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Construction of Local Atmospheric CH_4 and CO_2 Balance in Heavily Polluted Urban Areas on the Example of Kraków City

by J.M. Nęcki[1], M. Zimnoch[2], J. Mirosław[2] and J.Lasa[1*]

[1] *Institute of Nuclear Physics, Al. Radzikowskiego 152, Kraków 31-342*
[2] *Institute of Physics and Nuclear Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, Kraków 30-059*

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The application of analytical methods of atmospheric chemistry for balancing of greenhouse gases on the area under strong anthropogenic impact is presented. Gas chromatography and mass spectrometry analysis performed in two places (Kraków city–laboratory, Kasprowy Wierch–mountain station) gives opportunity to resolve constructed model and observe contributions of different sources influence on the total CO_2 concentration. It was possible also to point large leakage of city gas network as dominant source of methane in Kraków region.

Przedstawiono możliwość wykorzystania technik analitycznych stosowanych w chemii atmosfery do ilościowego zbilansowania emisji gazów cieplarnianych na obszarach silnej antropopresji. Pomiary z użyciem chromatografu gazowego oraz spektrometru mas wykonywane w dwóch punktach (Kraków i Kasprowy Wierch) dają możliwość rozwiązania założonego przez model układu równań i obserwacji wkładu poszczególnych źródeł emisji do całkowitej zawartości dwutlenku węgla w powietrzu Krakowa. Autorzy wskazują na przecieki w miejskiej sieci gazowniczej Krakowa jako główne źródło metanu na terenie Krakowa.

Wide scale investigations of greenhouse gases balancing are very important aim of environmental physics and chemistry. While powerful economical decision about emission limitation should be supported by the precise national greenhouse gas bud-

* Corresponding author

get, the sources and sinks of the gases should be quantitatively described and distinguish between natural and anthropogenic origin.

Different isotopic composition of carbon and oxygen of atmospheric CO_2 and CH_4 with different origin gives the possibility of source strength calculation [1]. This paper illustrates empirical method of estimation of Kraków agglomeration influence on methane and carbon dioxide concentration.

Large amplitude of diurnal fluctuation of trace gases concentration reveals high density of their sources inside the city boundary and frequently occurring temperature inversion. Local balance of CO_2 and CH_4 was constructed based on concentration and stable isotope data from chromatographic and mass spectrometry measurements performed in Kraków. Parallel measurements on Kasprowy Wierch in Tatry mountains, were used as reference point characterising continental air masses without local influence.

EXPERIMENTAL

Kraków is large (~ 800 000 habitants) agglomeration town situated in a Vistula river valley. Because of its location, a high frequency of boundary layer temperature inversion is observed in the city. Consequently we should expect high diurnal changes of trace gases concentration in Kraków. The sampling site is located on the roof of the Faculty of Physics and Nuclear Techniques building on Reymonta 19 street. Surroundings border to the recreation and sports grounds, full of green belt without direct anthropogenic sources of CO_2. Collected samples in this place represent average values for this region.

A fully automated gas chromatograph Hewlett–Packard series 6890 was used for quasi continuous measurements of atmospheric CO_2 and CH_4 concentration. Gas chromatograph is equipped with flame ionisation detector, nickel catalyst (heated to the 400 °C) reducing CO_2 to methane, Porapak Q packed column and thermostated 5ml sample loop.

Chromatographic analysis was performed at 80 °C. Single analysis including sample and standard injection was repeated every 30 min. Very high accuracy standards used in measurements were prepared at the University of Heidelberg by dr. Ingeborg Levin. CH_4 concentration is expressed in NIST (NOAA) scale while CO_2 in X87 mole fraction scale.

Precision of chromatographic results range around 0.1 ppmv (CO_2) and 5ppbv (CH_4).

Every four hours spot samples were collected directly to the 1 l glass flasks. Two times a day also to the 60 l steel tanks. After extraction on cryogenic glass vacuum line pure CO_2 was analysed for isotopic composition ($\delta^{13}C$, $\delta^{18}O$). Methane was converted to CO_2 on the platinum catalyst (800 °C) and then separated cryogenically. Stable isotope analysis was performed by mass spectrometer Delta S (Finnigan Mat) with precision 0.1‰ for both isotope ratios.

Parallel to the measurement carried out in Kraków, a separate monitoring programme was launched in a new remote station at Kasprowy Wierch in the Tatry mountains. Because of its location (1985 m a.s.l., 300 m above the tree line), under some meteorological conditions the site has the characteristics of the clean air station, free from local effects. Another fully automated HP 5890 GC was used for trace gases concentrations investigation every 30 min. For the analysis of interesting gases gas chromatograph on Kasprowy Wierch station was constructed similarly to the Kraków GC, however different column was used (Porapak QS) to keep temperature of separation at 40 °C. Reproducibility of concentration measurements by HP 5890 GC is better than 0.08 ppmv for CO_2 and 4 ppbv for CH_4. Also here every four hours the air was collected in the glass flasks and with less frequency into steel tanks. After collection the air was transferred to the Kraków laboratory and analysed for isotopic composition of methane and carbon dioxide.

RESULTS AND DISCUSSION

Local CO_2 balance

Based on measurements from Kraków and Kasprowy Wierch we drew out a CO_2 budget for Kraków region. We used the data from diurnal concentration changes and isotopic composition in Kraków and Kasprowy Wierch as well as the isotopic composition of CO_2 coming directly from different emission sources. For the facilitation of calculation we establish as follows.

1. Atmospheric CO_2 measured in Kraków contain components from background, biogenic origin and coming from the combustion of fossil fuels. Mass balance is described:

$$c_{tot} = c_{bg} + c_{bio} + c_{ant} \tag{1}$$

where: c_{tot} – concentration measured in Kraków, c_{bg} – continental background (may be compared with concentration measured at Kasprowy Wierch), c_{bio} – biospheric component of CO_2 in Kraków air, c_{ant} – CO_2 of anthropogenic origin.

2. Isotopic composition of individual component does not change in time and is introduced basing on measurements (for biogenic component $\delta^{18}O$ value changes reflecting variation of assimilation process and is taken from literature [2]). The $\delta^{13}C$ and $\delta^{18}O$ values, respectively –7.5 ‰ and –1 ‰ for background component are taken from Kasprowy Wierch measurements and for anthropogenic component values –29.1 ‰ and –17.2 ‰ are weighted averages from different fossil fuel combustion distribution in Kraków area (Fig. 1) [3].

Stable isotope composition of carbon and oxygen in CO_2 coming out directly from particular source was measured by [3]. Biogenic component composition approximates with –28 ‰ for $\delta^{13}C$ and from –10‰ to 10‰ for $\delta^{18}O$ during night and day respectively. Isotope balance for carbon and oxygen is described by equations 2 and 3.

$$c_{tot} \cdot \delta^{13}C_{tot} = c_{bg} \cdot \delta^{13}C_{bg} + c_{bio} \cdot \delta^{13}C_{bio} + c_{ant} \cdot \delta^{13}C_{ant} \tag{2}$$

$$c_{tot} \cdot \delta^{18}O_{tot} = c_{bg} \cdot \delta^{18}O_{bg} + c_{bio} \cdot \delta^{18}O_{bio} + c_{ant} \cdot \delta^{18}O_{ant} \tag{3}$$

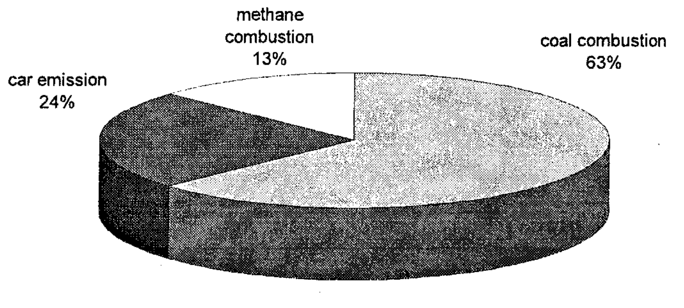

Figure1. Characteristic of CO_2 anthropogenic emission in Kraków area [3]

where index "tot" points values measured in Kraków, "bg" – values assumed using Kasprowy Wierch. Station measurements, "bio" – biospheric and "ant" anthropogenic component.

3. Sensitivity analysis proved high result dependence on background component isotopic composition. This fact implies possibility of application this method only to the short term changes of CO_2 (due to same mass circulation) using high quality stable isotope data [4].

Result of calculation based on the measurements performed in Kraków from 20 to 22 September 1994, during large biosphere activity and low anthropogenic emission (measurement campaign beside the heating season) are presented in Figure 2.

Especially interesting are the results of background component level. It is almost independent of time remaining on 353.5 ppmv, while average level of atmospheric CO_2 concentration in September on Kasprowy Wierch equals 352 ppmv [5]. It is surprisingly good agreement taking into account that we do not establish background concentration but only its isotopic composition. Figure 2 shows domination of biogenic component during the night time, when there is no photosynthesis reaction, only root respiration occurs. Temperature inversion limiting vertical mixing in atmosphere induces accumulation of trace gases from local emission sources. The soil CO_2 passes to the atmosphere mostly by the molecular diffusion processes and then, due to the turbulent diffusion, CO_2 concentration in inversion layer of atmosphere is equalised. Mixing volume of inversion layer is limited by its height usually placing at 300 m above the ground. If stable equilibrium occurs for longer time, trace gases concentration may reach extremely high values (CO_2 up to 700 ppmv, CH_4 up to 8 ppmv). During the day temperature inversion usually disappears, vertical mixing and photosynthesis reaction reduce amount of carbon dioxide in lower atmosphere. Biogenic component may even diminish background part in total CO_2 balance.

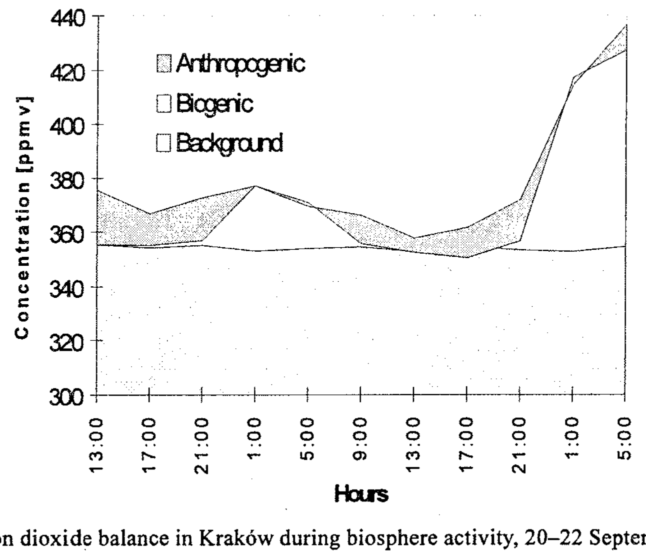

Figure2. Carbon dioxide balance in Kraków during biosphere activity, 20–22 September 1994

Anthropogenic component plays major role mostly during the day time, while industrial high emission is added to background level and car traffic is the most intensive. Contribution of this component ranges from 0 to 20 ppmv, what is confirmed by radiocarbon measurements in Kraków [6]. Different situation take place in the winter time, when anthropogenic component dominates during the day and night (Fig. 3). Temperature inversions in this season are longer and major CO2 source is ascribed to the house heating systems.

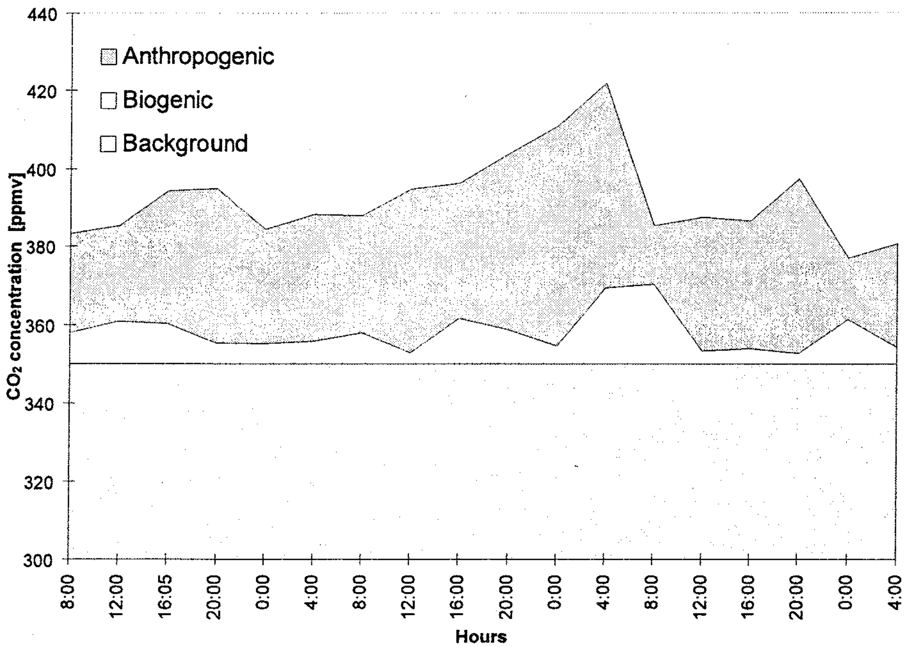

Figure3. Carbon dioxide balance in Kraków during heating season, 12–14 January 1995

Local CH_4 budget

In Kraków area CH_4 has not got any natural sources. Concentration of methane in the urban air has only one main component, city gas network leakage. Methane gets to the atmosphere independently of seasons and day time, so its emission occurs with the same intensity. Increase of methane concentration is observed during atmospheric stable equilibrium. Changes of CH_4 contents are parallel to CO_2 concentration fluctuations. A high correlation coefficient between changes of both gases (r^2=0.88) proofs their similarity as well as sources distributions. Because of low methane concentration in air (average concentration 1900 ppbv) for its isotope analysis it is necessary to use large air volume (60 l) and extraction of methane from air sample is time consuming. Therefore this measurements were done only twice a day, at 6 a.m. and 3 p.m., only when temperature inversion is observed. For methane budget calculation two component model was applied. As background parameters we can establish concentration and isotopic composition of CH_4 measured at Kasprowy Wierch [5]. A local budget of CH4 can be obtained using the equations:

$$c_{tot} = c_{bg} + c_{ant} \tag{4}$$

$$c_{tot} \cdot \delta^{13}C_{tot} = c_{bg} \cdot \delta^{13}C_{bg} + c_{ant} \cdot \delta^{13}C_{ant} \tag{5}$$

These equations let us calculate the average isotopic composition of anthropogenic methane source in Kraków. In years 1995–1996 we observed –54 ± 0.6 ‰. Isotopic composition of methane source we can also calculate without background parameters, based on correlation between $\delta^{13}C_{tot}$ and methane concentration reciprocal ($1/c_{tot}$) using equations (4) and (5). Result is reliable if there is strong correlation between both variables. For the described measurements the correlation coefficient was 0.85 (Fig.4). Isotopic composition of methane source received by this way (–53.3 ± 0.8 ‰) agrees with earlier calculated value.

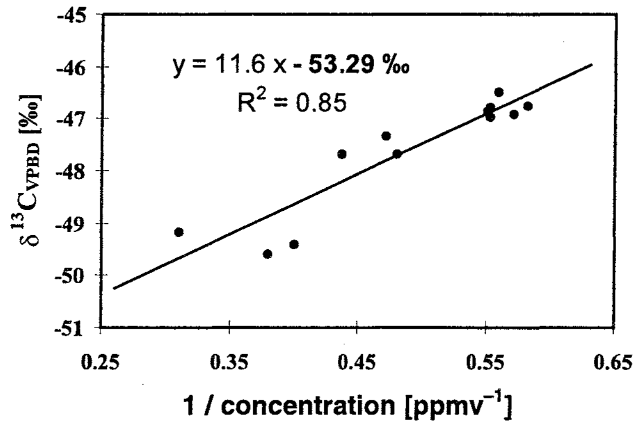

Figure 4. Correlation between carbon isotope composition of methane and reciprocal of its concentration for samples collected between March and October 1996

Based on measurement of methane isotopic composition from city gas network performed in 1995 and 1996 year average value of $\delta^{13}C$ for this gas oscillates around –54.4 ± 0.6 ‰ [7]. This agreement confirms rightness of model assumption. It shows that city gas network is the main methane source in Kraków. Contribution of this component might be obtained by difference between simultaneous measurement in Kraków and Kasprowy Wierch (equation 4). Average value of this component in concentration during temperature inversion in Kraków (*ca.* 12 h) is around 0.8 ppmv. Using effective height of inversion layer 150 m [5] and average part of Kraków area 25 km^2, methane emission from leakage rise up to $10^7 m^3 year^{-1}$. It is 5% of total consumption of methane in Kraków city. The highest uncertainty belongs to the "view area" of our measurements. Turbulent diffusion in town area during night time is taken from [8].

CONCLUSIONS

Parallel measurements of concentration and isotopic composition of atmospheric CO_2 and CH_4 allow to define contributions of anthropogenic and biogenic components of their concentration. Balances of both gases were created for Kraków based on measurement in town and remote station on Kasprowy Wierch. During the summer the biogenic component of CO_2 dominates while during the wintertime combustion of fossil fuels starts to play an important role in the budget of the atmospheric CO_2. Increase of methane concentration in night hours is connected with considerable city gas network leakage and often temperature inversion typical for Kraków.

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