

Long term measurements of the concentration of CFCs and SF₆ in air of urbanized area of Krakow

Ireneusz Śliwka



Department of Physicochemistry of Ecosystems

The Henryk Niewodniczanski Institute of Nuclear Physics

Polish Academy of Sciences (www.ifj.edu.pl)

Radzikowskiego Str. 152; PL-31342 Kraków





Schedule of the lecture

- ✓ Introduction
- ✓ Protection of the Earth ozone layer
- ✓ Halocarbons (CFCs) and greenhouse gases
- ✓ Montreal protocol
- ✓ CFCs investigations in Krakow
- ✓ Results of measurements in the years 1997-2007
- ✓ Conclusions



Introduction

The industrial activity of humane influence of the Earth chemical composition of atmosphere.

Chemical composition of atmosphere (trace gases) determine of the Earth surface temperature and quantities of solar UV radiation reach surface.

The observed phenomena are :

- **destruction of ozone layer in stratosphere**
- increase of the Earth temperature as a result of **intensification of greenhouse effect**



Composition of the Earth atmosphere

Compound	Concentration
	%
N ₂	78.08
O ₂	20.94
H₂O	variable 0 – 3.0
Ar	0.934
CO₂	0.0385
	ppm = 10⁻⁴%
Ne	18.2
He	5.24
CH₄	2.05
Kr	1.14
H ₂	0.55
N₂O	0.33
CO	0.12
	ppb = 10⁻⁷%
SO ₂	< 100
O₃	< 100
Xe	87
NO +NO ₂	< 10
C ₂ H ₆	< 5
other hydrocarbons (HC)	< 2
COS	0.5
	ppt = 10⁻¹⁰%
Halocarbons (CFCs)	< 500-1000
SF₆	6,1
SF₅CF₃	0.15
Perfluorocarbons (PFCs)	< 0.01



Protection of Earth's ozone layer

The main factor which evoke destruction of ozone layer in stratosphere (about 10ppm O₃) are chlorofluorocarbons (CFCs) i.e. Freons (**hypothesis of Rowland and Molina 1974**)

Freons are produced on industrial scale as refrigerants since 1930 and as aerosol spray propellants since 1965.



The chlorofluorocarbons (CFC`s)

Characteristics of selected CFCs (2002).

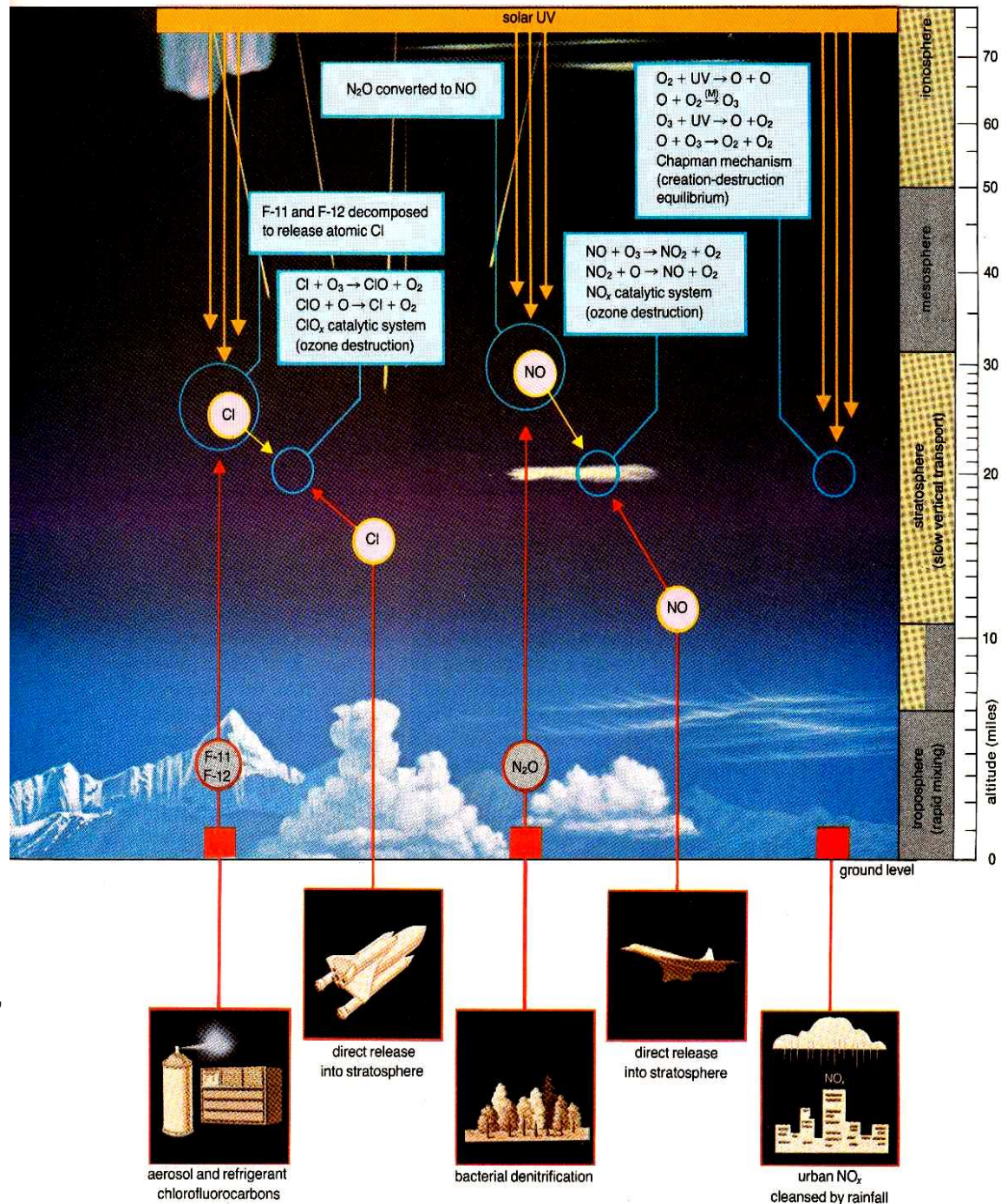
Compound	Concentration ppt	Production $\times 10^6$ kg/year	Lifetime years	ODP
F-11 (CCl₃F)	260	400	50	1
F-12 (CCl₂F₂)	560	460	120	1
F-13 (CF ₃ Cl)	15	10	400	0,1
F-22 (CHClF ₂)	50	206	12	0,05
F-113(CFCl₂CClF₂)	80	160	85	0,9
F-114(CClF ₂ CClF ₂)	13	24	200	0,8
F-115 (C ₂ ClF ₅)	15	15	400	0,2
F-116 (C ₂ F ₆)	3	5	500	0,1
CCl₄	100	830	35	1,2
H 1211 (CBrClF ₂)	3	10	25	3
H 1301 (CBrF ₃)	3,5	10	110	10



CFCs

The concentrations of chlorofluorocarbons (CFC`s) in the atmosphere are on the ppt level.

As radiatively active gases, they influence the depletion of the Earth's ozone layer and the increase of the greenhouse effect.

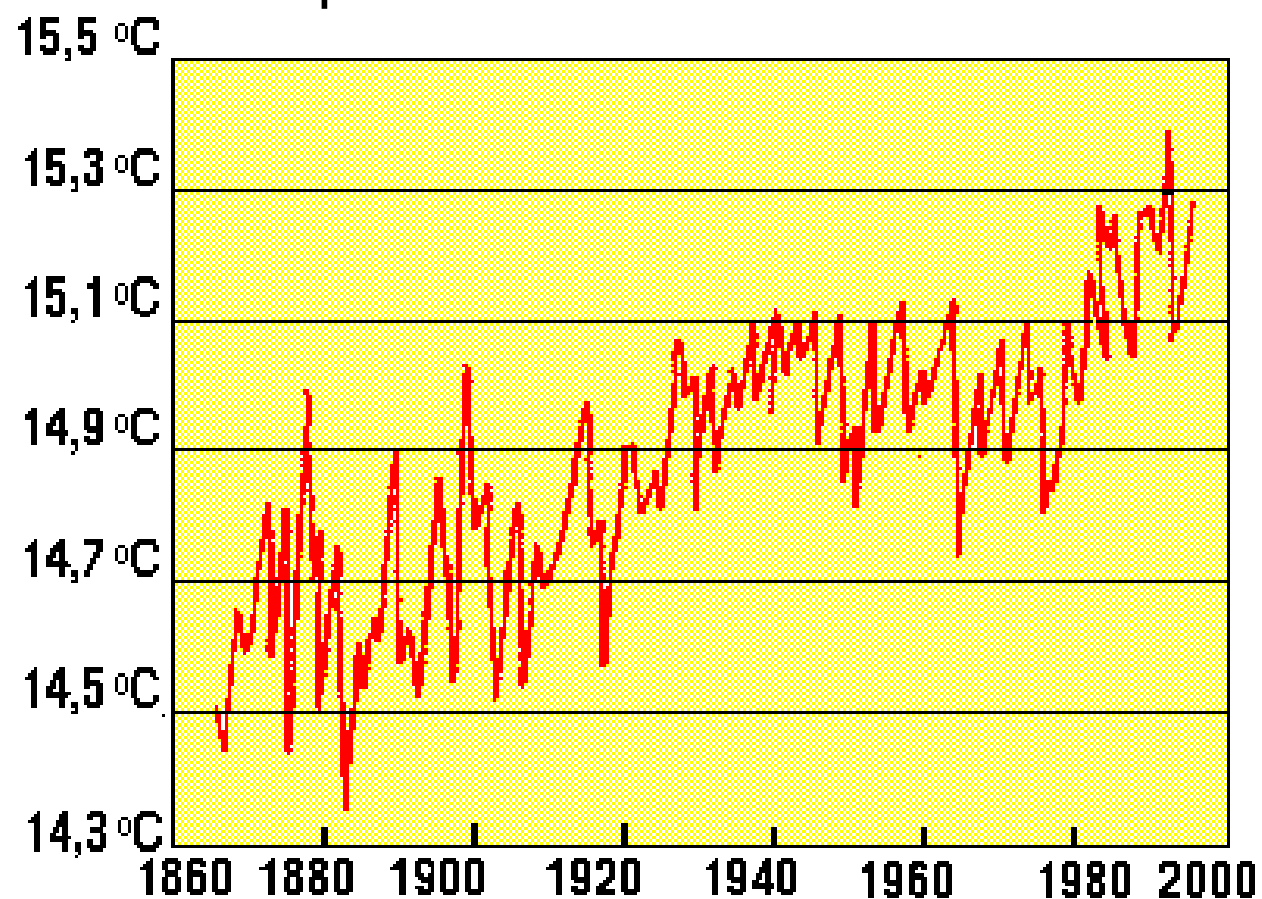


F.S. Rowland
Stratospheric Ozone: Earth's Fragile Shield
!979, Yearbook of Sciences and the Future,
Encyclopedia Britannica, Inc. p.170-191



The greenhouse effect

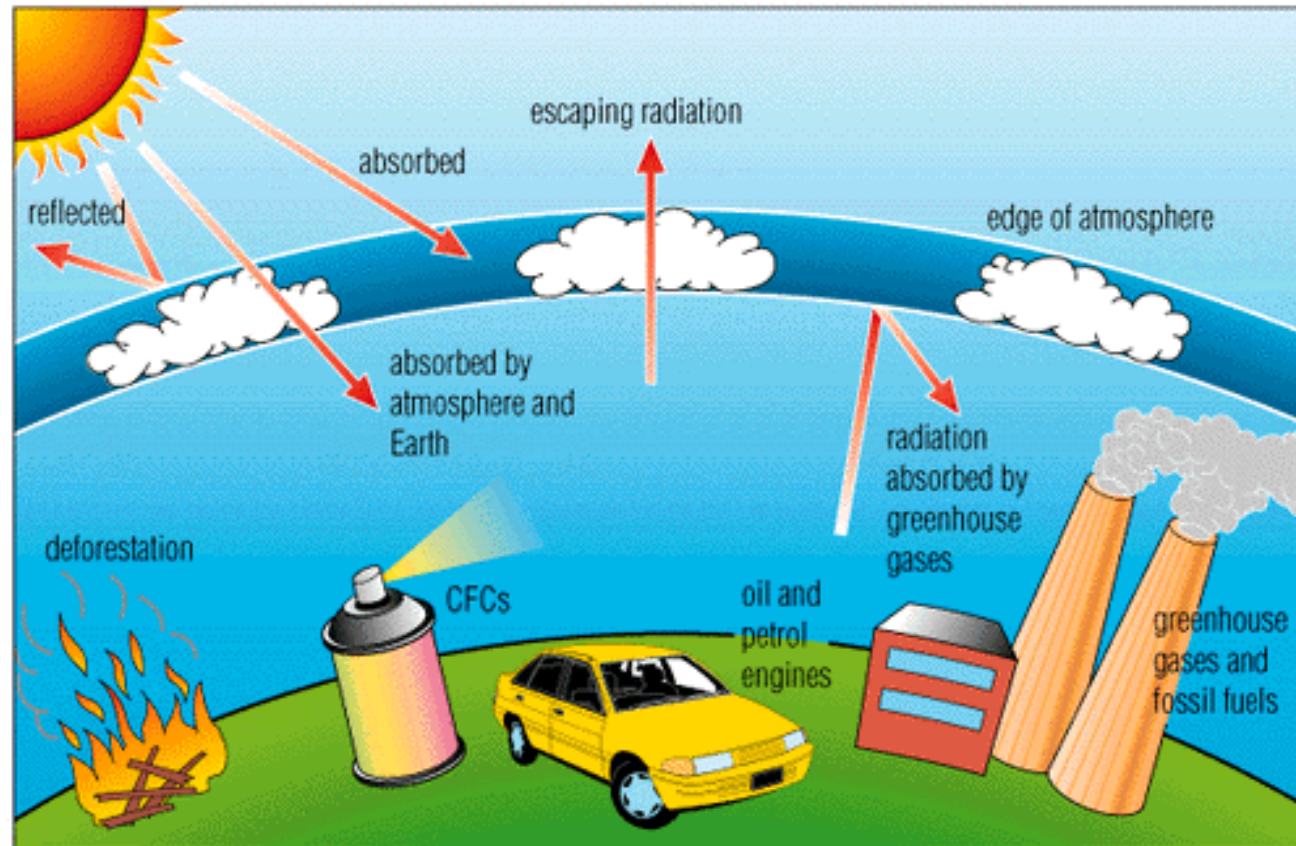
The observed growth of the mean Earth surface temperature since 1860 to 2000.





The greenhouse effect

<http://media.allrefer.com/s4/l/p0001164-greenhouse-effect.gif>





The greenhouse effect

Intensification of the greenhouse effect is connected with emissions of gases:

	share in %,	concentration
• water vapor (H_2O)	62	0,5 %
• carbon dioxide (CO_2),	22	370 ppm
• methane (CH_4),	2,5	2,0 ppm
• nitrous oxide (N_2O),	4	0,3 ppm
• ozone (O_3),	7	35 ppb
• halocarbons (CFCs),	2,5	1,0 ppb



The greenhouse effect

Greenhouse gases and their characteristics (2002).

Gas	Concentration before 1750	Concentration at present	Lifetime, years	GWP
CO ₂	280 ppm	372 ppm	120	1
CH ₄	730 ppb	1845 ppb	12	23
N ₂ O	270 ppb	317 ppb	115	300
O ₃	25 ppb	35 ppb	hours	
F-11	zero	260 ppt	50	4600
F-12	zero	550 ppt	120	10600
F-113	zero	80 ppt	85	6000
CCl₄	zero	100 ppt	35	1800
CH₃CCl₃	zero	45 ppt	5	140
F-22	zero	150 ppt	12	1700
F-23	zero	15 ppt	260	12000
C ₂ F ₆	zero	3 ppt	10000	11900
SF₆	zero	5,1 ppt	3200	22000
SF ₅ CF ₃	zero	0,12 ppt	3000	18000



The Montreal protocol (1987)

The Montreal protocol is an act of international law, which aim is reduction emissions of substances destructing ozone layer.

The present version of the Montreal protocol with amendments from London (1990), Copenhagen (1992), Montreal (1997), Peking (1999) include reduction emission of substances:

measurement by

- | | |
|-----------------------------------|-------|
| • 10 substances from CFCs group, | GC |
| • 3 halons, | GC-MS |
| • carbon tetrachloride, | GC |
| • 1,1,1-trichloroethane, | GC |
| • 20 substances from HBFCs group, | GC-MS |
| • 40 substances from HCFCs group, | GC-MS |



The Montreal protocol (1987)

Now into force is a next schedule of reduction :

- consumption of CFCs at 1996 – 2003, in yearly periods, should not be greater than in 1989 (100%).
- 35% reduction since 2004 r.,
- 65% reduction since 2010 r.,
- 90% reduction since 2015 r.,
- 99,5% reduction since 2020 r.,
- **total reduction since 2030 r.**



The world CFCs investigation program AGAGE

<http://agage.eas.gatech.edu/>

Advanced Global Atmospheric Gases Experiment

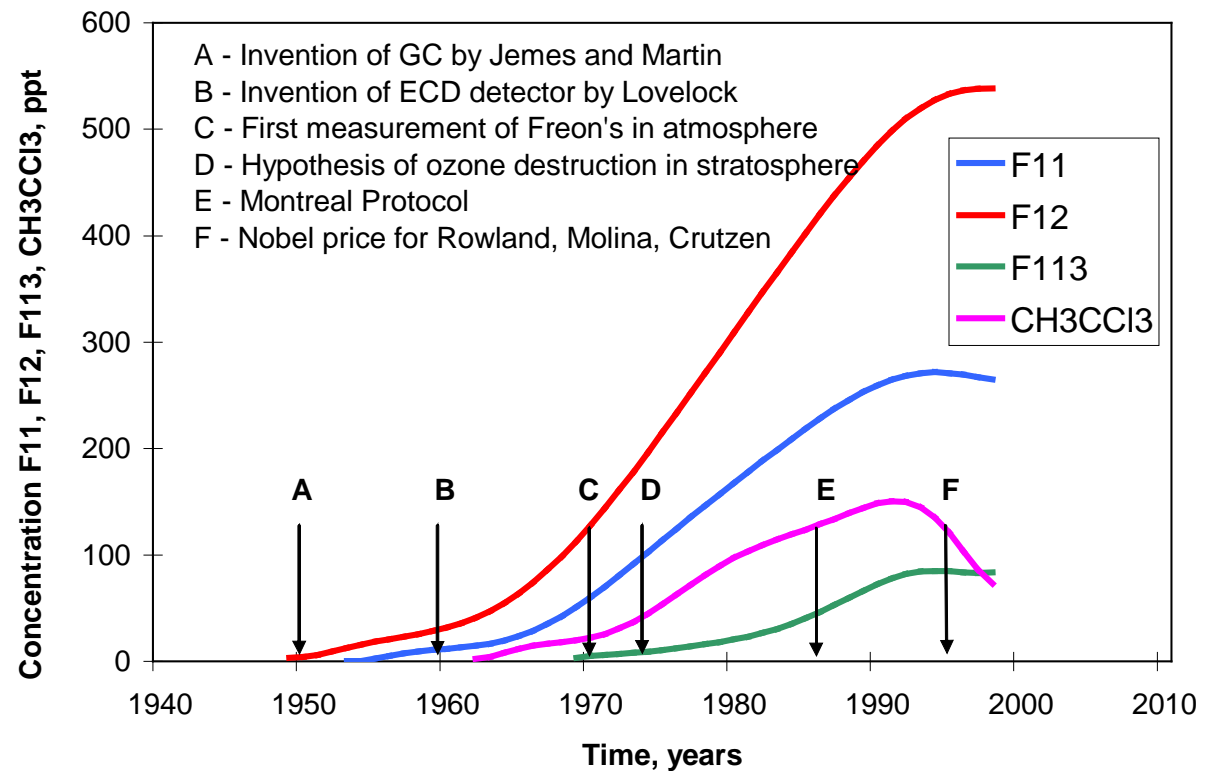




The results of measurements and historical facts

Concentrations of selected Freon's in atmosphere on the base of program AGAGE data (Advanced Global Atmospheric Gas Experiment).

Important historical facts concerning protection of ozone layer





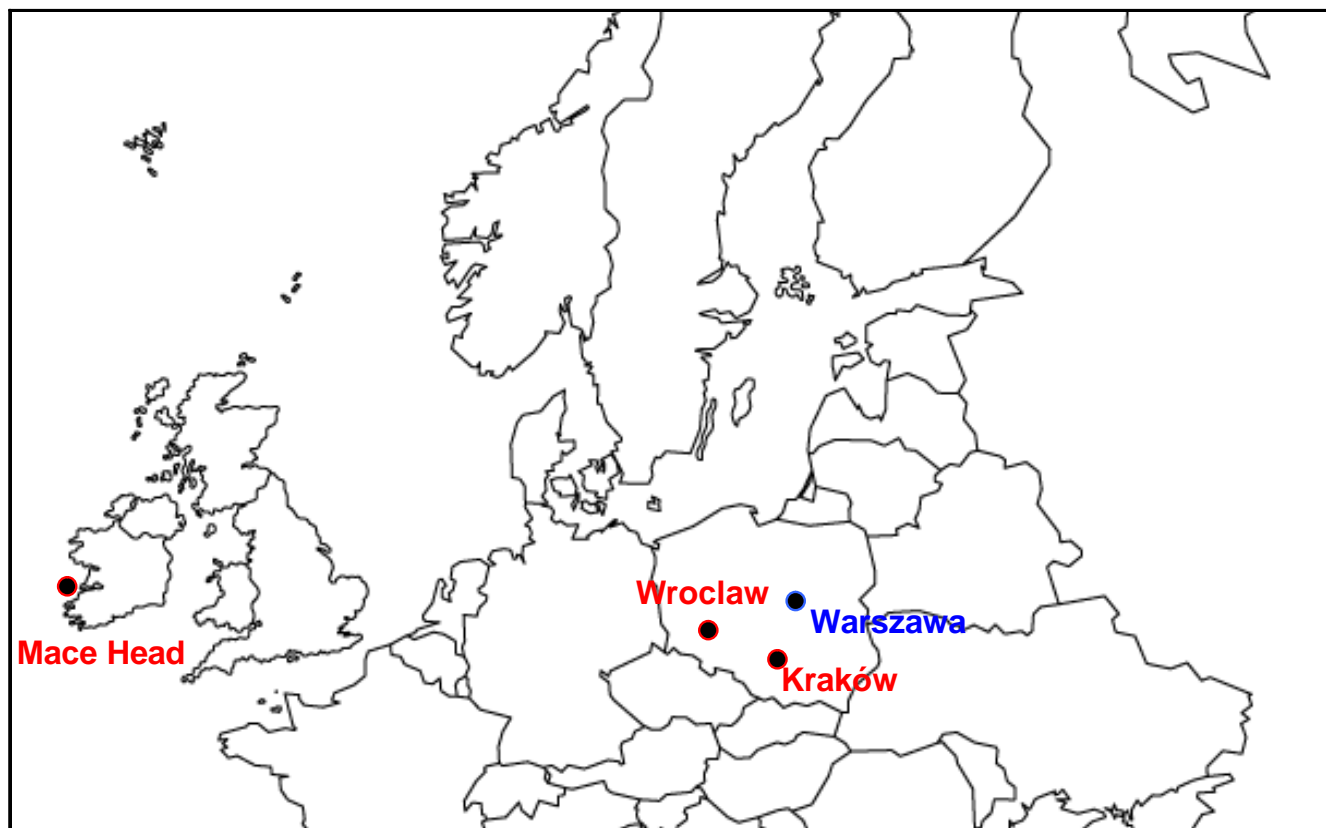
AGAGE

The investigations of the global trends of the concentration CFC`s in the atmosphere by Advanced Global Atmospheric Gas Experiment (AGAGE) program indicate that limitation of the world production of CFC`s by Montreal protocol agreement take effect in fall tendency of the concentration of several investigated compounds.



The investigations in Krakow

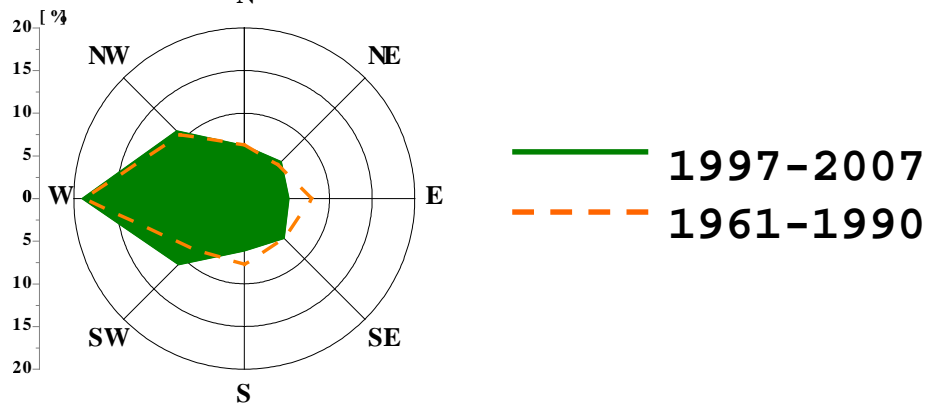
Location of Mace Head (53°N, 10°W) and Krakow (50°N, 20°E) in Europe



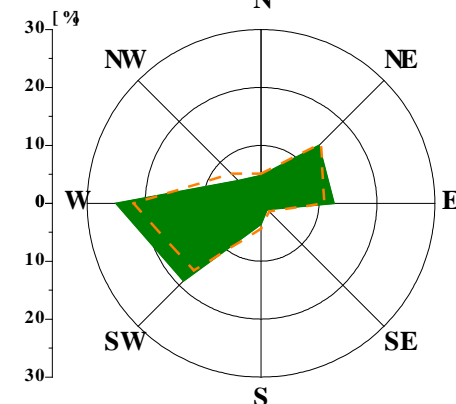


Meteorological data of Krakow

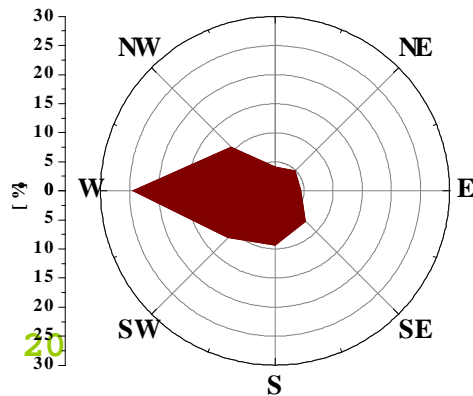
Advection frequency (%) of air mass



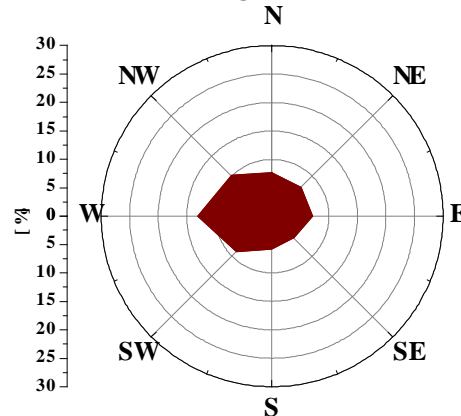
Wind frequency (%)



Autumn/Winter



Spring/Summer



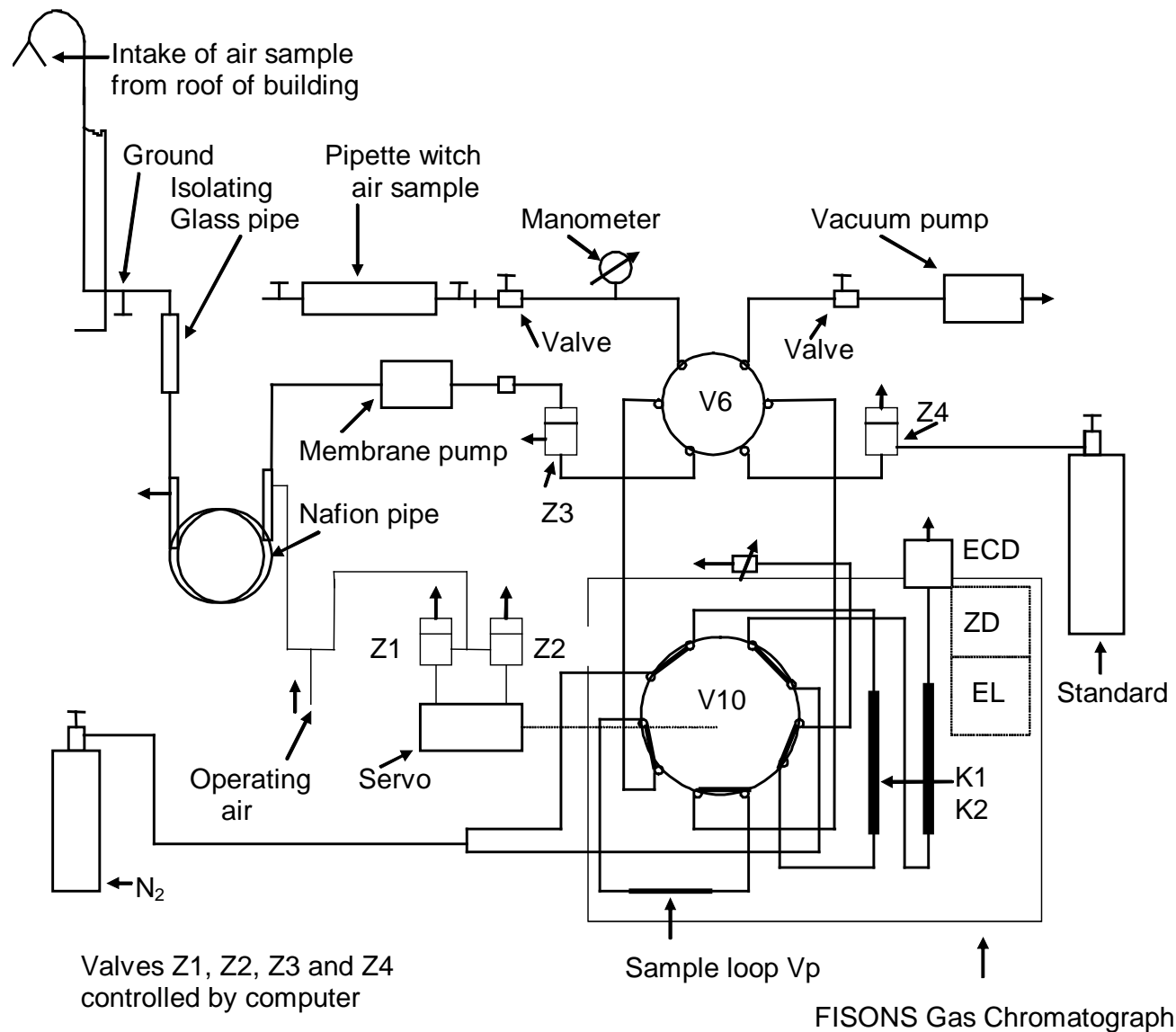


Experimental

- The continuous measurements of the concentrations of chlorofluorocarbons are conducted with the computer controlled GC Fisons, type 8000, equipped with two electron capture detectors (ECD) working in the constants current mode (channel A and B).
- The chromatograph uses four columns (10% SP 2100 and molecular sieve 5A, 80/100 mesh, 4 mm in diameter and 2, 10 ft and 1, 3 m long, respectively), working in a back flush system. The air samples are sucked from the roof of the laboratory building and dried in a Nafion tube.
- The air and standard samples, containing freons F-12, SF₆ (channel A) and F-11, F-113, CHCl₃, CH₃CCl₃, CCl₄ (channel B) are injected into GC alternatively every 30 minutes. The chromatograms of air and standard samples are registered in a computerized system HP ChemStation.
- As a standard, a cylinder filled with air, produced by Linde Firm was used. This secondary standard was calibrated relative to the primary standard of the Scripps Oceanography Institute, San Diego, USA (SIO-1993 scale).

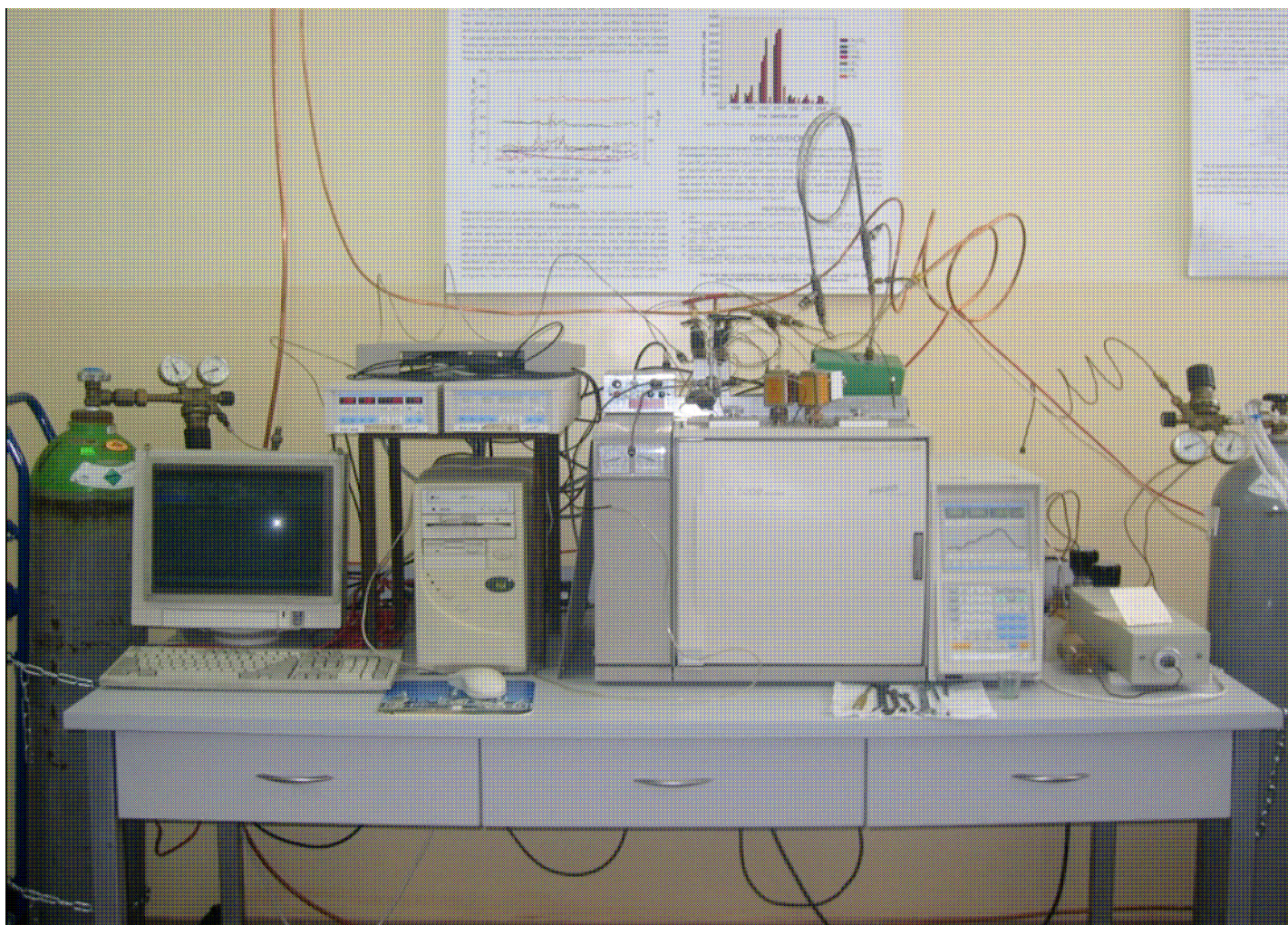


Scheme of the analytical system





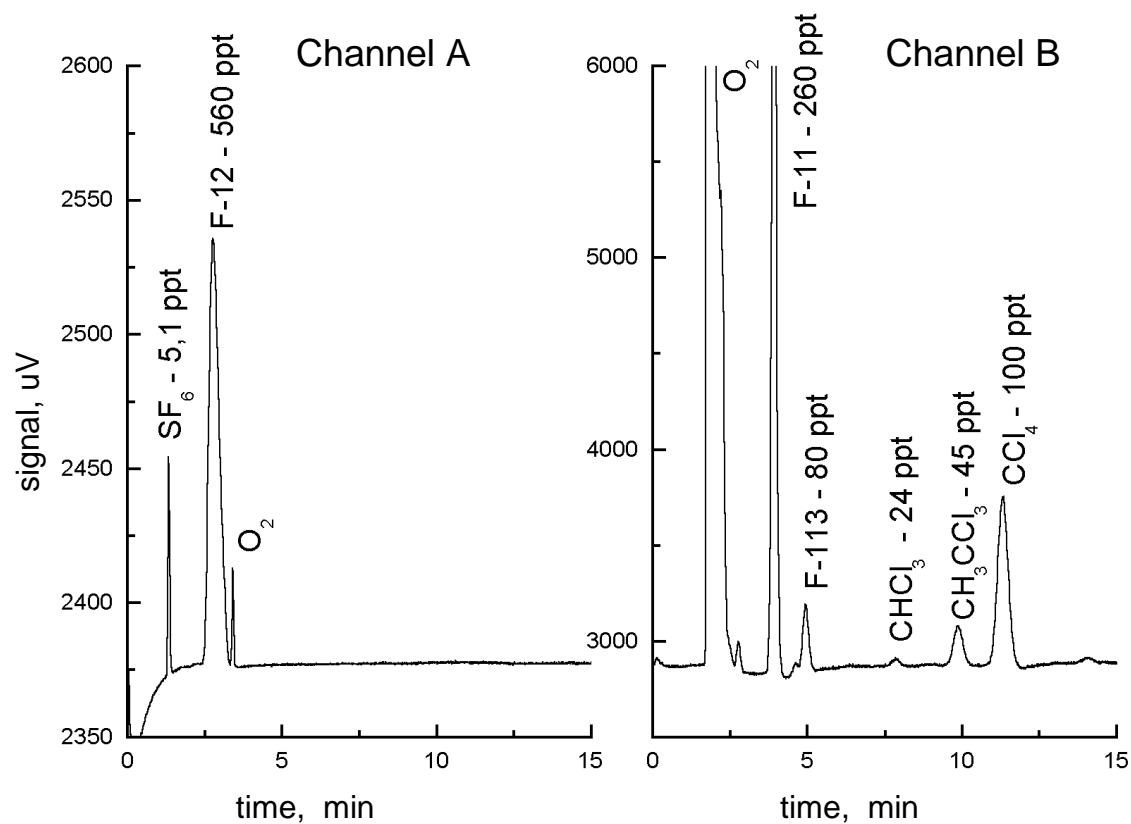
View of the measurements system





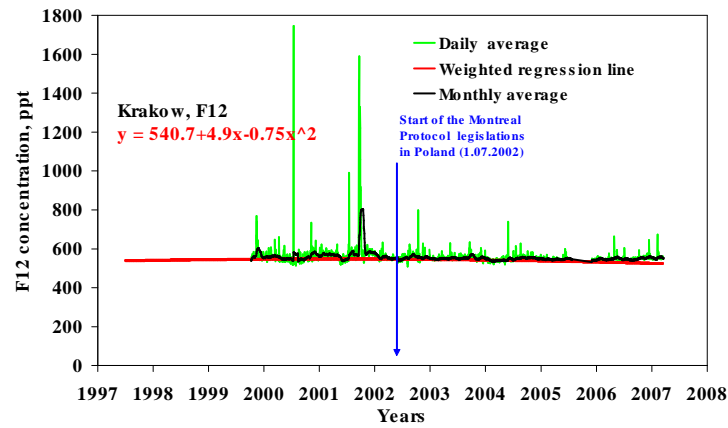
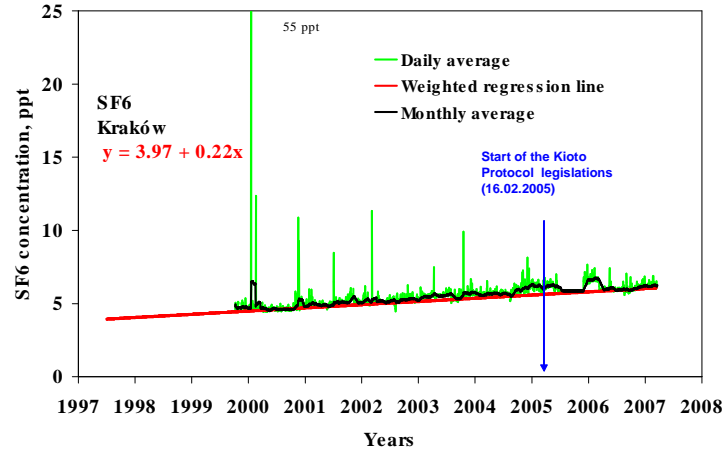
The chromatograms of CFCs

Example analysis of halocarbons in air of Krakow.





Results: Channel A

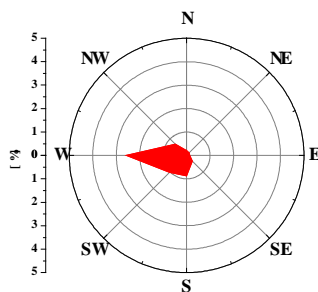
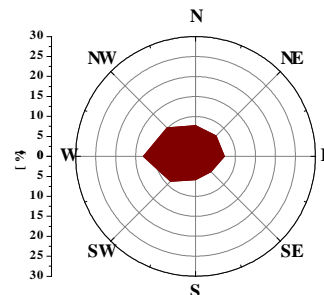
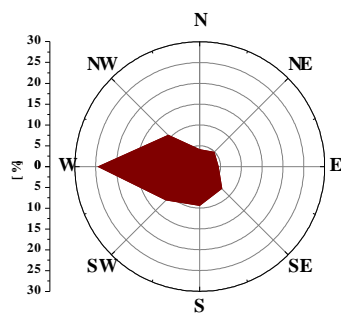




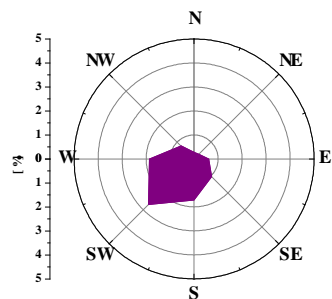
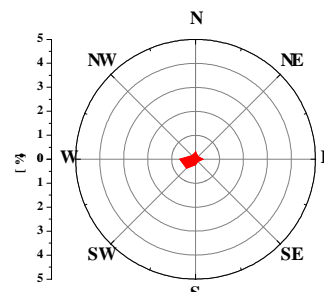
Autumn/Winter

Spring/Summer

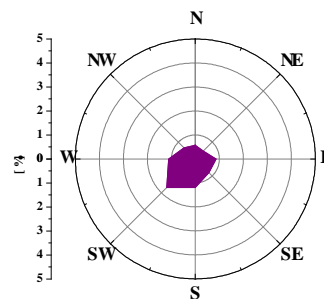
Channel A



SF6

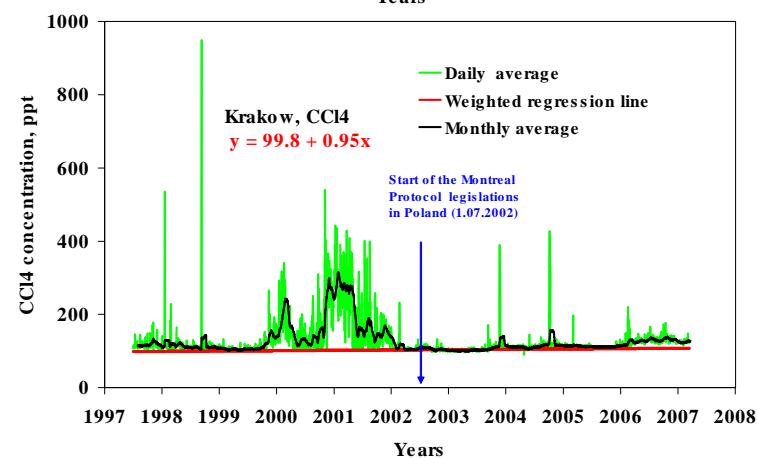
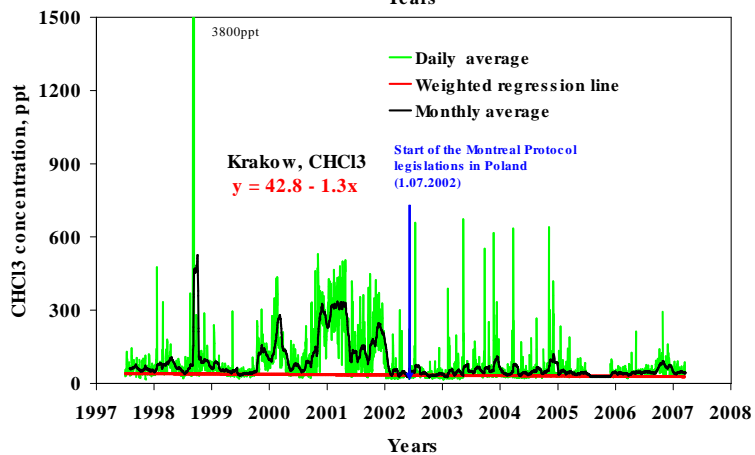
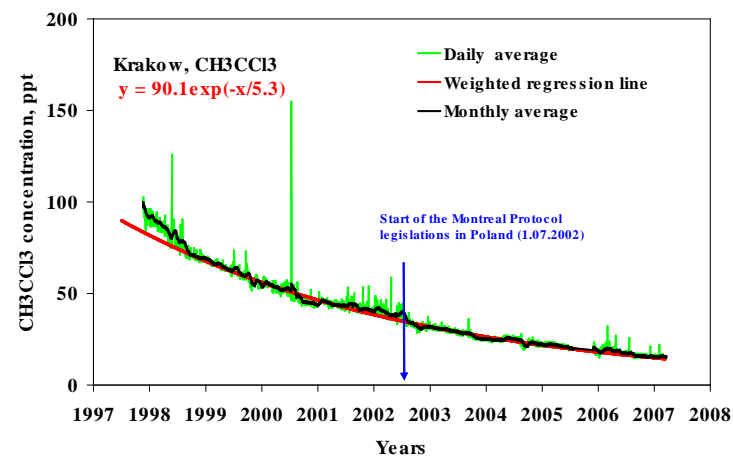
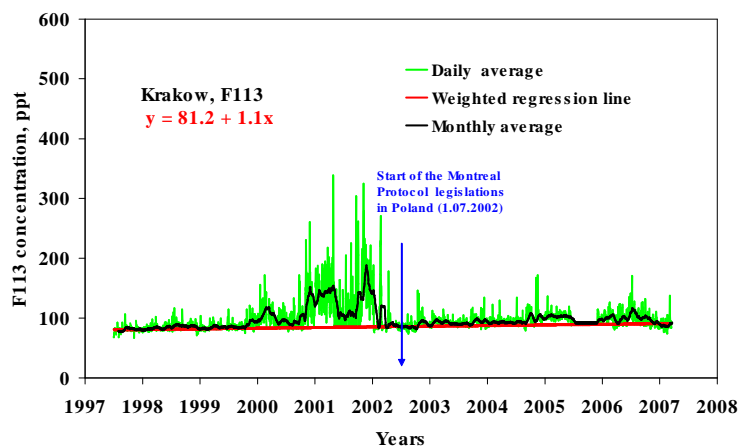
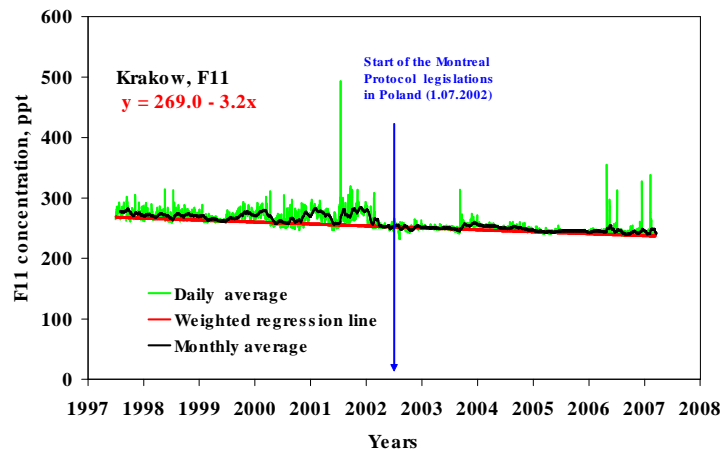


F-12





Results: Channel B

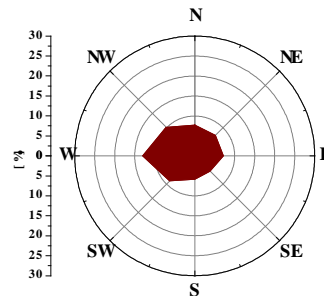
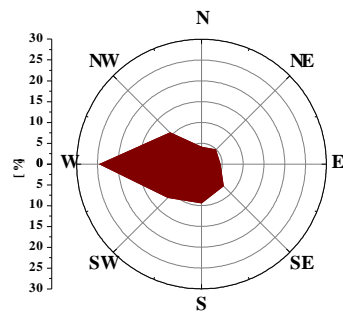




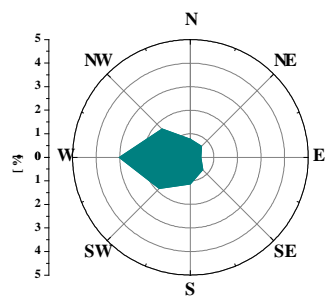
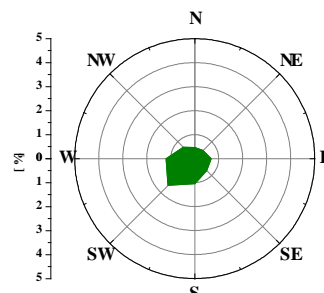
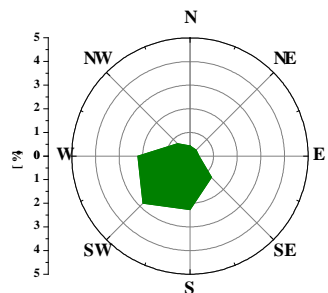
Autumn/Winter

Spring/Summer

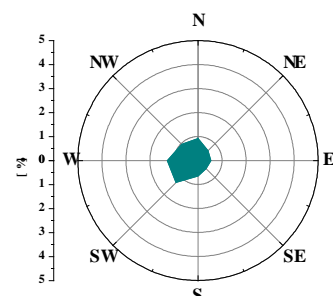
Channel: B



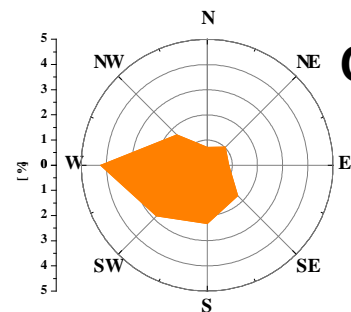
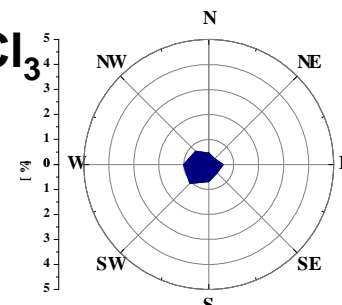
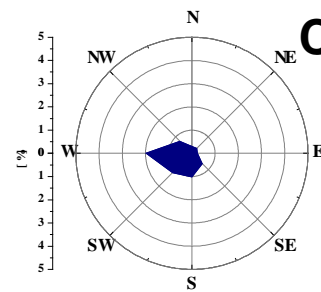
F-11



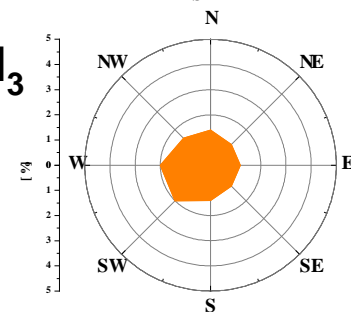
F-113



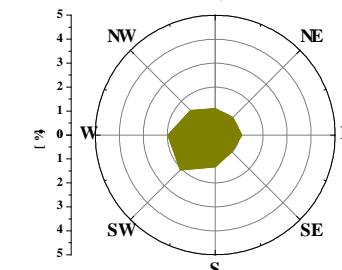
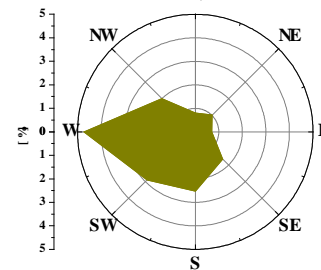
CH₃CCl₃



CHCl₃

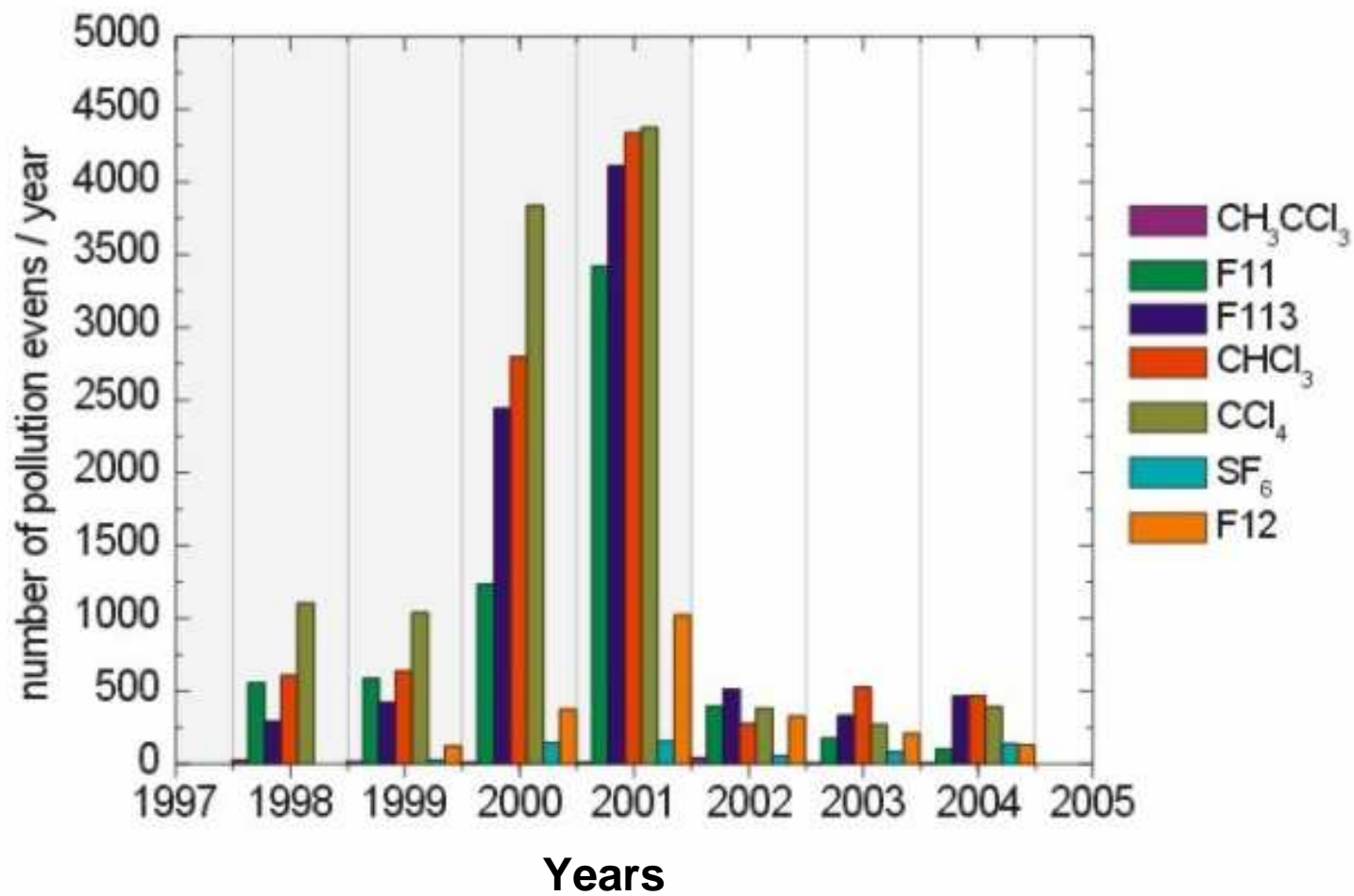


CCl₄





The number of pollution events





Act of law 2 March 2001 on proceedings in Poland with the Earth ozone layer depleting substances.

Dziennik Ustaw Nr 52

— 3510 —

Poz. 537

537

USTAWA

z dnia 2 marca 2001 r.

o postępowaniu z substancjami zubożającymi warstwę ozonową.

Rozdział 1

Przepisy ogólne

Art. 1. Ustawa ma na celu ograniczenie negatywnego oddziaływania niektórych substancji chemicznych na stratosferyczną warstwę ozonową oraz realizację zobowiązań wynikających z Konwencji wiedeńskiej o ochronie warstwy ozonowej, sporządzonej w Wiedniu dnia 22 marca 1985 r. (Dz. U. z 1992 r. Nr 98, poz. 488), oraz Protokołu montrealskiego w sprawie substancji zubożających warstwę ozonową, sporządzonego w Montrealu dnia 16 września 1987 r. (Dz. U. z 1992 r. Nr 98, poz. 490 i 491), zwanego dalej Protokołem Montrealskim.

Art. 2. 1. Wprowadza się kontrolę postępowania z substancjami zubożającymi warstwę ozonową, polegająca na ustanawianiu zakazów i ograniczeń dotyczą-

ułatwiającego niektóre procesy chemiczne, zawartego w innych substancjach chemicznych jako śladowe zanieczyszczenie, oraz emitowanych podczas produkcji wyrobów zawierających substancje kontrolowane i obrotu nimi,

- 2) współczynnika ODP — rozumie się przez to potencjał niszczenia ozonu, określający zdolność substancji kontrolowanej do zubożenia warstwy ozonowej i ustalony odrębnie dla każdej substancji kontrolowanej w umowach międzynarodowych, o których mowa w art. 1,
- 3) tonie ODP — rozumie się przez to iloczyn jednej tony danej substancji i ustalonego dla niej współczynnika ODP,
- 4) dozwolonych technologiach — rozumie się przez to technologie, których stosowanie jest dopuszczone na podstawie umów międzynarodowych, o któ-



The calculation results

The yearly trend coefficient (b) in the period since 07.1997 to 06.2007 and parameter (a) calculated in 1.07.1997 (using linear function $y=a+bx$).

Station	Krakow, Poland (50°N, 20°E, 250 m above MSL)	
Compound	b, ppt/year	a, ppt
F-11	-3.2 ± 0.1	269.1 ± 0.3
F-113	$+ 1.1 \pm 0.1$	81.2 ± 0.2
CHCl ₃	$- 1.3 \pm 0.2$	42.8 ± 0.9
CH ₃ CCl ₃ *	$- 4.4 \pm 0.2$	35.8 ± 0.3
CCl ₄	$+ 0.95 \pm 0.1$	99.8 ± 0.5
F-12*	-1.8 ± 0.1	546.5 ± 0.6
SF ₆	$+0.22 \pm 0.01$	3.97 ± 0.01

* (b) in the period since 07.2002 to 06.2007 and (a) calculated in 1.07.2002.



Conclusions

- The measured since 1997 concentrations of CFCs in Krakow air are characterized by seasonal variability. On the background of these changes four compounds i.e. F-11, F-12, CHCl_3 , CH_3CCl_3 have a tendency to decrease but F-113, CCl_4 and SF_6 concentrations tend to increase.
- A particular attention is necessary to call on investigations of CFCs pollutants advection from West sectors because increase of halocarbon concentrations in winter months distinctly correlate with air mass advection from these sectors.
- The observed diminishing frequency of the seasonal variability of CFC's concentration amplitude after the date of 1.07.2002 when the Montreal Protocol legislation have been started in Poland suggest that the limitations of CFC's emissions in Poland are being respected.



Thank you for attention