Long-Term Measurements of CFCs and SF₆ Concentrations in Air

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Abstract

The influence of Montreal Protocol legislation accepted by Polish Authority (in 2002) on concentration halogenated compounds (CFCs) in the atmosphere was observed. We present measurements made on atmospheric concentrations of seven halogenated compounds (freons F-11, F-12, F-113, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, and sulphur hexafluoride) between 1997 and 2008 from the densely polluted urban area of Kraków. The trend coefficients are calculated for the mean daily data measurements obtained at the Kraków stations (50ºN, 20ºE) using weighted regression method. The concentration of F-11, chloroform, 1,1,1-trichloroethane, and F-12 has a tendency to decrease, whereas F-113, carbon tetrachloride, and sulphur hexafluoride tend to increase. The results of the trend coefficient calculations expressed in ppt/year are F-11, -3.2; F-113, +0.4; CHCl₃, -1.3; CH₃CCl₃, -3.5; CCl₄, +1.9; F-12, -0.6; and SF₆, +0.22. The result of the measurements, particularly after 1 July 2002, shows a decrease in concentration of the mentioned compounds. This suggests that the Montreal Protocol limitations of CFC emissions are respected in Central Europe, especially in Poland, where those limitations have been in place since July 2002.

Keywords: trace gases, chlorofluorocarbons, gas chromatography, ECD, long-term measurements in the urban area

Introduction

The concentration of chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆) in the atmosphere are at ppt level (ppt = 10⁻⁶ ppm). As radiatively active gases they influence the depletion of the Earth’s ozone layer and increase the greenhouse effect. The hypothesis about destruction of the Earth’s ozone layer by freons was introduced by Rowland and Molina in 1974 [1]. The potential possibility of the destruction of the Earth’s ozone layer by anthropogenic chlorofluorocarbons increased the anxiety of the international community enough to lead to greater protection of the natural environment. International cooperation caused from production and emissions to the atmosphere to become almost entirely discontinued (Montreal Protocol, 1987). In 1995 S. Rowland, M. Molina, and P. Crutzen received the Nobel Prize in chemistry for explaining the chemical processes that influence the ozone layer. This discovery prevented an ecological crisis with potentially catastrophic after-effects. Important historical facts concerning protection of the ozone layer are presented in Fig. 1. The decisions of the Vienna Convention (1985) and of the Montreal Protocol (1987) mandate a 50% reduction in the World’s emissions of CFCs between 1986 and 2004.
In addition, they also suggest a total reduction of CFC emissions to the atmosphere by the year 2030. The Advanced Global Atmospheric Gas Experiment (AGAGE) program measurements of global CFC concentration trends in the atmosphere indicate that the limitations of the world production of CFCs has resulted in a decrease of the atmospheric concentration of several investigated compounds [1]. However, measurements of sulphur hexafluoride (SF₆) concentrations in the atmosphere indicate that its concentration is still growing [2]. Available data indicate that there are significant pollution events in the vicinity of large urban areas [3]. A good fraction of these events are caused by the use of SF₆ by the electrical power industry in high-voltage gas-insulated switchgears (GISs) and transmission lines from where it leaks into the atmosphere. Since urban centers have high population densities and large cumulative demand for electricity, there are also more GISs in and near these areas and more sources delivering SF₆ to the atmosphere [3].

CFC and SF₆ measurements in the atmosphere are usually carried out at the so-called clean stations situated far from urban areas. Such a clean station in Europe is situated at Mace Head (Ireland) and has been participating in the AGAGE program since 1987 [4]. The reason for monitoring CFC pollutants at such places is that the global change in CFCs is independent of local emissions. It would, however, be interesting to compare these global concentration changes with their variations in urban areas [5]. In central Europe such measurements have been carried out in Kraków since 1997 [6]. Kraków is situated 100 km East of the highly polluted, industrial area of Silesia. Finally, these investigations can show whether the Montreal Protocol limitations are respected in this part of Europe, especially in Poland, where those limitations were implemented in July 2002 [7].

CFCs and SF₆ also are used in hydrogeology as tracers for age-dating of young groundwaters. Such measurements have been carried out in the UK’s two largest cities (London and Birmingham) and a smaller urban area, Bristol [8]. Furthermore, Kraków’s outpost is engaged in such investigations [9]. From this point of view, measurements of CFCs and SF₆ in the atmosphere are very important, because in urban environments with many CFCs, point sources uncertainties in the delivery of CFCs to groundwater complicate interpretation of observed CFC distributions [10].

**Experimental Procedures**

Measurements of the concentrations of seven halogenated compounds, i.e. freons F-11 (CFCl₃), F-12 (CF₂Cl₂), F-113 (CCl₂FCClF₂), chloroform (CHCl₃), 1,1,1-trichloroethane (CH₂ClC₂), carbon tetrachloride (CCl₄) and SF₆ have been carried out in the densely populated urban area of Kraków between 1997-2008. The measurement of the indicated compounds are conducted with a computer-controlled two-channel gas chromatograph (GC Fisons, type 8000) equipped with both channels and electron capture detectors (ECD) working in a constant current mode [11]. In each channel, two columns are used, working in a back flush system. In the first channel, where F-11, F-113, CHCl₃, CH₂ClC₂ and CCl₄ are analyzed, the stainless steel columns are filled in with 10% SP 2100, 80/100 mesh, 2 mm in diameter, 2- and 10-ft. long. In the second channel, where SF₆ and freon F-12 are analyzed, the stainless steel columns are filled with molecular sieve 5A, 80/100 mesh, 4 mm in diameter, 1- and 3-m long. The temperature of column operation is 55°C and the temperature of detectors in both channels is 300°C. The detection limit of the detectors calculated as double amplitude of noise level is: F-11, 1.2±0.7 ppb; F-113, 6.2±0.9 ppb; CHCl₃, 16.2±2.7 ppb; CH₂ClC₂, 6.7±0.9 ppb; CCl₄, 2.9±0.6 ppb; F-12, 5.7±2.6 ppb and; SF₆, 0.15±0.08 ppb.

The air samples are sucked from the roof of two different laboratory buildings Institute of Nuclear Physics. The air samples were dried in a Nafion tube. The unknown air sample and standard sample containing a known concentration of the indicated compounds were injected to GC alternatively every 30 minutes. The chromatograms of air and standard samples are registered by a ChemStation of the Hewlett Packard computer program. As a standard, a cylinder filled with air produced by LINDE Plc was used. This secondary standard was calibrated relative to the primary standard of the Scripps Oceanography Institute, San Diego, USA (SIO-1993 scale). Primary standard contained the following concentration of chlorofluorocarbons: F-11, 264.87±0.089 ppb; F-113, 83.43±0.152 ppb; CHCl₃, 17.24±0.441 ppb; CH₂ClC₂, 97.45±0.235 ppb; CCl₄, 97.78±0.176 ppb; F-12, 533.52±0.258 ppb; and SF₆, 3.942±0.019 ppb. During the measurements, nine cylinders filled with air as secondary standard were prepared.

**Results and Discussion**

A typical monthly record of temporary data measurements of the concentration of the CFCs in air samples is calculated from the registered area of each of the chromatographic peaks corresponding to the components of the sample and the standard. The concentrations of the compounds
were calculated using the five-point Lagrange’s interpolation method that allows determination of detector sensitivity at the moment of air sample analysis. The procedure significantly improves measurement accuracy [12]. From a temporary measurement data, the daily and monthly arithmetic mean concentration values and its standard deviations are calculated.

Figs. 2 to 8 depict daily mean values and monthly mean values (black line) for the concentration of F-11, F-113, CHCl₃, CH₃CCl₃, CCl₄, F-12, and SF₆ measured in Kraków (Poland). The data from Kraków presented in the figures are converted to the SIO-2005 scale [13]. The daily-calculated concentration data indicate that the sudden increase of the CFCs concentration appears against the usual background level of these concentrations. The greatest changes of the concentration, reported for F-113, CHCl₃, and CCl₄ (Figs. 3, 4, and 6), are probably related to the use of these solvents at dry-cleaning facilities. The incidental changes of CFC concentrations, mentioned above influence the mean monthly values of these concentrations as is seen in the figures.

Figs. 2-8 illustrate regression curves in the form y=a+bx calculated using the weighted regression method (dashed line), to estimate the tendency for changes in concentration of the fluorocarbons in Kraków. For approximation of CH₃CCl₃ and F-12 data the exponential function and quadratic function have been used, respectively. The yearly tendency in the concentration (b, ppt/year) can be calculated from the formula given by Taylor [14], as well as parameter (a, ppt) for the equation of the line for weighted linear regression. Table 1 shows the values of coefficient (b) in time period of July 1997 to May 2008 and parameter (a) calculated for 1 July 1997, when measurements were started. It can be seen clearly from Figs. 2-8 that the concentration of CFCs, measured in urban areas of Kraków, are characterized by seasonal variability. In the background of these changes four compounds – i.e. F-11, F-12, CHCl₃, and CH₃CCl₃ – have a tendency to decrease, but for F113, CCl₄ and SF₆ concentrations increased (Table 1). Compounds F113, CHCl₃, and CCl₄ are characterized by higher seasonal variability of concentration amplitude than the other compounds.
The increase of investigated compound concentrations is probably connected with the wind directions over Poland, i.e. with advection under Kraków air mass from the Western part of Poland or Europe, as presented in Fig. 9. Fig. 9 illustrates the frequency of air mass advection and wind frequency over the Kraków area. The observed concentration increases during the winter seasons indicate that they have origins outside the Kraków region.

Figs. 2-8 present an interesting diminishing frequency of the seasonal variability of CFC concentration amplitudes after 1 July 2002, when the Montreal Protocol legislation was implemented in Poland [7]. This suggests that the most observed CFC pollution events have been emitted from sources localized on Polish territory, because the wind and air mass movements (Fig. 9) still have the same statistical character in Kraków region, as before legislation implementation. In Fig. 9 the time period 1961-90 and 1997-2008 (black solid line) are compared. Observed diminishing seasonal variability of CFC concentration amplitudes suggest that CFC emission limitations posed by the Montreal Protocol are respected in Poland.

Conclusions

This paper presents a general view of environmental pollution of Kraków air by selected halocarbons, i.e. freons F-11 (CFCl3), F-12 (CF2Cl2), and F-113 (CCl3FCCIF2), chloroform (CHCl3), 1,1,1-trichlororoethane (CH3CCl3), carbon tetrachloride (CCl4), and SF6. In spite of the constant amendment of Kraków air quality, the state of the atmosphere needs new measurements for reducing pollutant emissions.

The chlorofluorocarbons emitted in Kraków are the result of the superposition of the concentration of these compounds typical for this part of Europe and local, incidental concentration fluctuations.

The measured concentrations of CFCs are characterized by seasonal variability. On the background of these changes, F-11, F-12, CHCl3, and CH3CCl3 have a tendency to decrease, whereas F-113, CCl4, and SF6 concentrations tend to increase (Table 1).

Particular attention should be given to new investigations as to the origin of CFCs from the West, because an increase of halocarbon concentrations in winter months correlates with air mass advection from this region.

The observed diminishing frequency of the seasonal variability of CFC concentration amplitudes after the date of 1 July 2002, when the Montreal Protocol legislation was implemented in Poland, suggest that the limitations of CFCs emissions in Poland are adhered to.

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Table 1. Yearly trend coefficient (b) from 07.1997 to 05.2008 and parameter (a) calculated in 1.07.1997 (using linear function y=a+bx).

<table>
<thead>
<tr>
<th>Station</th>
<th>Kraków, Poland (50ºN, 20ºE, 250 m above MSL)</th>
<th>Compound</th>
<th>b, ppt/year</th>
<th>a, ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-11</td>
<td>-3.2 ± 0.1</td>
<td>269.0 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-113</td>
<td>+ 0.4 ± 0.1</td>
<td>81.2 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl3</td>
<td>-1.3 ± 0.2</td>
<td>42.8 ± 0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH3CCl3*</td>
<td>-3.5 ± 0.2</td>
<td>35.8 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCl4</td>
<td>+1.9 ± 0.1</td>
<td>98.0 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-12*</td>
<td>-0.6 ± 0.1</td>
<td>546.5 ± 0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF6</td>
<td>+0.22 ± 0.01</td>
<td>4.04 ± 0.01</td>
<td></td>
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</tbody>
</table>

* (b) from the period 07.2002 to 05.2008 and (a) calculated in 1.07.2002.
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Fig. 9. a) Air mass advection frequency (%) in Kraków 1961-90 and 1997-2008. b) Wind frequency (%) in Kraków 1961-90 and 1997-2008.

References

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