EnviroInfo 2007 (Warschau)
Environmental Informatics and Systems Research

Refrigerants ranked by Partial Order Theory

Guillermo Restrepo[1,2], Monika Weckert[1], Rainer Brüggemann[3],
Silke Gerstmann[1], Hartmut Frank[1]

Abstract

Forty refrigerants used in the past, used presently, and some proposed substitutes, were studied in respect to their ozone depletion potential, global warming potential, and atmospheric life times. They were ranked using the Hasse diagram technique, a mathematical method which permits to draw diagrams representing order relations among chemicals. The refrigerants were divided into 13 chemical classes (subsets) of which the most prominent ones are the chlorofluorocarbons (CFC), hydrofluorocarbons, hydrochlorofluorocarbons and hydrofluoroethers. Order relations among these subsets were calculated applying dominance and separability degrees. The dominance degree is a measure indicating the extent to which descriptors of members of one subset are higher than those of members of other subsets; the separability degree is a measure for the incomparability or lack of order relations between elements of two subsets. By application of these measures to the 13 chemical subsets it was found that more than half of the order relations among them are complete dominances; this means a high degree of comparability among subsets permitting to find the ones most problematic in environmental terms. This is the case for the CFC and for some of the hydrofluoroethers.

1. Introduction

Chlorofluorocarbons (CFC) have been used as refrigerants (Stemmler et al., 2004) but due to environmental problems, i.e. their high ozone depletion potential (ODP), their global warming potential (GWP) and their long atmospheric life times (ALT) (Molina and Rowland 1974, Rowland 1994, UNEP 1987, 1998, UNFCCC 1997) industry looked for substitutes; hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) became the first-generation alternatives (Haymann and Derwent, 1997). However, the latter still are not fully satisfactory; therefore, the search continues (Stemmler et al., 2004; UNFCCC 1997). Some of the newly proposed substances are chlorine-free fluorinated ethers, hydrocarbons (HC), alcohols, amines, and mixtures thereof (Sekiyaa and Misaki, 2000; Swaminathan, 2005a, b; Bivens, 1998). Prior to commencement of large-scale production, industry and regulatory agencies assess potential substitutes in respect ODP, GWP, ALT, toxicity, insulating ability, flammability, physical and chemical stability, solubility, cost, and other aspects of technical applicability (Sumantran et al., 1999; Swaminathan and Visco, 2005a, b;WMO 1991, 1992, 1995).

Normally an assessment implies that a decision is made based upon ranking of the substances under consideration (Lerche et al., 2002; Brüggemann, 1999); for this purpose, the Hasse diagram technique (HDT) (Brüggemann et al., 1993, 1994, 2001) is one of the most general and least subjective procedures (Lerche et al., 2002). In the present work, the HDT is applied to a set of 40 refrigerants taking ODP, GWP and ALT into consideration. After ranking, the refrigerants are divided into 13 subsets, and their order relations are studied by calculation of the two measures of comparability and incomparability, the dominance and the separability degrees.

[1] Environmental Chemistry and Ecotoxicology, University Bayreuth, Germany
email: guillermo.restrepo@uni-bayreuth.de, Internet: www.uni-bayreuth.de/departments/umweltchemie/
[2] Laboratorio de Química Teórica, Universidad de Pamplona, Colombia
[3] Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Berlin, Germany

2. Hasse diagram technique, dominance and separability degrees

2.1 Hasse Diagram Technique (HDT)

Important concepts of the HDT are illustrated in the following example; a detailed description of the technique is found in Brüggemann et al. (1994, 2001). Let us assume set P contains 6 substances: $P = \{a, b, c, d, e, f\}$ of which each is described by three properties: q_1, q_2 and q_3 (Table 1). The HDT permits to compare any two chemicals considering simultaneously all their properties. A substance x is ranked higher than another y ($y \leq x$) when all its properties are higher than those of y, as is the case for $c \leq e$ (Table 1, Figure 1); in this case it is said that the two substances are "comparable". If x, y and z are substances and if $x \leq y$ and $y \leq z$, then $x \leq z$; for example $c \leq e$, $d \leq c$, then $d \leq e$ (Figure 1). If the property q_i of x is higher than q_j for y and the value of the property q_j for x is lower than q_j for y, then x and y are said to be "incomparable" ($x \parallel y$), for instance $e \parallel f$ (Table 1, Figure 1). Two substances are in a "cover-relation" if they are comparable and if there is no third one in between; all the pairs of substances with cover-relations are graphically represented in a Hasse diagram (Figure 1) drawn and analysed with the software WHASSE (Brüggemann et al., 1995). In general, the HDT permits to study order relations among the elements of a set by analysing the partially ordered set given by the couple (P, $\leq$), where $\leq$ is the order relation discussed above.

Table 1:
Properties q_1, q_2 and q_3 of the chemicals a, b, c, d, e and f.

	q_1	q_2	q_3
a	0	5	1
b	1	1	1
c	3	6	4
d	2	4	1
e	4	9	7
f	5	7	7

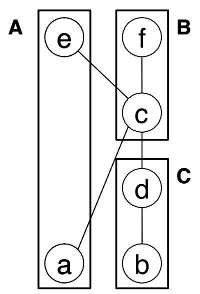

Figure 1: Hasse diagram of the substances in Table 1; the three boxes represent three subsets of chemicals (see text).

If the chemicals are described by properties whose values increase with the extent of their adverse impact, as is the case of ODP, GWP and ALT, then these substances located at the top of the diagram will be the "most hazardous" ones; in Figure 1 these substances correspond to *e* and *f*; in contrast, the chemicals found at the bottom (*a* and *b*) will represent the "least hazardous" ones.

Normally, a Hasse diagram is interpreted by analysing the order relations of single elements of *P*, but in some cases the order relations among different subsets is also of interest, for example among classes of similar chemicals. For doing this, two measures have been developed (Restrepo et al., 2007a, b, c), one indicating the extent to which members of one subset hold higher values in their descriptors than the members of other subsets, called the dominance degree (Restrepo et al. 2006a, 2007a, b, c); the second measure quantifies the number of incomparabilities among the members of two compound subsets and is called the separability degree (Restrepo et al., 2007c).

2.2 Dominance and separability degrees

Given a Hasse diagram of $(P, \leq)$ and two disjoint subsets $P_1, P_2 \subset P$, the dominance degree between P_1 and P_2 is given by Dom $(P_1, P_2) = N_R / N_T$, where $N_R = |\{(x, y), x \in P_1, y \in P_2 \text{ and } y \leq x\}|$ and $N_T = |P_1| \cdot |P_2|$; $|X|$ means the cardinality or number of elements in a set *X*. The separability degree between P_1 and P_2 is given by Sep $(P_1, P_2) = N_I / N_T$, where $N_I = |\{(x, y), x \in P_1, y \in P_2 \text{ and } y \parallel x\}|$.

Dom (P_1, P_2) and Sep (P_1, P_2) range from 0 to 1; Dom $(P_1, P_2) = 1$ means that all elements in P_1 have descriptor values higher than the ones of the elements of P_2; in this case it is said that P_1 completely dominates P_2 (Restrepo et al. 2007c). Dom $(P_1, P_2) = 0$ means that for no element *x* of P_1 and *y* of P_2 the relation $y \leq x$ holds; in this case P_1 does not dominate P_2. Because of the antisymmetry of $\leq$ (Trotter 1992), Dom (P_1, P_2) is not necessarily equal to Dom (P_2, P_1) (Restrepo et al. 2007b, c). Furthermore, Sep $(P_2, P_1) = 1$ means that all possible relations between P_1 and P_2 are incomparabilities; Sep $(P_1, P_2) = 0$ means that there are no incomparabilities between P_1 and P_2, and therefore all their relations are ruled by $\leq$. Additionally, it was proved that Dom (P_1, P_2) + Dom (P_2, P_1) + Sep $(P_1, P_2) = 1$ (Restrepo et al. 2007c). The values of dominance and separability degrees for the three subsets shown in Figure 1 are the following: Dom $(A, B) = 1 / 4 = 0.25$, Dom $(B, A) = 2 / 4 = 0.5$, Sep $(A, B) = 1 / 4 = 0.25$; Dom $(B, C) = 4 / 4 = 1$, Dom $(C, B) = 0 / 4 = 0$, Sep $(B, C) = 0 / 4 = 0$; and Dom $(A, C) = 2 / 4 = 0.5$, Dom $(C, A) = 0 / 4 = 0$, Sep $(A, C) = 2 / 4 = 0.5$.

The set *P* of 40 refrigerants (Table 2) was divided into the following 13 subsets: CFC, HFC, HCFC, HC, di(fluoroalkyl)ethers (DFAE), alkylfluoroalkylethers (AFAE), chloromethanes (CM), and the single-compound subsets trifluoroiodomethane (FIM), octafluorocyclobutane (PFC), carbon dioxide (CO_2), bromochlorodifluorobutane (BCF), dimethyl ether (DME) and ammonia (NH_3). These subsets were formed taking into consideration the common classification of the refrigerants into different chemical families. Each refrigerant is represented by its ALT, ODP and GWP (Restrepo et al. 2007b).

Table 2:
Refrigerants included in this study, their labels, chemical subsets, molecular formulae and non-proprietory names

Label	**Subset**	**Molecular formula**	**Non-proprie-tory name**	**Label**	**Subset**	**Molecular formula**	**Non-proprie-tory name**
1	CFC	CCl_3F	R11	**21**	CO_2	CO_2	R744
2	CFC	CCl_2F_2	R12	**22**	BCF	$CBrClF_2$	R12B1
3	HCFC	$CHClF_2$	R22	**23**	PFC	C_4F_8	RC318
4	HCFC	$C_2HCl_2F_3$	R123	**24**	HFC	C_3HF_7	R227ea
5	HCFC	C_2HClF_4	R124	**25**	AFAE	$C_4H_3F_7O$	HFE-7000
6	HCFC	$C_2H_3Cl_2F$	R141b	**26**	AFAE	$C_5H_3F_9O$	HFE-7100
7	HCFC	$C_2H_3ClF_2$	R142b	**27**	AFAE	$C_6H_5F_9O$	HFE-7200/ HFE-569mccc
8	HFC	CHF_3	R23	**28**	AFAE	$C_9H_5F_{15}O$	HFE-7500
9	HFC	CH_2F_2	R32	**29**	DFAE	C_2HF_5O	HFE-125
10	HFC	C_2HF_5	R125	**30**	DFAE	$C_2H_2F_4O$	HFE-134
11	HFC	$C_2H_2F_4$	R134a	**31**	CM	CH_2Cl_2	R30
12	HFC	$C_2H_3F_3$	R143a	**32**	CM	CH_3Cl	R40
13	HFC	$C_2H_4F_2$	R152a	**33**	CFC	$C_2Cl_3F_3$	R113
14	HFC	$C_3H_3F_5$	R245fa	**34**	HCFC	$CHCl_2F$	R21
15	HFC	$C_3H_2F_6$	R236fa	**35**	CFC	$C_2Cl_2F_4$	R114
16	HC	C_3H_8	R290	**36**	FIM	CF_3I	R13I1
17	HC	C_4H_{10}	R600	**37**	DME	C_2H_6O	
18	HC	C_4H_{10}	R600a	**38**	NH_3	NH_3	R717
19	HC	C_5H_{12}	R601	**39**	AFAE	$C_2H_3F_3O$	HFE-143
20	HC	C_3H_6	R1270	**40**	AFAE	$C_3H_3F_5O$	HFE-245

3. Results and discussion

The Hasse diagram of the considered refrigerants is depicted in Figure 2 with the marked boxes representing the 13 subsets mentioned in Table 2.

Since high values of ALT, ODP and GWP indicate a refrigerant with adverse effects on the environment, the most problematic substances are 1, 2, 8, 22, 23, 29, 33 and 35, while 19 and 20 are considered as benign ones. Problematic substances belong to DFAE, CFC, BCF, HFC and PFC subsets, and the benign ones to the HC subset. It is important to note the identification of 29, a difluoroalkyl ether, as hazardous refrigerant although this chemical has been introduced as potential replacement of CFC, HFC and HCFC (Tai, 2005), while 31, although a chlorocarbon, is relatively benign.

From the total of $13 \times 13 = 169$ ordered pairs (P_i, P_j), dominance and separability degrees are defined for 156 (169 minus 13 self comparisons $P_i = P_j$). Hence, for each of the 78 non-ordered pairs {P_i, P_j}, Dom (P_i, P_j), Dom (P_j, P_i) and Sep (P_i, P_j) were calculated (Table 3).

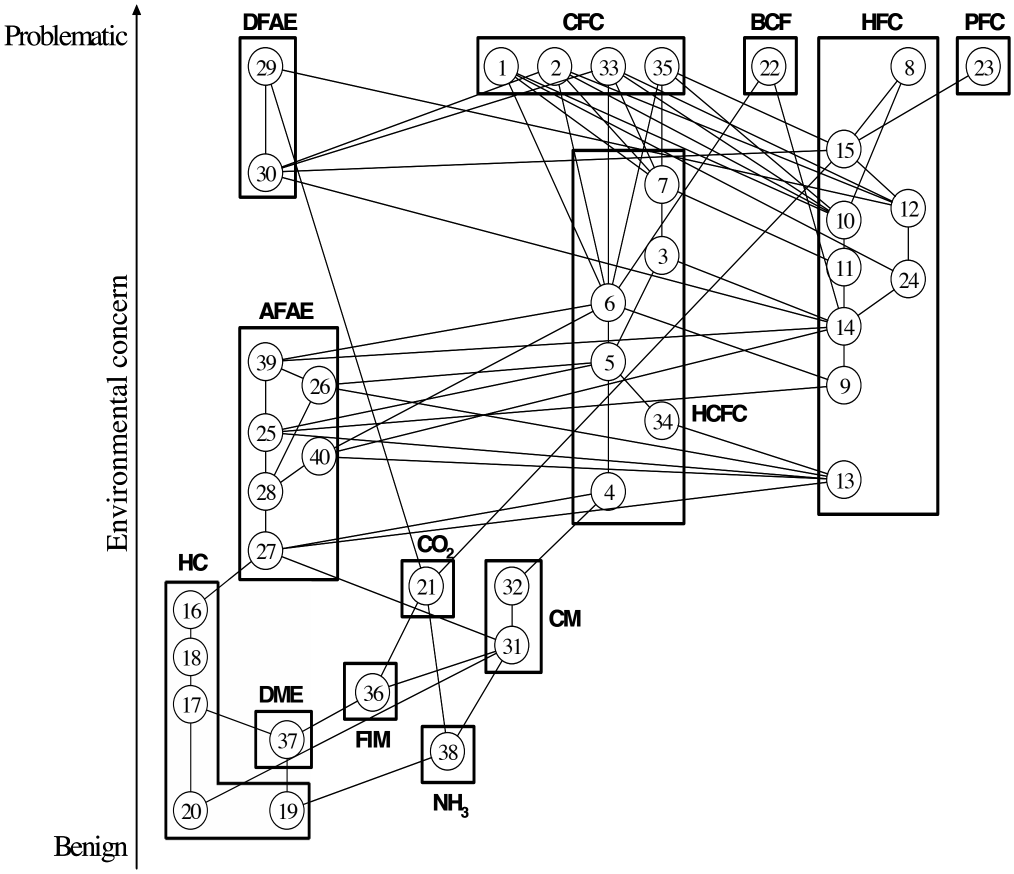

Figure 2: Hasse Diagram of 40 refrigerants and its subsets shown as boxes. CFC: chlorofluorocarbons, HFC: hydrofluorocarbons, HCFC: hydrochlorofluorocarbons, HC: hydrocarbons, DFAE: di(fluoroalkyl)ethers, AFAE: alkylfluoroalkylethers, CM: chloromethanes, FIM: trifluoroiodomethane, PFC: octafluorocyclobutane, BCF: bromochlorodifluorobutane, DME: dimethyl ether, CO_2 and NH_3.

Table 3:
Dominance and separability degrees for the 13 subsets shown in Figure 2

{P_i, P_j}	**Dom (P_i, P_j)**	**Dom (P_j, P_i)**	**Sep (P_i, P_j)**
{DFAE, AFAE}, {DFAE, HC}, {DFAE, FIM}, {DFAE, DME}, {DFAE, NH_3}, {BCF, AFAE}, {BCF, CM}, {BCF, HC}, {BCF, FIM}, {BCF, DME}, {BCF, NH_3}, {CFC, HCFC}, {CFC, AFAE}, {CFC, CM}, {CFC, HC}, {CFC, FIM}, {CFC, DME}, {CFC, NH_3}, {PFC, AFAE}, {PFC, CO_2}, {PFC, HC}, {PFC, FIM}, {PFC, DME}, {PFC, NH_3}, {HCFC, HC}, {HCFC, FIM}, {HCFC, DME}, {HCFC, NH_3} {HFC, HC}, {HFC, FIM}, {HFC, DME}, {HFC, NH_3}, {AFAE, HC}, {AFAE, FIM}, {AFAE, DME}, {AFAE, NH_3}, {CM, FIM}, {CM, DME}, {CM, NH_3}, {CO_2, FIM}, {CO_2, DME}, {CO_2, NH_3}, {FIM,DME}	1	0	0
{HCFC, CM}	0.92	0	0.08
{HFC, AFAE}	0.85	0.07	0.08
{CFC, HFC}	0.78	0	0.22
{HCFC, AFAE}	0.73	0	0.27
{BCF, HCFC}	0.67	0	0.33
{PFC, HFC}	0.63	0	0.37
{HC, DME}	0.6	0.2	0.2
{DFAE, CM}, {DFAE, CO_2}, {PFC, CM}, {HFC, CM}, {AFAE, CM}, {PFC, DFAE}	0.5	0	0.5
{DFAE, HFC}	0.44	0.11	0.45
{CM, HC}	0.4	0	0.6
{CFC, DFAE}	0.38	0	0.62
{BCF, HFC}	0.33	0	0.67
{CFC, CO_2}	0.25	0	0.75
{HFC, CO_2}	0.22	0	0.78
{HCFC, HFC}, {CO_2, HC}, {FIM, HC}, {NH_3, HC}	0.2	0	0.8
{DFAE, BCF}, {DFAE, HCFC}, {BCF, CFC}, {BCF, PFC}, {BCF, CO_2}, {CFC, PFC}, {PFC, HCFC}, {HCFC, CO_2}, {AFAE, CO_2}, {CM, CO_2}, {FIM, NH_3}, {DME, NH_3}	0	0	1

According to Table 3, for 55% of all pairs {P_i, P_j} there is complete dominance of one subset over another, they are not separable (Sep (P_i, P_j) = 0). This indicates a high degree of comparability among the studied subsets, implying the possibility of finding order relations among the majority of subsets. According to a previous investigation (Restrepo et al., 2007b), one of the subsets dominating the majority of the subsets is CFC (Table 3) with high values of dominance over the other subsets.

When none of the compared subsets dominates any others, these are completely separated and therefore all their elements are incomparable (Restrepo et al., 2007c); in this case the dominance degree drops to 0 and the separability degree grows to 1. One example is the pair {CFC, PFC} (Figure 2). In this study, 15% of the pairs have this distribution for the three calculated parameters (Table 3); this means that less than a sixth of the relations among subsets do not follow an order relation, thereby it is not possible to find a most hazardous susbset for these cases because of their mutual incomparability. A strategy for looking for comparabilities in these cases is to prioritise the properties of the chemicals in order to aggregate them into a new superdescriptor which yields a linear order of the original Hasse diagram. The application of this strategy to the refrigerants will be published in a forthcoming paper.

The remaining pairs of Table 3, 30% of the total, are representing intermediate situations where one subset partially dominates the other one, both being partially separable. One example is { DFAE, HFC }, where 15% of their possible relations are of the kind $y \leq x$, with $x \in$ HFC and $y \in$ DFAE; 40% hold $x \leq y$, and 45% are incomparabilities between x and y.

The fact that more than half of the refrigerant subsets dominate others can be regarded as evidence of the relationship between the ranking of single compounds and the ranking of their families. This also suggests a relationship between the criteria for selecting members of each class and their ranking. Since the criteria of forming the subsets is the common chemical classification, i.e. chlorofluorocarbons, hydrofluorocarbons, and so on, it is interesting to form the classes by unsupervised classification, such as hierarchical cluster analysis using molecular descriptors for describing the refrigerants. It will be interesting to compare the resulting ranking of subsets with the ones found in the current work.

Acknowledgements

This study was financially supported by the Bavarian Environmental Agency. G. Restrepo thanks the Universidad de Pamplona and COLCIENCIAS in Colombia for a grant received during this research.

Bibliography

Bivens, D.B., Minor, B. (1998): Fluoroethers and other next generation fluids. Int. J. Refrig. 21: 567 - 576.

Brüggemann, R., Münzer, B. (1993): A graph-theoretical tool for priority setting of chemicals. Chemosphere, 27: 1729-1736.

Brüggemann, R., Münzer, B., Halfon, E. (1994): An algebraic/graphical tool to compare ecosystems with respect to their pollution - the German river “Elbe” as an example - I: Hasse-diagrams. Chemosphere, 28: 863-872.

Brüggemann, R., Halfon, E., Bücherl, C. (1995): Theoretical base of the program “Hasse”, GSF–Bericht 20/95, Neuherberg. (WHASSE available from R. B.).

Brüggemann, R., Bücherl, C., Pudenz, S., Steinberg, C.E.W. (1999): Application of the Concept of Partial Order on Comparative Evaluation of Environmental Chemicals. Acta Hydrochim. Hydrobiol., 27: 170-178.

Brüggemann, R., Halfon, E., Welzl, G., Voigt, K., Steinberg, C.E.W. (2001): Applying the Concept of Partially Ordered Sets on the Ranking of Near-Shore Sediments by a Battery of Tests. J. Chem. Inf. Comput. Sci., 41: 918-925.

Haymann, G.D., Derwent, R.G. (1997): Atmospheric Chemical Reactivity and Ozone-Forming Potentials of Potential CFC Replacements. Environ. Sci. Technol., 31: 327-336.

Lerche, D., Brüggemann, R., Sørensen, P., Carlsen, L., Nielsen, O. J. (2002): A Comparison of Partial Order Technique with Three Methods of Multi-Criteria Analysis for Ranking of Chemical Substances. J. Chem. Inf. Comput. Sci., 42: 1086-1098.

Molina, M.J., Rowland, F.S. (1974): Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. Nature, 249: 810-812.

Restrepo, G., Brüggemann, R. (2006): Modelling the Fate of Alkanes in Rivers. In Recent Progress in Computational Sciences and Engineering; Simos, T.; Maroulis, G., Eds.; VSP: Leiden, 1386-1389.

Restrepo, G., Brüggemann, R. (2007a): Partially ordered sets in the analysis of alkanes fate in rivers. Croat. Chem. Acta. In press.

Restrepo, G., Weckert, M., Brüggemann, R., Gerstmann, S., Frank, H. (2007b): Order relationships between sets of refrigerants. Submitted to Environ. Sci. Technol.

Restrepo, G., Brüggemann, R. (2007c): Dominance and separability in posets, their application to isoprotonic-isoelectronic species. Submitted to J. Math. Chem.

Rowland, F.S., Molina, M.J. (1994): Ozone depletion: 20 years after the alarm. Chem. Eng. News, 8-13.

Sekiyaa, A., Misaki, S. (2000): The potential of hydrofluoroethers to replace CFCs, HCFCs and PFCs. J. Fluorine Chem., 101: 215-221.

Stemmler, K., O'Doherty, S., Buchmann, B., Reimann, S. (2004): Emissions of the Refrigerants HFC-134a, HCFC-22, and CFC-12 from Road Traffic: Results from a Tunnel Study (Gubrist Tunnel, Switzerland). Environ. Sci. Technol., 38: 1998-2004.

Sumantran, V., Khalighi, B., Saka, K., Fischer, S. (1999): An Assessment of Alternative Refrigerants for Automotive Applications based on Environmental Impact. SAE International Automotive Alternate Refrigerant Systems Symposium. Scottsoale, http://www.sae.org/altrefrigerant/presentations/present 99.htm

Swaminathan, S., Visco, D.P. Jr. (2005a): Thermodynamic Modeling of Refrigerants Using the Statistical Associating Fluid Theory with Variable Range. 1. Pure Components. Ind. Eng. Chem. Res., 44: 4798-4805.

Swaminathan, S.; Visco, D.P. Jr. (2005b): Thermodynamic Modeling of Refrigerants Using the Statistical Associating Fluid Theory with Variable Range. 2. Applications to Binary Mixtures. Ind. Eng. Chem. Res., 44: 4806-4814.

Tsai, W.T. (2005): Environmental risk assessment of hydrofluoroethers (HFEs). J. Hazard. Material., 119: 69-78.

Trotter, W.T. (1992): Combinatorics and Partially Ordered Sets Dimension Theory; The Johns Hopkins University Press: Baltimore.

UNEP. (1987): Montreal Protocol on Substances that Deplete the Ozone Layer; United Nations Environment Programme: Nairobi, Kenya.

UNEP. (1998): Montreal Protocol on Substance that Deplete Ozone Layer; United Nations Environment Programme: Montreal, Canada.

UNFCCC. (1997): Kyoto Protocol to the United Nations Framework Convention on Climate Change, United Nations Framework Convention on Climate Change.

WMO. (World Meteorological Organization) (1991): Scientific Assessment of Stratospheric Ozone: 1989; Volume II, Appendix AFEAS Report; Global Ozone Research and Monitoring Project Report 20, Geneva, Switzerland.

WMO. (World Meteorological Organization) (1992): Scientific Assessment of Stratospheric Ozone: 1991; Global Ozone Research and Monitoring Project Report 25, Geneva, Switzerland.

WMO. (World Meteorological Organization) (1995): Scientific Assessment of Stratospheric Ozone: 1994; Global Ozone Research and Monitoring Project Report 37, Geneva, Switzerland.