Introduction

Lower Silesia is a province in southwestern Poland located at the contact point of Polish, German, and Czech Republic borders. The presence of old and diverse geological structures makes this region rich in various natural resources, like copper ores, coal, brown coal, and mineral waters of proved healing properties. But simultaneously, the exploration and processing of natural resources, which are fundamental for the local economy, appeared to be – indirectly – the source of environmental deterioration. In the 1980s and ’90s the region, where the borders of Poland, Germany, and the Czech Republic adjoin, was called the “Black Triangle.” It was considered one of the most polluted regions in Europe because of numerous power plants without efficient gas cleaning techniques, wide open coal mining areas, and domestic heating based on brown coal. Since the early 1970s deforestation has been the major concern due to the extent and severity of the observed damage. Massive areas of forest suffered serious deterioration presenting strong visual symptoms of ecological damage [1, 2]. After the political changes great effort was made to reduce the emissions from the highest industrial companies. Permanent air monitoring carried out since 1997 proved the evident decrease of gaseous and particulate pollution [3, 4].

The overall results of our field studies in two health resorts located in the Polish part of the former “Black Triangle” region have been analyzed in this paper in relation to the background material and methods presented earlier. The main aim of this research was to determine the sources of PM10, SO2, NOx, CO2, and CO metabolites. The results of our field studies in the Czerniawa and Cieplice health resorts in Lower Silesia were presented in the last section of this paper.

The relationship between aerosol particle concentration and traffic intensity was quite clear. The present paper is a part of the research project which was financially supported by the Polish State Committee for Development of Science (KBN) under the project number 3 T0D 015 28.

Air Pollution Origins Using PM10 Data and CO2 Isotopic Analysis

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Abstract

PM10 concentrations (in relation to main gaseous pollutant levels and prevailing meteorological conditions) and carbon isotopic composition of atmospheric CO2 have been analysed in two health resorts in SW Poland (Cieplice and Czerniawa) to determine the main air pollution sources. In Cieplice, PM10 concentrations followed the variations in NO2 and CO, as well as SO2, suggesting traffic and domestic heating to be the main sources of aerosol particles. Conversely, in Czerniawa periodically pollutant rich air masses originating from regional sources contribute to increases in SO2 and NO2 levels, whereas the PM10 concentrations are at the background level. The analyzed δ13C(CO2) values reinforced the conclusions drawn on the basis of traditional methods and indicated the different impact of pollution sources between the investigated regions. Czerniawa was controlled by regional sources of CO2, whereas Cieplice was dominated by multiple local sources of pollutants (mainly traffic pollutants).

Keywords: PM10, SO2, NOx, episode, carbon isotope

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Triangle” area [5] indicated that the monthly average concentrations of SO$_2$, NO$_x$, and PM$_{10}$ (particulate matter diameter below 10 µm) have been decreasing since 1996, but episodically both local and regional influences are still evident. Air quality in these two health resorts has improved significantly compared to the 1990s. Nevertheless, pollution by PM$_{10}$ is believed to remain a concern.

Based on the above-mentioned survey, we have undertaken a more detailed evaluation of air pollution sources. We have analyzed PM$_{10}$ concentrations in relation to main gaseous pollutant levels and prevailing meteorological conditions. Moreover, we report the results of the atmospheric carbon dioxide analyses concerning its concentration and carbon isotopic signatures, comparing them with the above described investigations. The geochemical and isotopic analyses of CO$_2$ have been carried out as a part of complex investigations of atmospheric pollutants in that area [5, 6]. The major goals of our investigations presented here are:

(i) to indicate the processes that probably influence the pollutant concentrations and carbon isotopic composition of atmospheric CO$_2$;

(ii) to assess air quality in the investigated area.

Isotopic analyses enable tracing of the pollution origin. The total concentration and carbon isotopic composition of atmospheric carbon dioxide consists of background gases and additional inputs of anthropogenic and/or biogenic gases [7, 8]. The biogenic gases are derived from plant leaf respiration or from two pathways for production of CO$_2$ in soil. The biogenic isotopic fractionation factor depletes atmospheric CO$_2$ through absorption by terrestrial photosynthesis. This results in the shift of $\delta^{13}$C value of C3 plants from -16 to -20‰ and of C4 plants from -2 to -8‰ [9]. Therefore, the $\delta^{13}$C(CO$_2$) values derived from C3 plant respiration processes at night (biogenic gases) can reduce to -20‰ [10, 11]. Carbon dioxide produced in the inter soil processes can originate from two main sources: root respiration and decompnsition of organic matter by soil microorganisms [12]. The $\delta^{13}$C(CO$_2$) values originated from the first inter soil process reach values close to the whole plant respiration, i.e. ca. -20‰. On the contrary, the second inter soil process generates the CO$_2$ enriched in $^{13}$C [12]. In contrast, the $\delta^{13}$C(CO$_2$) values derived from burning fossil fuels (anthropogenic sources) obtained by Widory and Javoy [13] varied in the wide range from 40.5‰ (natural gas burning fumes) to -24.6‰ (coal burning fumes). In winter the photosynthesis input is almost negligible (non-vegetation period), hence the CO$_2$ is derived from anthropogenic sources (heating period) or soil respiration [14, 15]. Conversely, in summer season the anthropogenic input is negligible and the biological input is dominant [8]. Obviously, the natural system is more complicated; usually a combination of all the above processes can be observed [15]. Therefore, our winter observations, when biogenic input did not complicate the whole system, are the most useful in order to correctly access the processes controlling air quality in the region under study.

### Experimental Procedures

#### Study Area

Field sampling campaigns were performed in July 2006 and 2007, and in February 2007 and 2008 in order to represent two different seasons: summer and winter. Two sites were selected to represent health resort areas: Cieplice (50°54’N, 15°44’E, 330 m asl) and Czerniawa (50°54’N, 15°20’E, 645 m asl) situated in SW Poland (Lower Silesia region) in the Sudety Mts. Cieplice is part of Jelenia-Góra city (about 90,000 inhabitants), whereas Czerniawa (30 km west of Cieplice) is part of Świeradów (about 5,000 inhabitants). Świeradów health resort with the Spa House is situated 200 m below the Czerniawa site. Moreover, data from other two monitoring stations representing regional rural background: Wlen (51°00’N, 15°40’E, 303 m asl) and Jeleniow (51°13’N, 15°15’E, 244 m asl) were also used to compare the temporal and spatial variations in PM$_{10}$ concentrations in order to recognize the local and regional influences. The location of the sampling sites is shown in Fig. 1.

#### NO$_2$, O$_3$, CO, SO$_2$, and PM$_{10}$ Sampling

Methodology

Air quality data (NO$_x$, O$_3$, CO, SO$_2$, and PM$_{10}$) and meteorological parameters were obtained from the Voivodship Inspectorate for Environment Protection in Wroclaw (www.wroclaw.pios.gov.pl). PM$_{10}$ measurements were conducted with the Environment S.A. MP101M monitor (based on β-attenuation). Continuous trace gas measurements of NO$_x$ (NO and NO$_2$), SO$_2$, CO, and ozone were made using chemiluminescence for NO$_x$ (Environment S.A., Model 142M), UV fluorescence for SO$_2$ (Environment S.A., Model 22M), infrared gas filter correlation for CO (Environment S.A., Model 12M), and UV absorption (Environment S.A., Model 41M) for ozone, respectively.

Meteorological parameters measured during the period of field studies were wind speed and direction, temperature, relative humidity, pressure and solar radiation, which were obtained from an automatic station equipped with LSI-LASEM weather sensors and installed near the sampling point. The backward trajectories of the air masses were calculated by the HYSPLIT [16] model run by the U.S. National Oceanic and Atmospheric Administration (http://www.arl.noaa.gov/).

All data were quality-controlled in the data management network system operated by the Voivodship Inspectorate for Environment Protection in Wroclaw.

#### CO$_2$ Sampling Methodology

The atmospheric samples were collected using glass (July 2006 and February 2007) or steel (July 2007 and February 2008) 2-litre vacuum containers [17]. Each container was evacuated to about 10$^{-3}$ hPa in the laboratory before field usage. In each sampling action the flask stopcock was opened into the wind direction and the air was...
Fig. 1. Location of sampling points.

Fig. 2. Daily concentrations of PM$_{10}$ at the selected monitoring stations in July 2006 and 2007, and February 2007 and 2008.
sucked in. After filling, the flask was immediately closed and transported to the laboratory within a few days (max. 3 days) for further carbon isotopic analysis of atmospheric CO₂.

The atmospheric CO₂ concentration [ppm] and temperature [ºC] were measured using a Telaire 7001 portable instrument.

Carbon Isotopic Analysis

From air samples for carbon isotopic analyses CO₂ was obtained by cryogenic purification and collected in hermetic glass ampoules [10, 11, 18]. Carbon isotopic ratios were measured using the Finnigan Mat Delta E mass spectrometer (Laboratory of Isotope Geology and Geocology at University of Wroclaw, Poland). The standard uncertainty of the δ¹³C determination was less than 0.1‰. IAEA NBS-22 and USGS-24 standards were used as the carbon stable isotope standards. The additive correction of +0.22‰ was included for N₂O contribution in each final calculated δ¹³C(CO₂) value [19, 20].

Results and Discussion

General Weather Conditions during Field Studies

The summers of 2006 and 2007 (campaigns I and III) were characterized by sunny weather and high air temperature. In winter 2006/07 and 2007/08 (campaigns II and IV) the weather conditions were rather cloudy, with foggy and snowy episodes. However, days with the rebuilding baric field and the growth of Eastern European anticyclone with the centre over Ukraine were also observed. Air temperature in campaigns II and IV oscillated about 0ºC. Minimum daily air temperature was reported on 13 February 2008 in Czerniawa (-0.4ºC), while the maximum was 22 July 2006 in Cieplice (32.4ºC).

Spatial and Temporal Variations of PM₁₀ Data

Diurnal time series of PM₁₀ (particulate matter, diameter below 10 µm) concentrations registered in July 2006 and 2007, and February 2007 and 2008 in the selected air monitoring stations are shown in Fig. 2. For Czerniawa these results were available only for July 2006 and have not been measured afterwards. Therefore, data from the other air monitoring stations were used to show the spatial and temporal variations in PM₁₀ concentration and to see how comparable the sites are within the area under study. Clearly, there is a great similarity in temporal variations of the PM₁₀ concentration between the sites, although the data show that during both summer and winter the PM₁₀ concentrations in Cieplice are higher than those in the other sites. The daily EU PM₁₀ standard of 50 µg/m³ [21] was exceeded several times a month (allowing 35 days per year). However, the regional background of PM₁₀ levels registered in Wlen and Jeleniow was also very high during some episodes in winter. During wintertime, an extremely high PM₁₀ concentration (up to 175 µg/m³ in February 2007) was noticed in Cieplice, most likely due to the high load of local pollutants and local meteorology. During summertime, the PM₁₀ concentrations significantly decreased both in Cieplice (up to 50 µg/m³ in July 2006) and in Jeleniow and Wlen (up to 35 µg/m³ in July 2006).

Comparable temporal patterns in the PM₁₀ concentration for all sites can be explained as being strongly influenced by similar dust sources and/or similar meteorological characteristics of the area [22-24]. In order to understand these processes, we had to analyze the different trends of PM₁₀ levels, taking into account the gaseous pollutants and some meteorological factors. Figs. 3 and 4 show two examples of air pollution episodes registered in Cieplice and Czerniawa during the field studies. Similar patterns were also recorded in July 2007 and February 2008 (not presented here).

On 20-21 July 2006 (Fig. 3) high PM₁₀ (up to 55 µg/m³) and very high ozone concentrations (up to 180 µg/m³) were noticed in Cieplice, a result of which was most likely due to stagnant conditions with weak winds combined with high temperatures and high solar radiation. The region was in a low pressure gradient between two high pressure areas, one centred east of Poland (Ukraine) and the...
second west of Poland (the Alps). Large temperature differences occurred between day and night (up to 22ºC) in Cieplice, which indicated intensive cooling processes during the night. In general, the radiational cooling of the surface at night generates a temperature inversion. The magnitude of the inversion can be estimated based on simultaneous temperature measurements at stations located at different altitudes. The temperature difference (12ºC) between Czerniawa and Cieplice can be deduced from data in Fig. 3. These data confirmed a substantial inversion over the city that reduced air turbulence and led to a well-known accumulation of pollutants as observed in Cieplice. This process seems to be responsible for early morning (5:00-6:00 LT) and late evening (20:00-21:00 LT) CO and NO2 peaks, rather than rush hour traffic, which occurs later in the morning (8:00-9:00 LT) and earlier in the evening (17:00-18:00 LT). In addition to these local influences, regional pollutants sometimes can be recognized. The most prominent SO2 event took place (simultaneously in Czerniawa) on the morning of 21 July, when the SO2 levels reached 22 μg/m3, rising from 5 ug/m3. At the same time, NO2 (but not CO) concentrations noted a slight peak. Air masses contained more SO2 and NO2 but were not distinctly depleted in ozone. This episode was associated with trajectory from W-SW (Fig. 5), and most probably originated from lignite power plants located 30 km in that direction.

In Czerniawa the pollutants showed markedly different patterns. The variations in the ozone level proved that we dealt with different air masses in Cieplice and Czerniawa. At night, when temperature inversion occurred, the ozone concentration in the valley decreased more efficiently, but in Czerniawa (300 m higher) its concentration was still high. This behaviour indicates that Czerniawa (650 m asl) lies above the nocturnal boundary layer. The variations in the SO2 and PM10 concentrations over the 24-hour period show significant diurnal increases and decreases, which probably reflect the interplay between regional sources’ impact and daily evolution of the boundary layer. The confirmation of the impact from regional sources may be the simultaneous significant increase in SO2 and NO2 levels,

Fig. 4. Temporal variations of temperature and pollutant concentrations in Cieplice and Czerniawa (only SO2 and NO2) on February 18, 2007. All hours are in local time.

Fig. 5. Vertically modelled transport back-trajectories from (a) an altitude of 700 m asl (Czerniawa 650 m asl) ending at 18:00 UTC (+2 h – local time) 21 July 2006 and (b) an altitude of 330 m asl (Cieplice) ending at 00:00 UTC (+1 h – local time) 19 February 2007.
more evident on 21 July than 20 July. On 20 July air masses arrived from southern directions (Fig. 5a, the trajectory 06am07/21), and the next day from western directions. High SO₂ values were observed at both Czerniawa and Cieplice associated with winds from the west, where the lignite power plant is situated, being the main source of gaseous pollutants in that area.

Fig. 4 shows data for 18 February 2007, which gives an example of a local-emission-dominated winter-pollution episode with high concentration of PM₁₀ (up to 117 μg/m³) and both traffic-generated pollutants (NO₂, CO) and wintertime central heating (SO₂). An area of high pressure was centered over the Ukraine, leading to very low pressure gradients and low surface winds. The continuous process of sinking observed on February 18 (Fig. 5b) was attributed to the existence of large-scale anticyclonic subsidence. Because of the lower ventilation factor (mixing layer height (MLH) and wind velocity – weak air flow and a shallow mixing depth (MD)) the measured concentrations of all components were very high in Cieplice, most probably due to accumulation of local pollutants. On the contrary, we dealt with different air masses in Czerniawa, where regional SO₂ and NO₂ background concentrations have been noted.

Concentration and Carbon Isotopic Composition of Atmospheric CO₂

The obtained CO₂ concentration and carbon isotopic signatures of carbon dioxide (δ¹³C(CO₂) values) show a seasonal variability (Fig. 6). Minimum value in atmospheric CO₂ concentration was noted on 13 February 2008 in Czerniawa (349 ppm) and a maximum on 17 July 2007 in Cieplice (566 ppm). Minimum δ¹³C(CO₂) values were noted on 17 February 2007 in Cieplice (-11.51‰) and maximum in July 2006 in Cieplice (-9.12‰). The concentration and δ¹³C(CO₂) values reported in this study are similar to those reported by other authors for southern Poland [7, 25-27].

The observation of the concentration and δ¹³C(CO₂) values are summarized in Fig. 6. The data of CO₂ concentration and δ¹³C(CO₂) values measured at Czerniawa in summer season (Fig. 6) reach similar values in both summer periods (2006 and 2007). In contrast, the data of CO₂ concentration and δ¹³C(CO₂) values measured at Cieplice in summer 2007 show higher CO₂ concentration and lower δ¹³C(CO₂) values than those obtained in summer 2006. Probably, we observed a larger input of air masses characterized by more anthropogenic character [8, 13] in summer 2007 in Cieplice. These theoretical considerations are confirmed by episodes and air mass trajectory observations for the summer period, which have indicated the regional sources (mainly lignite power plant) as the major impact controlling air quality in the region.

The δ¹³C(CO₂) values obtained at Czerniawa in winter (Fig. 6) are characterized by similar values in both 2007 and 2008. This suggests the same level of anthropogenic impact (biogenic is negligible in non-vegetative season) in both years. However, the winter data of CO₂ concentrations measured in Czerniawa show a radical decrease in CO₂ concentration (about 100 ppm) in 2008. The very similar carbon isotopic composition of CO₂ in both years, and the contemporary decrease of CO₂ concentration indicate a substitution of one anthropogenic source by another during the 2-year observations. In contrast, the data of CO₂ concentrations measured in Cieplice in winter (Fig. 6) suggest the improvement of air quality between 2007 and 2008. This hypothesis can be tested more precisely by the simultaneous analysis of concentrations and carbon isotopic composition of CO₂. For the sample at Cieplice the lower CO₂ concentration (about 100 ppm) in 2008 is associated with higher δ¹³C(CO₂) values (about 1.5‰). We postulate that it is caused by lower anthropogenic impact concerning the fuels (coal and wood) burning contribution in the total balance of CO₂. These theoretical considerations are confirmed by episodes and air mass trajectory observation for the winter period, which indicate the regional background...
sources influencing air quality in Czerniawa, whereas the air quality in Cieplice is controlled by local pollutants (central heating and traffic). Therefore, the obtained data of concentration and carbon isotopic composition of atmospheric CO₂ indicate the improvement of air quality only for Cieplice health resort during the 2-year monitoring period.

In order to better characterize the sampling environment and exclude accidental episodes, the average carbon isotopic signature of atmospheric carbon dioxide has been calculated. The arithmetic average values of all the samples obtained for each period are presented in Fig. 7.

The average carbon isotopic signatures for Czerniawa CO₂ samples most probably result from regional impacts (controlled by long-transport processes) and rather exclude the local influences. In contrast, the average isotopic composition of Cieplice samples has not indicated the clear seasonal repeatability (Fig. 7) that has been observed at Czerniawa. In our opinion, the irregular seasonal variations in Cieplice are caused by different mixing of local carbon dioxide sources and traffic pollutants in winter with occasional regional pollutant inputs in summer. The lack of typical seasonal variations suggests that the atmospheric pollution in Cieplice is governed mainly by local processes and the regional influences have minor influence on air quality. However, the average δ¹³C(CO₂) data have confirmed the earlier conclusions concerning the improvement of air quality in Cieplice between 2007 and 2008.

Conclusions

In summary up, the data obtained from analyses of concentration and isotopic composition of the atmospheric CO₂ with comparison to traditional monitored pollutants (PM₁₀, NOₓ, CO, SO₂, O₃) and meteorological conditions can provide comparable information about air quality.

The results about the seasonal data point out much higher PM₁₀ concentrations during the cold season than during the warm one, with the highest peaks observed at Cieplice in each sampling, exceeding the EU standards. Some meteorological (high pressure system, low winds, temperature inversion) and topographical (a relatively flat valley in Cieplice) factors were likely to be of significant importance during the episodes considered. In Cieplice the PM₁₀ concentrations followed the variations in NO₂ and CO in summer and in SO₂, NO₂, and CO in winter, suggesting that traffic could be the main source of aerosol particles in summer and domestic heating in winter. Conversely, Czerniawa was subjected to periodic pollutant-rich air originating from regional sources, which contributed to the increase in SO₂ and NO₂ levels, both in summer and winter months.

The data obtained from carbon isotopic analyses of CO₂ confirmed the different impact of pollution sources between the investigated regions. Czerniawa is mainly controlled by regional sources of CO₂. Conversely, Cieplice is dominated by multiple local sources of pollutants (mainly traffic pollutants). The seasonal characteristics of carbon dioxide pollutant indicate the improvement of air quality in Cieplice (in the 2-year monitoring period), and only a slight change of pollutants’ impact in Czerniawa.

Stable isotopic analyses applied in this study constitute an innovative tool for tracing atmospheric pollution origin. Here we have demonstrated, coupling stable isotopic analyses with traditional monitoring of air quality, that the information obtained using both methods is consistent and complementary.

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References


17. LONGINELLI A. AND SELMO E. Seasonal and diurnal variations of δ13C and concentration of atmospheric CO2 at Parma, Italy, Geol. Q. 49, (2), 127, 2005.