta^{13}C[CH_4]_{bg} \qquad (2)$$

Separating CH_4 sources using isotopic signatures is complicated by enrichment during uptake processes such as bacterial CH_4 oxidation, or methanotrophy (Chanton et al., 2005 cited by Cuna et al. 2008). Thus, the methane mixing ratio changes over time according to Eq. (3), where $[CH_4]_S$ is the sum of all sources and τ is the lifetime of methane with respect to its destruction by OH and addition from other processes (Montzka et al., 2000; Hein et al., 1997 cited by Cuna et al. 2008):

$$d[CH_4] / dt = [CH_4]_S - ([CH_4] / \tau) \qquad (3)$$

The $\delta^{13}C$ of methane measured in an air sample results from several different sources, such that

$$\delta^{13}C_S = \delta^{13}C_{bg} + \varepsilon \qquad (4)$$

In Eq. (4) $\delta^{13}C_S$ is the flux-weighted isotopic ratio of all sources expressed in δ notation, $\delta^{13}C_{bg}$ is the atmospheric background isotopic ratio and ε is the average isotopic fractionation associated with these processes (Cantrell et al., 1990 cited by Cuna et al. 2008). Using the values of measured concentrations of methane $[CH_4]_T$ in the same time and in the same air as the measurements of δ^{13}, it is possible to estimate the contribution of all sources at the atmospheric methane budget. Thus, Moriizumi (Moriizumi et al., 1998) analyzing the CH_4 in Nagoya, Japan found that "*the contribution of fossil CH_4 to local CH_4 released from the urban area was calculated to be 102±8%, and its $\delta^{13}C$ was −40.8±3.0‰. In a suburban area of Nagoya fossil, CH_4 contributed to less than 10% of local release and the calculated value of $\delta^{13}C$ for non-fossil CH_4 was approximately −65‰, which is within the range of reported values of $\delta^{13}C$ for CH_4 derived from bacterial CH_4 sources such as irrigated rice paddies*". Kuc (Kuc et al. 2003), measuring the CH_4 in Krakow found that "*The linear regression of $\delta^{13}C$ values of methane plotted versus reciprocal concentration yields the average $\delta^{13}C$ signature of the local source of methane as being equal to −54.2‰. This value agrees very well with the measured isotope signature of natural gas being used in Krakow (−54.4±0.6‰) and points to leakages in the distribution network of this gas as the main anthropogenic source of CH_4 in the local atmosphere*". Nakagawa (Nakagawa et al., 2005), using the stable carbon and hydrogen isotopic compositions ($\delta^{13}C$

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and δD) of methane quantified the contribution of automobile exhaust to local CH_4 budget. The authors estimated that for local sources, automobile exhaust in Nagoya, Japan, contribute significant amounts (up to 30%) of CH_4 to the troposphere in the studied area.

Studies performed in wetlands showed that the isotopic signature $\delta^{13}C$ of methane is situated between -67.4 and -53.3‰ with lower values in the summer and higher values in the winter (Cuna et al., 2008; Tarasova et. al., 2006). These values confirm that in the wetlands, the biogenic CH_4 is the main source of atmospheric CH_4.

5.3 Isotopic $^{13}CO_2$ measurements in Cluj county. Case study

In order to study the role of CO_2 resulted from anthropic activities in the urban atmosphere of Cluj county, the variation of CO_2 concentrations and the corresponding $\delta^{13}C$ values, in samples collected in the three areas (Cluj-Napoca, Turda, Huedin) were measured (by flask sampling) during a whole year (July 2008-June 2009). For each area two points of measurements were selected, one in the city and one reference outside of the city. The determination of CO_2 concentrations was done with an infrared gas analyzer, and the isotopic ratios were measured with a DELTA V Advantage, Thermo Finnigan mass spectrometer. A graphic representation of the isotopic ratios as a function of $1/[CO_2]$ gives a Keeling plot and the value of the intercept of Keeling slope provide information about the isotopic signature of the source. Depending on the climatic conditions and the size of the urban agglomeration, correlations between $\delta^{13}C$ values and corresponding CO_2 concentrations were between -11 ‰ for Cluj-Napoca, -10.0‰ for Turda and -9.0‰ for Huedin (Tables 5-7). If we consider $\delta^{13}C = -8$‰ the isotopic composition of natural CO_2, the anthropogenic contribution for CO_2 budget is higher for Cluj-Napoca and near the natural level for small town Huedin. As the data in tables show, for the locations in the interior of the cities, the isotopic values are displaced from the average values by 0.5-1.5 ‰ compared with the reference points, which suggests that the CO_2 source in the urban location is composed from the zone with $\delta^{13}C = -8$‰, with clean air, and an anthropic source which can be CO_2 resulted from burning fossil fuels (mainly gasoline and methane) plus a biogenic source of CO_2 resulted from the respiration of the local vegetation. The largest difference occurred in the municipality of Cluj-Napoca (1.376), where the average values of $\delta^{13}C = -$

Measurement mounth	Time	City Point (Mărăşti)		Reference Point	
		CO_2 (ppm)	$\delta^{13}C$ (‰)	CO_2 (ppm)	$\delta^{13}C$ (‰)
July 2008	12.30	386	-8.773	373	-8.670
August 2008	12.30	433	-10.529	409	-8.928
September 2008	12.30	435	-10.683	400	-8.901
October 2008	12.30	530	-10.926	416	-8.936
November 2008	12.30	526	-10.836	444	-8.940
January 2009	12.30	538	-10.200	450	-8.949
February 2009	12.30	773	-11.012	438	-8.939
March 2009	12.30	665	-10.543	455	-8.943
April 2009	12.30	682	-10.657	428	-8.921
May 2009	12.30	458	-9.542	420	-8.901
June 2009	12.30	425	-9.230	395	-8.763

Table 5. Values of CO_2 (ppm) and $\delta^{13}C_{PDB}$ (‰) in Cluj-Napoca city

Measurement mounth	Time	City Point (Potaisa)		Reference Point	
		CO_2 (ppm)	$\delta^{13}C$ (‰)	CO_2 (ppm)	$\delta^{13}C$ (‰)
July 2008	12.30	380	-8.797	371	-8.720
August 2008	12.30	403	-8.826	382	-8.762
September 2008	12.30	416	-8.802	391	-8.851
October 2008	12.30	450	-8.973	406	-8.878
November 2008	12.30	502	-10.620	450	-8.953
January 2009	12.30	463	-9.274	425	-8.900
February 2009	12.30	483	-9.560	450	-8.940
March 2009	12.30	450	-9.200	420	-8.760
April 2009	12.30	490	-10.146	435	-9.120
May 2009	12.30	399	-8.870	371	-8.832
June 2009	12.30	425	-9.132	355	-8.900

Table 6. Values of CO_2 (ppm) and $\delta^{13}C_{PDB}$ (‰) in Turda city

Measurement mounth	Time	City Point (O.Goga)		Reference Point	
		CO_2 (ppm)	$\delta^{13}C$ (‰)	CO_2 (ppm)	$\delta^{13}C$ (‰)
July 2008	12.30	376	-8.180	370	-8.168
August 2008	12.30	408	-8.438	379	-8.187
September 2008	12.30	387	-8.175	379	-8.141
October 2008	12.30	405	-8.382	376	-8.138
November 2008	12.30	404	-8.390	387	-8.221
January 2009	12.30	422	-9.455	411	-8.324
February 2009	12.30	416	-9.342	385	-8.122
March 2009	12.30	406	-9.142	400	-8.786
April 2009	12.30	409	-10.620	390	-9.200
May 2009	12.30	402	-8.761	379	-8.100
June 2009	12.30	355	-8.956	350	-8.212

Table 7. Values of CO_2 (ppm) and $\delta^{13}C_{PDB}$ (‰) in Huedin town

10.266‰ were obtained in the city center, compared with the $\delta^{13}C$ = -8.890‰ for the reference point. For the other locations studied (Turda and Huedin) the isotopic concentrations are close to the atmospheric background, namely -9,291‰ for Turda and -8,895‰ for Huedin, comparable with the average values for the reference points (-8.874‰ for Turda and -8.327‰ and Huedin) suggesting that anthropic CO_2 is not contributing to the pollution.

5.4 Isotopic $^{13}CH_4$ measurements in Cluj county. Case study

For the evaluation of the role of CH_4 resulted from anthropic activities in the urban atmosphere in the Cluj county, the variation of CH_4 concentrations and the corresponding $\delta^{13}C$ values were measured in air samples collected in three areas: Cluj-Napoca (Piaţa

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Mărăşti), Turda (Potaisa School) and Huedin (O. Goga High School) during the period between January-June 2009, using the flask sampling. Again, the $\delta^{13}C$ values were measured with a ThermoFinnigan Delta V Advantage mass spectrometer. The methane concentrations in the same samples were measured with a gas chromatograph equipped with a FID detector.

The observed variation of methane concentrations (Table 8) is rather large, between 4.7 and 11.5 ppm. The values measured are above the atmospheric background, which suggests that there is an anthropic source of CH_4 in all investigated areas. The average value of $\delta^{13}C$ = - 40 ‰ suggests that the source of methane in the atmosphere is the gas fuel network of the urbane zone investigated.

Measurement month	Cluj-Napoca		Turda		Huedin	
	CH_4 (ppm)	$\delta^{13}C$ (‰)	CH_4 (ppm)	$\delta^{13}C$ (‰)	CH_4 (ppm)	$\delta^{13}C$ (‰)
January 2009	11.5	-39.21	10.4	-39.45	10.6	-39.78
March 2009	8.0	-37.90	6.3	-38.75	5.5	-38.97
April 2009	11.5	-39.80	11.0	-38.92	10.5	-38.98
May 2009	8.4	-38.02	7.4	-38.80	4.7	-38.85

Table 8. Simultaneous value of CH_4 (ppm) and $\delta^{13}C$ (‰) in the Cluj district.

6. Correlation between CO₂ trend variation in urban area and variation of meteorological parameters

6.1 Case study Cluj-Napoca city

For this study a daily measurements of the CO_2 concentration and the main meteorological parameters (temperature, relative humidity and wind velocity) were recorded for a whole calendar year, beginning with July 2008 until June 2009. The measurements were carried out in the centre of Cluj-Napoca city, the time of midday (12.30), at the selected latitude. The results of measurements revealed a daily variation of CO_2 concentrations correlated with the meteorological factors and biological cycles of plants. Thus, the largest values of CO_2 were recorded in the fall and winter in the absence of vegetation, and the lowest values in the summer months, when the biologic cycle of plants is at the maximum.

The graphic representation of the CO_2 values as a function of meteorological parameters indicates a direct correlation with temperature and an inverse correlation with the wind velocity and relative humidity.

A computation of linear regression slopes of CO_2 versus air temperature for two months from winter (January and February) and two months from summer (July and August) gives positive slopes for both seasons with a highest correlation factor (0.666) in winter in the absence of photosynthesis (figure 7).

The same representation for CO_2 and for relative humidity shows a negative slope in summer and a positive slope in the winter. The computation of linear regression slopes for CO_2 versus wind velocity show a negative slopes both in summer and in winter (figure 7).

The results of this case study show that in urban area it is difficult to estimate by correlation coefficient analyses the influence of meteorological parameters over the CO_2 variation. In order to correlate the variation of CO_2 concentrations with the variation of meteorological parameters a statistic analysis of data is necessary. For the statistical approach the regression analysis and principal component analysis (PCA) has been used.
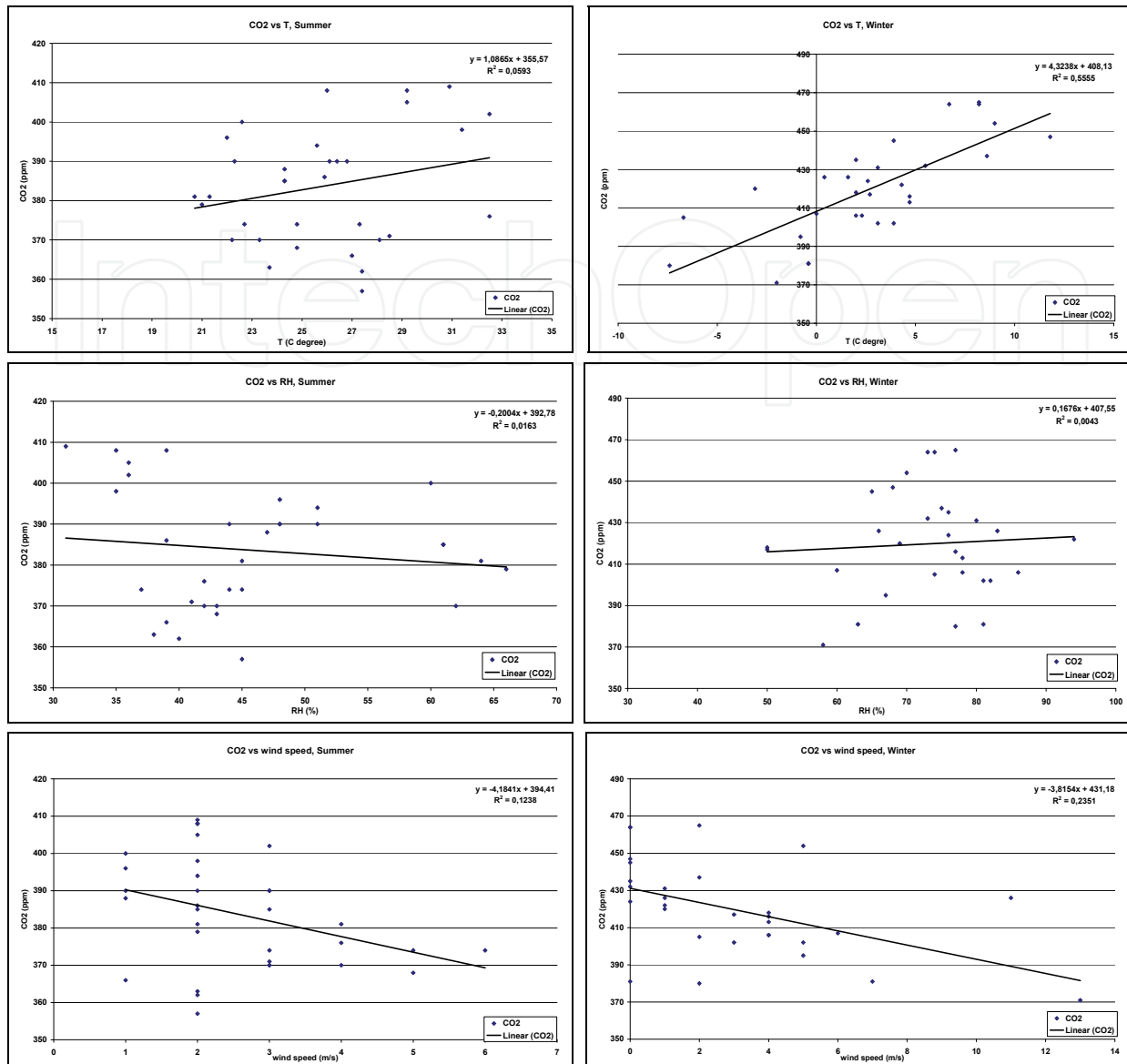
Fig. 7. Corelation between CO_2 variation and meteorological parameters in two seasons

6.1.1 The regression analysis

The regression analysis was performed with the aid of Curve estimation model of SPSS statistics program and the regression coefficients were calculated, having the CO_2 concentration as independent variable and the meteorological parameters as dependent variables. For analysis the squares of regression coefficients and the regression curves were used. The regression coefficients R^2 were computed for the most frequently used types of regression, namely linear, logarithmic, polynomial and exponential (Table 8).

The analysis of regression coefficients leads to some important conclusions.

The only meteorological parameter which correlated with the CO_2 concentration over the 0.6 threshold is the air temperature. Both the air humidity and the wind velocity have very low regression coefficients, suggesting that there is a low probability that the variation of the CO_2 is influenced by these meteorological factors. However, there are singular situations, when the correlation coefficients are close to the 0.6 threshold. Thus, for the relative

Month	Rt	Ta °C	RH %	V m/s
I (January)	Li	.842	.042	.014
	Lo	.843	.040	.013
	Po	.	.040	.
	Ex	.	.041	.
II (February)	Li	.802	.000	.426
	Lo	.789	.000	.430
	Po	.	.001	.
	Ex	.	.000	.
III (March)	Li	.461	.011	.166
	Lo	.456	.011	.168
	Po	.550	.003	.090
	Ex	.549	.003	.087
IV (April)	Li	.392	.034	.064
	Lo	.392	.033	.064
	Po	.368	.037	.012
	Ex	.368	.039	.012
V (May)	Li	.750	.462	.546
	Lo	.741	.462	.544
	Po	.865	.454	.380
	Ex	.869	.455	.381
VI (June)	Li	.632	.485	.000
	Lo	.632	.489	.000
	Po	.673	.520	.020
	Ex	.673	.516	.019
VII (July)	Li	.117	.158	.003
	Lo	.121	.159	.004
	Po	.116	.161	.019
	Ex	.113	.160	.018
VIII (August)	Li	.028	.271	.088
	Lo	.026	.278	.082
	Po	.025	.166	.120
	Ex	.027	.160	.126
IX (September)	Li	.368	.033	.337
	Lo	.376	.035	.342
	Po	.481	.004	.287
	Ex	.471	.003	.283

X (October)	Li	.121	.045	.088
	Lo	.123	.047	.092
	Po	.206	.	.065
	Ex	.202	.	.061
XI (November)	Li	.270	.189	.143
	Lo	.269	.180	.144
	Po	.	.152	.
	Ex	.	.160	.
XII (December)	Li	.571	.172	.028
	Lo	.581	.176	.027
	Po	.667	.196	.024
	Ex	.656	.193	.023

Table 9. The Estimation of regression coefficients (R^2). Note: The types of regression R are: Li – linear, Lo – logaritmic, Po – polynomial, Ex – exponential

humidity the highest regression coefficient was 0.52, for the type polynomial in June 2009. For the wind velocity the largest coefficient was 0.56 in May 2009, for the linear regression.

The regression between CO_2 concentration and temperature reveals two interesting aspects. The 0.6 threshold of the correlation coefficient was overfull filed in the three months of winter, at the end of spring and beginning of the summer, in May and June. The lowest value of the correlation coefficient was observed in August when the measurements were made at high temperatures over 30 Celsius degree. Large values, above 0.8 were observed in January and May. To illustrate the correlations we present in table 9 all the situations when the correlation coefficient was higher than 0.6.

6.1.2 The analysis of main components (PCA)

This type of analysis was necessary, because we wanted to see, which is the weight of meteorological parameters and CO_2 concentrations in the explanation of total variations. The PCA (Principal Component Analysis) method without factor rotation was used and the results are shown in Table 10.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	1.760	44.002	44.002	1.760	44.002	44.002
2	1.066	26.646	70.648	1.066	26.646	70.648
3	.900	22.491	93.139	.900	22.491	93.139
4	.274	6.861	100.000			

Table 10. Explanation of total variations. Extraction Method: Principal Component Analysis

After the value of 0.5 was selected for the Eigenvalue, three components were extracted which together explain 93.139% of the total variation. The first component explains 44.002 %

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of the variation, the second 26.649 and the third 22.5 %. The difference to 100 % is due to a fourth component, which was eliminated because it had an Eigenvalue of only 0.274.

The matrix of components (Table 11) allows the identification of each factor. Thus, the first factor is very well correlated with the air temperature (inverse correlation) and with the air humidity (direct correlation). The second component is very well correlated with the wind velocity. The concentration of CO_2 is very well correlated with the third component.

	Component		
	1	2	3
CO_2	.480	-.283	.824
Ta	-.897	-.245	.045
V	-.045	.961	.234
RH	.850	-.048	-.406

Table 11. Matrix of components

7. Conclusions

The monitoring of the CO_2 levels in urban area could estimate the contribution of anthropic activities over the global CO_2 level. This contribution is essential in order to establish the presence of CO_2 dome over the cities. The results of presented case study confirm the presence of a CO_2 dome over the urban studied area. More than that, it confirms that the anthropogenic CO_2 emissions are the primary source of the urban CO_2. Taking into account the obtained results it can be observed that the level of CO_2 in urban areas is influenced by the size of the city and by the amplitude of anthropic activities. Thus the highest values of CO_2 were obtained in the biggest city Cluj-Napoca (between 380 and 530 ppm at Mărăşti Square, 376-456 at Grigorescu and 373-444 at reference point) followed by Turda (380-502 ppm at Potaisa School and 371-450 ppm at the reference point) and Huedin (355- 433 ppm at O. Goga High School and 350-411 ppm at the reference point. It is also observed that the concentration of urban CO_2 has an annual variation with the lower value in the summer and the highest value in the autumn and spring. Regarding the daily CO_2 variation it also observed that it is dominated by the photosynthesis.

The results of the atmospheric methane measurements show a signficant variation depending on the season and the urban aglomeration degree. Thus, the methane concentrations in the three investigated areas indicate a similar profile for the measurements carried out in the cities, with minima in the summer months and maxima during the spring. The highest values were recorded in the city of Cluj-Napoca (11.5 ppm in April 2009) and the lowest values were recorded in the month of August 2008 (2.5 ppm). In Turda the concentrations of atmospheric methane were comprised between 2.2 and 8.6 ppm, with the lowest values measured in August 2008 (2.2 ppm) and the highest values recorded in April 2009 (8.6 ppm) while in Huedin the concentrations of methane varied between 1.4 and 7 ppm, with the lowest values recorded in July 2008 (1.4 ppm) and the highest ones in April 2009 (7 ppm). Significant differences are also observed between te methane concentrations in the interior of the cities and the reference points located outside. These differences prove that the anthropic activities, in particular the automobile traffic, are an important source of methane in the urban atmosphere.

The carbon isotopic composition measurement of CO_2 and CH_4 is the best way to establish the biogenic and anthropic contribution at CO_2 and CH_4 budget in urban areas. Regarding the case study performed in three Romanian cities the results of $^{13}CO_2$ show that the value of $\delta^{13}C$ is depending on the size of the urban agglomeration. Thus, the lower value -11 ‰ were obtained for Cluj-Napoca, followed by Turda (-10.0‰) and Huedin (-9.0‰). If we consider $\delta^{13}C = -8‰$ the isotopic composition of natural CO_2, the anthropogenic contribution for CO_2 budget is higher for Cluj-Napoca and near the natural level for small town Huedin. More than, the recorded data show a difference of 0.5-1.5 ‰ between the measurements city points and reference points which suggests that the CO_2 source in the urban location is composed from the zone with $\delta^{13}C = -8‰$, with clean air, and an anthropic source which can be CO_2 resulted from burning fossil fuels (mainly gasoline and methane) plus a biogenic source of CO_2 resulted from the respiration of the local vegetation. The largest difference occurred in the municipality of Cluj-Napoca (1.376), where the average values of $\delta^{13}C = -10.266‰$ were obtained in the city center, compared with the $\delta^{13}C = -8.890‰$ for the reference point. For the other locations studied (Turda and Huedin) the isotopic concentrations are close to the atmospheric background, namely -9,291‰ for Turda and -8,895‰ for Huedin, comparable with the average values for the reference points (-8.874 for Turda and -8.327 and Huedin).

Regarding the $^{13}CH_4$ measurements the results obtained in the case study are above - 40 ‰ which suggests that there is an anthropic source of CH_4 in all investigated areas. We think that these values are a consequence of methane resulted from gas fuel network of the urbane investigated areas.

Regarding the correlation between CO_2 variation in urban area and variation of meteorological parameters the results of the case study indicate a direct correlation of CO_2 level with temperature and an inverse correlation with the wind velocity and relative humidity. Although, these correlations are poor and the analysis of regression coefficients showed that only the air temperature is correlated with the CO_2 concentration over the 0.6 threshold. The 0.6 threshold of the correlation coefficient was overfull filed in the three months of winter, at the end of spring and beginning of the summer, in May and June. The lowest value of the correlation coefficient was observed in August when the measurements were made at high temperatures, over 30 degrees Celsius. Large values, above 0.8 were observed in January and May. The air humidity and the wind velocity have very low regression coefficients, suggesting that in the urban areas studied, there is a low probability that the variation of the CO_2 is influenced by these meteorological factors. Thus, for the relative humidity the highest regression coefficient was 0.52, for the type polynomial in June 2009 while for the wind velocity the largest coefficient was 0.56 in May 2009, for the linear regression.

Taking into account the results obtained, the present case study shows that the variation of CO_2 in urban area is in agreement with other results reported in the scientific literature. Thus, according to the carbon isotopic composition measurements of CO_2 the anthropogenic CO_2 emissions are the primary source of the urban CO_2 dome; the dome is generally stronger in city centers, in winter, under conditions of heavy traffic, with little or no wind, and in the presence of strong temperature inversions.

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9. References

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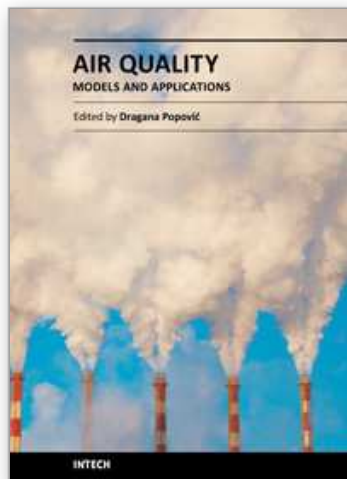
Air Quality-Models and Applications

Edited by Prof. Dragana Popovic

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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