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Variation of CFCs and SF_6 Concentration in Air of Urban Area, Kraków (Poland)

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Chlorofluorocarbons, both of natural and industrial origin, currently exist as trace gases in the entire human environment. The CFCs cause ozone depletion in the stratosphere. Moreover, CFCs and SF_6 take part in intensification of the greenhouse effect. On account of international agreements, the measurements of CFCs and SF_6 in air were started. Measurement stations of these gases were situated at places outside of urban areas influence and gathered on the world-wide program — AGAGE (Advanced Global Atmospheric Gases Experiment). One of these stations is Mace Head (Ireland, 53° N, 10° W), which participates in AGAGE since 1987 and in InGOS (Integrated non-CO_2 Greenhouse Gas Observing System) program since 2011. Similar research is also conducted in Central Europe, in urban area of Kraków (Poland, 50° N, 19° E) since 1997. This work discusses the results of concentration measurements (1997–2012) of selected halocarbons and SF_6 in Kraków. To obtain concentrations of the measured compounds the mathematical procedure has been used, where concentrations were calculated using a five points Lagrange interpolation method. Daily arithmetic means of the measured mixing ratios and their standard deviations were determined. Based on these data, efficiency of Montreal Protocol legislation, implemented in Poland could be assessed.

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1. Introduction

Atmospheric concentrations of chlorofluorocarbons (CFCs) are currently at the ppt level. They cause both loss of stratospheric ozone [1], revealing the presence of periodic "ozone hole" over the poles, as well as they contribute to intensification of the greenhouse effect. The analyzes of air trapped in ice cores retrieved in the polar regions clearly show that these compounds have mainly anthropogenic sources [2], and their highest emissions were recorded in the '70 and '80 of the last century [3]. The emission of these compounds to the atmosphere mainly comes from industry (solvents, refrigerants) and all kinds of products in which they are used as a carrier gas, e.g. aerosol containers [4, 5].

Concerns of a substantial part of the international community led to several agreements, from which the most important was the Montreal Protocol with its numerous amendments [6, 7]. This made it possible to bring about a gradual reduction and elimination of the production and emission of these compounds. This fact is reflected in the currently observed decline in global trends of atmospheric concentrations of CFCs compounds [1, 8]. In 2002, Poland became a member of the group of countries which fully respect all international agreements on the management of chemical compounds active in destruction of the Earth ozone layer. On the basis of Montreal Protocol the special law in Poland has been implemented in July 2002 (The Journal of Laws No. 52) under the name "The management of ozone-depleting substances". The document regulates production and use of these substances on the Polish territory [9].

Continuous measurements of atmospheric mixing ratios of trace compounds, such as: CFC11, CFC113, $CHCl_3$, CH_3CCl_3, CCl_4, SF_6 and CFC12 are conducted from July 1997, in an urban area of Cracow [10]. They reflect the impact of local, regional and global emissions of those gasses and atmospheric mixing patterns. Based on this, the influence of international protocols could be assessed.

This work mainly focuses on the analysis of seasonal changes in chlorofluorocarbons and SF_6 concentration over the area of Kraków. In addition, mathematical identification method of pollution incidents was employed.

2. Results

The CFCs and SF_6 analyses are performed with Fisons chromatograph series 8000. It is equipped with two measurement channels with ECD detectors working in a constant current mode. First channel is used to analyze CFC11, CFC113, $CHCl_3$, CH_3CCl_3 and CCl_4. In the second channel SF_6 and CFC12 is measured. The scheme of analytical setup and its description can be found in the work [10].

Daily quasi-continuous measurements of CFCs and SF_6 concentration in the air of Kraków, revealed short-term variability of the measured mixing ratios superimposed on the long-term trends. On the basis of long-term measurements conducted at first at AGH (University of Science and Technology) until 2005, and later in the IFJ PAN (Institute of Nuclear Physics, Polish Academy of Sciences) from 2005 till now, it was possible to determine the nature of the concentration changes. The concentrations of measured compounds were obtained by the mathematical procedure, the measured mixing ratios were calculated using five points Lagrange interpolation method. The concentrations of measured compounds were obtained by the mathematical procedure, the measured mixing ratios were calculated using five

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points Lagrange interpolation method. Using raw measurement data daily arithmetic means and their standard deviations were determined. Daily arithmetic averages and monthly weighted averages of the measured gases are shown in Fig. 1.

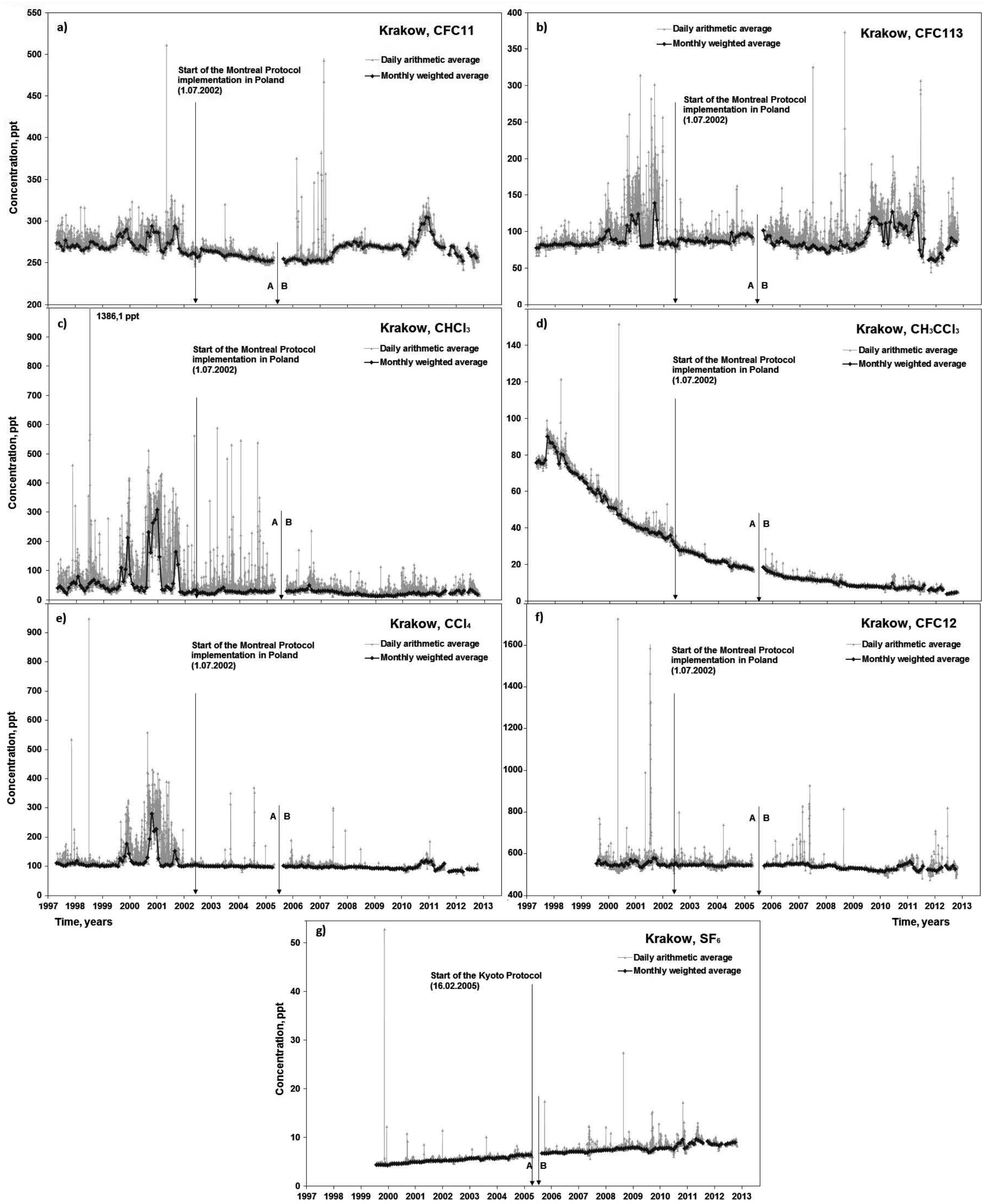

Fig. 1. Records of atmospheric mixing ratios of CFCs and SF_6 measured at AGH during the period 1997–2005 (A) and at IFJ PAN, Kraków during the period 2005–2012 (B).

The daily average data were filtered by the cut-off method. The method is based on determination of the weighted linear regression ($y = ax + b$), with width of the value of cut-off criterion. The cut-off criterion was designated as the five times average value of the standard deviation, which was calculated on the basis of the standard deviations of the daily measurements obtained in the months in which the measurement performance was equal or greater than 95%. Knowing the width of the baseline the number of exceedances could have been identified for all measured compounds in the atmosphere over Kraków during the period 1997–2012. The negative exceedances were not taken into account and were rejected. The results are presented in Fig. 2.

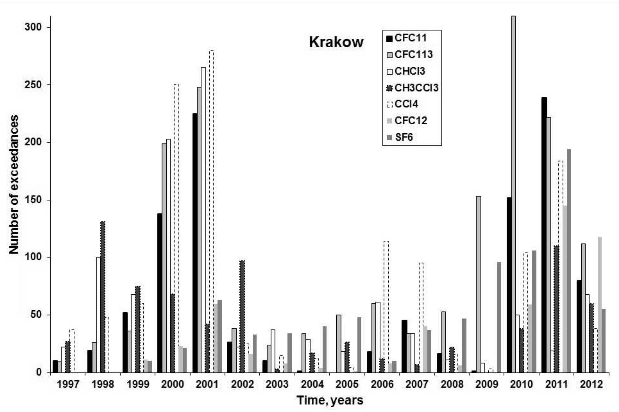

Fig. 2. Number of concentration exceedances of the analyzed compounds during the period 1997–2012.

By usage of weighted linear regression function the trend of baseline for the individual compounds was defined. The following values were obtained (growths rates after 2005): CFC11 (−2.8 ppt/year), CFC113 (−2.6 ppt/year), $CHCl_3$ (−1.3 ppt/year), CH_3CCl_3 (−1.5 ppt/year), CCl_4 (−1.8 ppt/year), CFC12 (−5.1 ppt/year) and SF_6 (+0.29 ppt/year).

3. Concluding remarks

Analysis of long-term trends of chlorofluorocarbons and SF_6 in the urban atmosphere of Kraków reveals general decline of CFCs levels and consistent increase of SF_6 concentration.

The measured mixing ratios vary seasonally; higher concentrations are generally recorded in autumn and winter. This may be due to the fact that in the area of Kraków, during autumn and winter, there is a large number of days with thermal inversion in the lower atmosphere, which can limit the vertical dispersion of pollutants.

Analysis of the number of exceedances leads to the conclusion that their appearance was significantly large before 2001 and then got lowered. Most likely, this can be connected with the entry into force of Polish law "The management of ozone-depleting substances" (1st of July, 2002). Unfortunately, from 2008 onwards an upward trend in number of exceedances is recorded. The reasons for this unexpected trend are unclear.

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References

[1] R.G. Prinn, R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R.H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Sturrock, P.M. Midgley, A. Mcculloch, *J. Geophys. Res.* **105**, D14, 17751 (2000).

[2] J.H. Butler, M. Battle, M.L. Bender, S.A. Montzka, A.D. Clark, E.S. Saltzman, C.M. Sucher, J.P. Severinghaus, J.W. Elkins, *Nature* **399**, 749 (1999).

[3] D. Qin, *Atmos. Environ.* **41**, 8424 (2007).

[4] B.M. Coldiron, *Dermatol. Surg.* **22**, 296 (1996).

[5] F. Zhang, L. Zhou, B. Yao, M.K. Vollmer, B.R. Greally, P.G. Simmonds, S. Reimann, F. Stordal, M. Maione, L. Xu, X. Zhang, *Atmos. Environ.* **44**, 4454 (2010).

[6] K.-H. Kim, Z.-H. Shon, H.T. Ngu, E.-C. Jeon, *Atmos. Environ.* **45**, 1369 (2011).

[7] N. Santella, D.T. Ho, P. Schlosse, E. Gottlieb, W.J. Munger, J.W. Elkins, G.S. Dutton, *Atmos. Environ.* **47**, 533 (2012).

[8] P.G. Simmonds, R.G. Derwent, A. McCulloch, S. O'Doherty, A. Gaudry, *Atmos. Environ.* **30**, 4041 (1996).

[9] *The Journal of Laws* No. 52, pos. 537 (2001), Poland.

[10] I. Śliwka, J. Lasa, J. Bielewski, D. Limanówka, *Polish J. Eviron. Stud.* **19**, 811 (2010).