

Stable isotope composition of carbon dioxide emitted from anthropogenic sources in the Kraków region, Southern Poland

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Abstract. The summary of the measurements of CO₂ stable isotopic composition emitted from different anthropogenic sources in the Kraków region is presented. The sources are divided into three main groups – high emission (electric and heat power plants), low emission (coal and methane burning in the households) and car traffic (gasoline, diesel and LPG supplied engines equipped and not equipped with catalyst). Presented results include two measurement campaigns made in the years 1995 and 2000. The measurements revealed three well-defined groups with respect to carbon isotope composition ($\delta^{13}\text{C}_{\text{VPDB}}$): $-30.60 \pm 0.37\text{‰}$ (car traffic) $-23.82 \pm 0.10\text{‰}$ (coal burning) and $-51.8 \pm 1.1\text{‰}$ (methane burning). The oxygen isotope composition ($\delta^{18}\text{O}_{\text{VPDB-CO}_2}$) of CO₂ varied in a broad range, from ca. -11‰ to ca. -22‰ , the most negative values being observed for coal and methane burning and the most positive for cars equipped with a catalyst. No significant isotopic shift has been observed between two measurement campaigns.

Key words: stable isotopes • carbon dioxide • anthropogenic sources • Kraków

Introduction

Attempts to quantify the role of urban areas in the global carbon budget have so far focused mainly on inventories of emissions originating from burning of fossil fuel and from cement production, complemented by the assessments of carbon sequestration based on urban biomass estimates [3]. In the case of Germany the emission inventories having hourly temporal resolution and high spatial (e.g. 1 km × 1 km) exists but in case of other countries like Poland, and other Eastern European countries the emission data based on inventories have a number of limitations in terms of their temporal and spatial resolution, and tend to rely on simplified assumptions linking specific activities to expected carbon dioxide fluxes. Thus, alternative ways of assessing carbon dioxide fluxes and their temporal and spatial variability for range of urban environments are needed.

Observations of atmospheric CO₂ mixing ratios alone are not sufficient to provide information on contribution of biogenic and fossil-fuel related sources of CO₂ to the atmosphere. Several methods have been employed to address this question. One of the most reliable methods are based on the isotopic composition of atmospheric CO₂. Isotopic investigations of atmospheric CO₂ can be particularly useful when studying

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the carbon cycle in heavily polluted urban areas, with high input of carbon dioxide from fossil fuel burning (heating, car traffic) and from industrial activities [6, 7]. The most adequate isotope in case of investigation the fossil fuel component contribution to the atmosphere is radiocarbon. Unfortunately, the ^{14}C measurements of small atmospheric samples are very expensive and thus not suitable for characterization of temporal and spatial variability with high resolution. Another possibility is utilization of stable isotope composition (^{13}C and ^{18}O). This approach is based on the three component mass balance equations assuming that the local atmospheric CO_2 near the ground level consists of three components: background representing the regional atmosphere, the local biogenic component representing decay of organic matter, root respiration and CO_2 uptake by photosynthesis and anthropogenic CO_2 emitted by cars, domestic heating and industrial emissions. Detailed description of this approach was published by [10, 11]. The method utilizing stable isotope composition of CO_2 for apportionment of biogenic and fossil-fuel related CO_2 sources in the urban environment requires input data on carbon and oxygen isotope composition of various sources of this gas [2, 10].

The primary aim of this study was to provide the data on carbon and oxygen isotope composition of major anthropogenic CO_2 sources in the Kraków region as well as qualitatively assess, if any long term trend of these values can be observed. The study was carried out in Kraków, a second largest city in Poland. With about 1 million inhabitants, heavy car traffic and significant industrial activities, it represents a typical urban environment. Coal, gas, and oil burned for heating and transport purposes generate the main flux of anthropogenic carbon dioxide within the region. In addition, because of prevailing western circulation, the exhaust gases from two big power plants (Skawina and Jaworzno) localised up to 60 km to the west of Kraków were measured.

Methodology

The samples were collected using a 1/8" diameter stainless steel tube connected directly to exhaust pipes of various CO_2 sources. The sampled exhaust gases were pumped through a drying trap filled with magnesium perchlorate and a 500 ml glass flask used as storage volume. Prior to sampling, the collection flasks were flushed with the exhaust gases for approximately 10 min. One pair of samples was collected for each type of CO_2 source. In the laboratory, the CO_2 was separated cryogenically from the collected exhaust gases. For the second campaign, a modification of mobile sampling device was introduced made it possible a sequential, *in situ* collection of several samples of exhaust gases (Fig. 1). The sampling device was placed in a plastic case providing more compact construction easier to handle in the field and enhanced two stage drying system consisting of the Nafion tube immersed in silicagel and of an additional trap filled with magnesium perchlorate. Two and three extractions using a small amount of collected exhaust gas (ca. 100 ml) from the flask were made for each collected sample in the case of the first and second

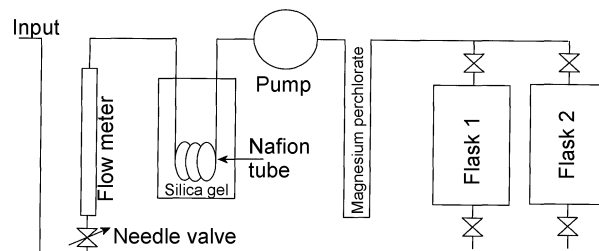


Fig. 1. Schematic diagram of a mobile sampling unit used to sample exhaust gases for stable isotope analyses of carbon dioxide. Removable glass flasks allow collection of several samples of exhaust gases during a single sampling campaign.

campaign respectively. The carbon and oxygen isotopic composition of CO_2 was then analysed using a Finnigan Delta-S mass spectrometer and expressed as relative deviations from the internationally accepted standard. The isotope results are reported on the VPDB- CO_2 scale [1]. Gaseous mixtures prepared from synthetic air and CO_2 of known isotopic composition were employed to test the extraction method for presence of systematic errors and to assess the overall uncertainty of the isotope analyses performed. The resulting uncertainty, including extraction and mass spectrometric analysis, turned out to be of the order of 0.08‰ and 0.07‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively [9].

Results

An investigation of isotopic composition of different urban anthropogenic CO_2 sources has been carried out during spring months of 1995 and summer months of 2000. The investigated CO_2 sources were classified into three categories: (i) cars of different make; (ii) domestic heating systems relying on coal and methane burning (low emission) and (iii) centralized heating systems relying on coal burning localised in Kraków and the surroundings (high emission). The first group was next subdivided with respect to the type of engine, presence of catalyst and the type of fuel used. The results of isotope analyses averaged by category for both campaigns are reported in Table 1.

The carbon isotope composition of CO_2 emitted by different types of sources investigated in the framework of this study turned out to be well defined. The data presented in Fig. 2 reveal three distinct groups of $\delta^{13}\text{C}$ values. The CO_2 emitted by cars is characterized by uniform $\delta^{13}\text{C}$ values, around $-30.60 \pm 0.37\text{‰}$, irrespectively of the type of engine. Slightly higher $\delta^{13}\text{C}$ values (around -29.1‰) were obtained for gasoline engines without catalyst. These cars are using the so-called universal fuel mixed with alcohol which is produced from corn or potatoes and is characterized by $\delta^{13}\text{C}$ values of around -25‰ . Spread of individual $\delta^{13}\text{C}$ data within the given group is distinctly smaller for diesel engines, when compared to cars supplied by LPG (liquefied petroleum gas) and gasoline. The CO_2 associated with burning of methane in domestic heating systems reveals very low $\delta^{13}\text{C}$ values ($-51.8 \pm 1.1\text{‰}$), while burning of coal in industrial plants supplying heat and electricity to the town and in households yields CO_2 with distinctly higher $\delta^{13}\text{C}$ values ($-23.82 \pm 0.10\text{‰}$).

Table 1. Mean carbon and oxygen isotope composition of the investigated sources of anthropogenic CO₂. The delta values represent mean values calculated from the set of samples collected from a specified source. Each number has assigned a standard deviation of mean value. LPG means liquefied petroleum gas

Type of source	1995			2000		
	Samples	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^{18}\text{C}_{\text{VPDB-CO}_2}$ (‰)	Samples	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	$\delta^{18}\text{C}_{\text{VPDB-CO}_2}$ (‰)
Diesel engines without catalyst	2	-30.36±0.03	-17.79±0.07	5	-30.95±0.06	-19.57±0.18
Gasoline engines without catalyst	4	-28.98±0.18	-16.74±0.19	5	-29.24±0.36	-16.33±0.45
Gasoline engines with catalyst				5	-31.06±0.13	-13.11±0.83
LPG engines without catalyst	4	-31.72±0.11	-17.48±0.06	2	-31.88±0.72	-19.82±0.70
LPG engines with catalyst				3	-30.64±0.28	-11.59±0.75
Low emission – methane burning	7	-52.86±0.17	-18.47±0.37	5	-50.72±0.28	-21.68±0.23
Low emission – coal burning	8	-24.01±0.07	-20.53±0.25			
High emission – coal burning	2	-23.67±0.18	-18.37±0.16	3	-23.80±0.03	-20.53±0.16

The $\delta^{13}\text{C}$ values of CO₂ associated with burning of coal and methane are similar to that measured directly for the respective fuels. Carbon isotopic composition of coal all over the world varies in a narrow range, between -22‰ and -25‰. The coal being mined in Poland is characterized by $\delta^{13}\text{C}$ values from -23.8±0.5‰ to -24.7±0.4‰ [4]. $\delta^{13}\text{C}$ values of methane reveal higher variability, depending on the origin (microbial or thermogenic). Direct, regular measurements of methane present in the city gas network of Kraków, carried out during the period 1995–1996, revealed rather homogeneous isotopic composition of carbon in methane with the mean $\delta^{13}\text{C}$ value equal to -54.42±0.16‰ [8]. A comparison of $\delta^{13}\text{C}$ values measured in 1995 and 2000 revealed no significant trend, but most of the values were slightly lower for the year 2000. The difference between the results from 1995 and 2000 is not statistically significant with one exception, i.e. for methane. In this case the difference is ca. 2.1‰ showing more positive value in the year 2000. One of the possible explanations which should be confirmed by direct measurements is the change in the contribution of methane originating from different stocks in the city gas network.

Oxygen in CO₂ originating from different anthropogenic sources of this gas stems predominantly from air. The isotopic composition of atmospheric oxygen is uniform with $\delta^{18}\text{O}$ value equal to +23.5±0.3‰ when reported on VSMOW scale [5]. When converted to VPDB-CO₂ scale, this value becomes -17.27‰.

The measured $\delta^{18}\text{O}$ values presented in Fig. 3 range from ca. -11‰ (LPG engines with catalyst) to ca. -22‰ (low emission – methane burning). Comparison of data obtained in 1995 and 2000 shows systematic small enrichment in ¹⁸O for 1995 measurements. One possible explanation is that during sampling campaign in 1995 a simpler drying system was used. This could lead to isotopic exchange between CO₂ and small amounts of water condensed on the walls causing shift in the obtained values. The application of enhanced drying system used during 2000 campaign eliminated this effect. The observed shift in oxygen-18 results is small comparing to the observed variability between different sources. In general, the measured $\delta^{18}\text{O}$ values for gasoline and LPG cars are much more variable than those observed for diesel cars. The mean $\delta^{18}\text{O}$ value for diesel cars is equal to ca. -19.1‰ (weighted mean value

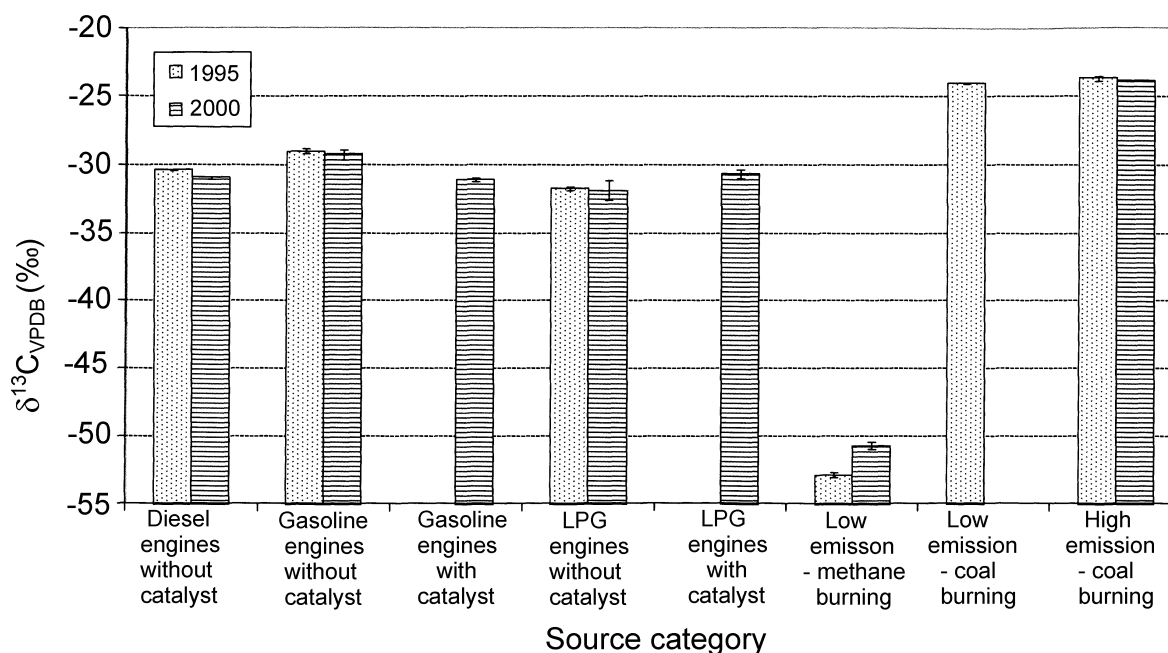


Fig. 2. Carbon isotope composition of CO₂ extracted from exhaust gases collected from different sources within the Kraków urban area.

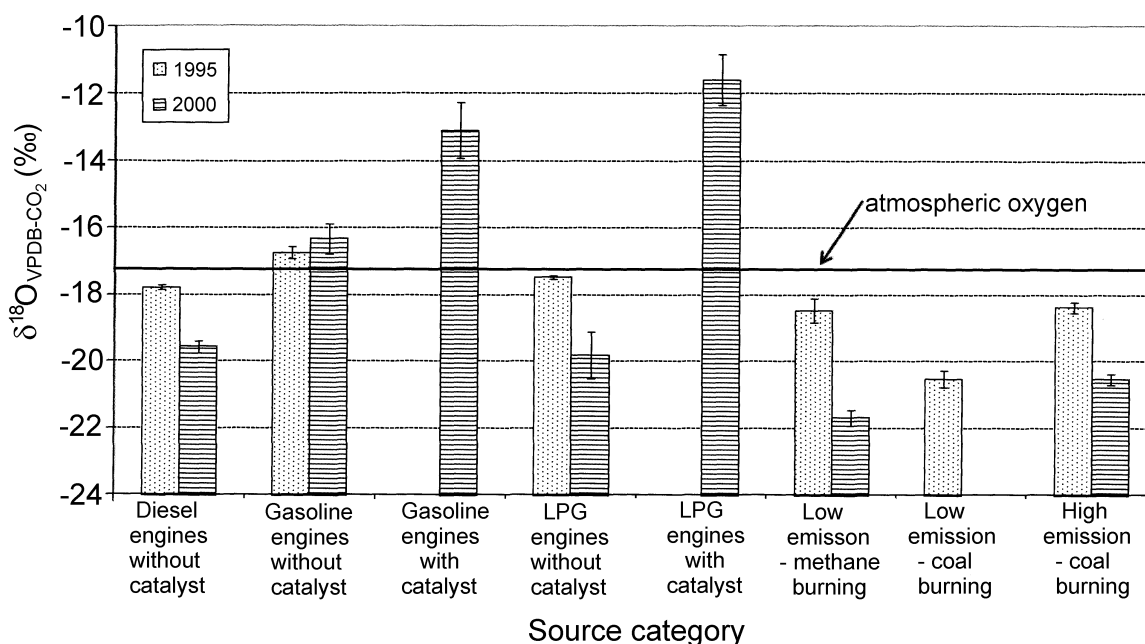


Fig. 3. Oxygen isotope composition of CO₂ extracted from exhaust gases collected from different sources within the Kraków urban area.

for 1995 and 2000 measurement) and is comparable with CO₂ emissions associated with methane burning (ca. -19.8‰), as well as with coal burning (-20.2‰). Similarity of the δ¹⁸O values and a relatively small spread of data suggest stable burning conditions in the presence of surplus of oxygen. In general, both more negative and less negative δ¹⁸O values are observed, when compared to the δ¹⁸O value of atmospheric oxygen reservoir. Carbon dioxide emitted by cars with catalyst is enriched in ¹⁸O when compared to atmospheric oxygen, while other sources are depleted in the ¹⁸O isotope.

Conclusions

The study aimed at providing background data and a long-term trend on carbon and oxygen isotope composition of CO₂ originating from various anthropogenic sources of carbon present in a typical urban environment revealed a substantial variability in both δ¹³C and δ¹⁸O values. Three distinct groups of δ¹³C values characterizing different sources of CO₂ have been identified: car traffic (around -30.6‰), emissions associated with burning of methane in domestic heating systems (around -51.8‰) and burning of coal in domestic heating systems and industrial plants supplying heat and electricity to the town (around -23.8‰). All these three sources contribute to the overall carbon budget in the urban atmosphere and modify the ¹³C isotope signature of free-air background carbon dioxide.

The oxygen isotope composition of CO₂ emitted from various anthropogenic urban sources also revealed a wide range of delta values, indicating that the emitted carbon dioxide can be enriched or depleted in ¹⁸O when compared to atmospheric oxygen reservoir. This depletion amounts up to 3‰, on the average, for CO₂ from coal and methane burning. Cars with catalyst yield CO₂ which has more variable δ¹⁸O values, being in general more enriched in ¹⁸O when compared to atmospheric oxygen.

A comparison of the measurements done in 1995 and 2000 shows no significant trend for carbon isotopes with one exception, i.e. for methane burning giving ca. 2‰ enrichment during the five year period. One possible explanation of this effect is a change in the contribution of methane originating from different stocks in the city gas network. In the case of oxygen isotopes in most cases a small depletion in oxygen-18 for 2000 measurements comparing to 1995 is observed but this effect is small comparing to the observed variability between different sources groups.

Based on the obtained data as input characterizing the isotopic composition of anthropogenic sources, one can use the isotope mass balance models for calculation of contribution of these sources to the atmospheric CO₂ in urban areas.

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