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IWONA GROMBIK*, MARCIN JACKOWICZ-KORCZYŃSKI*,***,
DANUTA LIMANÓWKA**, IRENEUSZ ŚLIWKA*

ADVECTION OF CFC POLLUTANTS IN KRAKÓW AREA

Gas chromatographic measurements of selected CFC (chlorofluorocarbons) in dense urbanized area of the city of Kraków conducted since July 1997 show a downward trend in the concentration of CFC11 (–3.1 ppt/year) and CFC12 (–1.0 ppt/year); however, the concentration of CFC113 is still increasing (+1.6 pp/year). Background concentration levels of CFC are subjected to seasonal variability with a distinct amplification in autumn–winter. In measurements, incidental events that testify to exceeding base-line pollution levels are recorded. In 2001, the highest number of such events was recorded, and in 2002 their number was significantly reduced. The inventory of advection events responsible for air pollution showed domination of the western air masses if the events occurred in 2000 and 2001. Currently, as in the year 2002, SW air mass advections are connected with CFC pollution occurring in Kraków.

1. INTRODUCTION

Chlorofluorocarbons (CFC) as stable anthropogenic compounds have a negative influence on the Earth stratospheric ozone layer and additionally increase the greenhouse-effect warming. Current atmospheric concentration of CFC is on the ppt level, but the analysis of air bubbles trapped in polar firn samples shows that before 1950 those compounds were not present in the Earth's environment [1]. This proves that CFC are of anthropogenic origin. The highest emission of CFC into the atmosphere was recorded in the seventies and eighties of the twentieth century [2].

In July 1997, the Laboratory of Environmental Physics (LEP) with financial support from the Polish State Committee for Scientific Research (project 3 T09B 120 08) began continuous measurements of air concentration of five halogenated compounds, i.e., CFC11, CFC113, $CHCl_3$, CH_3CCl_3 and CCl_4, and in October 1999 (project T7

* Laboratory of Environmental Physics, Institute of Nuclear Physics, Polish Academy of Sciences, Polish Academy of Sciences, Radzikowskiego 152, 31-342 Kraków, Poland.

** Regional Meteorology Department, Institute of Meteorology and Water Management (IMGW), Piota Borowego 14, 30-215 Kraków, Poland.

*** Corresponding author: mjkorcz@novell.ftj.agh.edu.pl

T09D 042 21) the measurements of CFC12 and SF_6 concentration were started [3]. Measurements are carried out with fully automated gas chromatographic system (GC) Fisons 8000 equipped with two electron capture detectors (ECD) working in a constant current mode [4]. Air samples sucked on the roof of the laboratory building are analyzed alternatively with gaseous standard sample in one-hour intervals. In routine measurements, the secondary standard sample is injected. Concentration of selected CFC in the secondary standard is determined using a primary standard calibrated by Scripps Institute of Oceanography, San Diego, U.S.A. [3]

Currently LEP is still conducting the above mentioned experiment in the city of Kraków, southern Poland, which is a unique event in this part of Europe.

2. DATA AND METHODS

The analysis is based on hourly CFC concentration records being collected for eight years of GC measurements (since 1997) and on synoptic circulation classification developed and described for the upper Vistula basin by NIEDŹWIEDŹ [5].

In this classification, for each day of the year, one of the 20 specified synoptic situations is assessed. According to Niedźwiedź in mesosynoptic scale the most important elements regulating weather conditions are as follows: the air mass advection direction or the lack of air mass advection and the type of the pressure system over the area of interest. Following that in Niedźwiedź's classification for both cyclonic and anticyclonic situations, eight advection types were determined (from eight main directions over the horizon) and four situations without advection related to air mass stagnation over the area of interest. Synoptic situations that do not fit into the 20 classes described above are to be included in the additional 21st class.

Table

The baseline and the cut off level coefficients for each of CFC measured in Kraków

Compound	b/b', ppt	a, ppt/year
CFC11*	270.1 / 297.1 ± 0.3	–3.1 ± 0.1
CFC12**	551.8 / 606.8 ± 0.6	–1.0 ± 0.1
CFC113*	80.9 / 101.1 ± 0.2	+1.6 ± 0.1

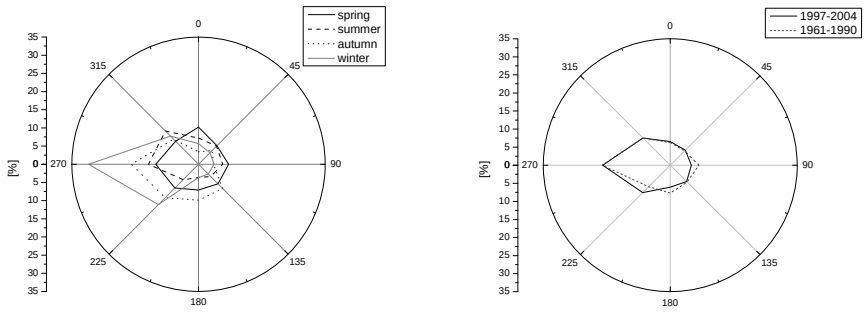
* Calculated for July 1st 1997.
** Calculated for October 8th 1999.

The inventory of advection events responsible for pollution is based on comparing the number of events characterized by the background CFC concentration exceeding permissible level in Krakow and the directions of air mass advection obtained from

Niedźwiedź's classification. Baseline levels of CFC concentration were calculated based on the weight linear regression for daily mean concentration values and their standard deviation ($y = ax + b$) [6] (see the table).

3. AIR MASS ADVECTION IN KRAKÓW IN 1997–2004

The analysis of synoptic charts for the period of 1997–2004 shows seasonal character of the air mass advection over the region of interest. In autumn (IX–XI) and winter (XII–II), a significant increase in western air mass advection was recorded. In spring (III–V) and summer (VI–VII), a homogeneous distribution of air mass advection was noticed (see figure 1a). The distribution of air mass advection over the Kraków area recorded for the years 1997–2004 is similar to that recorded for thirty-year period (1961–1990) (see figure 1b).



a) b)

Fig. 1. The distribution of air mass advection over Kraków in 1997–2004:
a) seasonal, b) against the background of thirty-year records in 1961–1990
(on the basis of NIEDŹWIEDŹ classification [5])

4. CLASSIFICATION METHOD OF POLLUTION EVENTS

Classification of the CFC pollution events is based on the cut off criterion. The cut off criterion was defined as a pollution level parallel to the pollution base-line calculated with the use of weight linear regression for daily average concentration and standard deviation of those values ($y = ax + b$). The cut off level position ($y = ax + b'$) compensates for natural variability characteristic of the place of measurement. The distance between the base-line and cut off level was calculated as a triple value of standard deviation σ of measurements recorded during the period when the least number of pollution events were observed. For the measurement conducted in Kraków this period lasted in summer (VI–VIII). The table shows weight linear regression coefficients (a, b, b') de-

scribing both base-line and cut off level for each of the CFC considered.

5. ANALYSIS OF ADVECTION EVENTS RESPONSIBLE FOR POLLUTION

The number of the events responsible for pollution each year recorded in Kraków increased significantly in 2000 and 2001. Since 2002 a decrease in the number of the events responsible for pollution and recorded yearly has been noticed for CFC11 and CFC12, but for CFC113 the number of these events began to stabilize at the level of ~500 events per year (see figure 2).

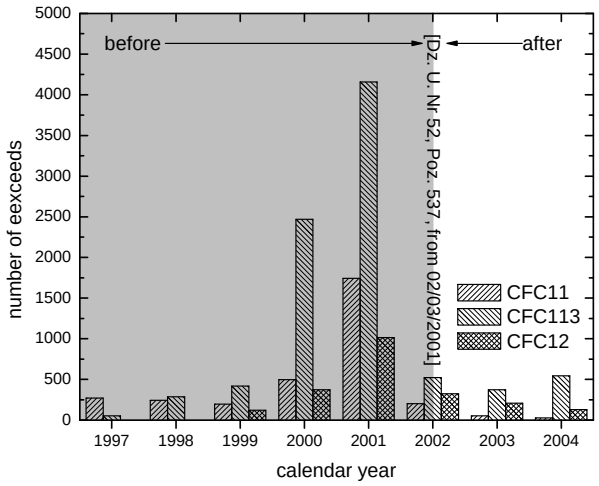
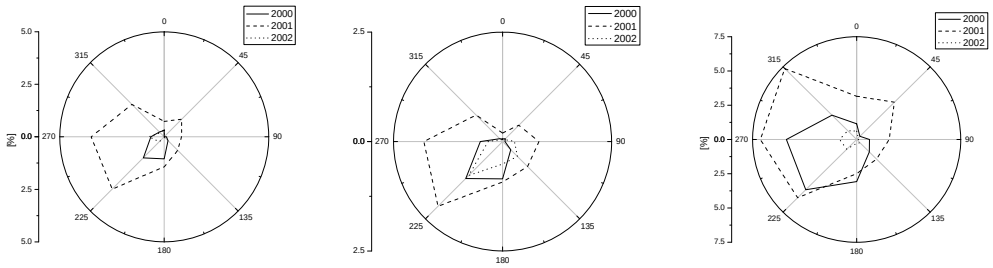


Fig. 2. The number of classified events responsible for pollution

Figure 3 shows the distribution of air mass advection recorded when a significant number of events associated with CFC pollutants occurred in Kraków (2000 and 2001). Such a distribution recorded in 2002 is also presented. The distributions presented are based on the types of advection of air masses described by NIEDŹWIEDŹ [5].



a) b) c)

Fig. 3. Distribution of advection events responsible for pollution in 2000, 2001 and 2002 for each of the CFC investigated: a) CFC11, b) CFC12, c) CFC113

6. CONCLUSIONS

Long-term GC measurements in urbanized area of the city of Kraków testify to a decreasing trend in the concentration changes for CFC11 (–3.1 ppt/year) and CFC12 (–1.0 ppt/year), but the concentration of CFC113 (+1.6 ppt/year) is still increasing.

The analysis of the classified events responsible for pollution shows that after a significant increase in CFC concentration exceeding the permissible levels recorded in 2000 and 2001, a successive reduction (CFC11 and CFC12) and stabilisation (CFC113) are observed. This was due to passing an effective law in Poland [7] which states how to deal with chemical compounds having negative influence on the Earth's ozone layer. The results obtained prove that since 2002 Poland has belonged to the World Community respecting the regulations defined by the Montreal Protocol.

The analysis of air mass advection accompanying the classified events responsible for exceeding the pollutant levels shows that during a strong release of CFC (years 200 and 2001), advections of western air masses prevailed, and after 2002 when a significant reduction in pollutant concentration was observed, SW directions were mostly related to those events.

A constant level of CFC113 pollutants and their still increasing atmospheric concentration indicate that active sources of CFC113 can be easily found in the area of Kraków.

ACKNOWLEDGEMENTS

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SEKTOROWA ANALIZA NAPŁYWU ZWIĄZKÓW CHLOROWCOWYCH DLA KRAKOWA

Prowadzone od 1997 r. ciągłe pomiary stężenia związków chlorowcowych wskazują, iż w zurbanizowanym obszarze Krakowa zwiększanie się stężeń CFC11 (–3,1 ppt/rok) oraz CFC12 (–1,0 ppt/rok) zostało zahamowane, nadal jednak obserwuje się wzrost stężenia CFC113 (+1,6 ppt/rok). Poziom rejestrowanych stężeń zmienia się sezonowo, a wyraźnie wzrasta w miesiącach jesienno-zimowych. Codzienne pomiary świadczą o incydentalnych przekroczeniach poziomu podstawowego mierzonych stężeń zanieczyszczeń, których ilość została wyraźnie zredukowana w 2002 r. Przeprowadzona sektorowa analiza napływu zanieczyszczeń CFC nad obszar Krakowa wskazuje, iż notowany w 2000–2001 r. wzrost ilości zanieczyszczeń był związany głównie z adwekcją z kierunków zachodnich.