GREEN CHEMISTRY AND THE NEXT GENERATION OF OXYGEN CLEANING CHEMICALS

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IUCT

- NASA Headquarters has tasked the Technology Evaluation for Environmental Risk Mitigation Principal Center (TEERM) to investigate industry and government progress on identifying environmentally friendly replacements for Class II ODS used in precision cleaning application for aviation oxygen systems.

◆ The TEERM has found that, to date, little tangible progress has been made in finding replacements for Class II ODSs. Only two chemical products are under development by industry.

- QwikClean® from Mainstream Engineering Corp.

  - 25% 4-bromo-3-chloro-3,4,4-trifluoro-1-butene.
  - 75% 1-chloro-2,2,2-trifluoroethyl difluoromethyl ether.

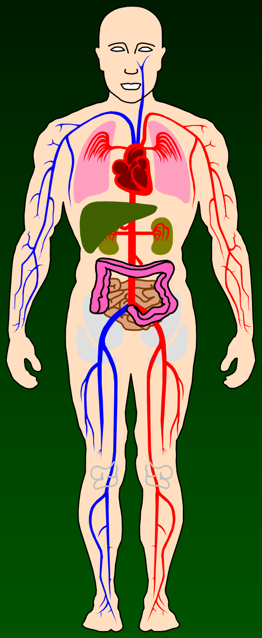
- QwikClean® appears to perform well in cleaning tests, but still requires additional toxicology testing.

- The second product is a reformulation of DuPont's Vertrel MCA® cleaning product.

  - 46% Vertrel XF
  - 40% *trans*-1,2-dichloroethylene
  - 14% Cyclopentane

- DuPont states that the new product will still be a hydrofluorocarbon (HFC), but not a regulated Class II ODS

Environment & Health
Adverse Effects



PHYSICO-CHEMICAL PROPERTIES GREATLY DETERMINE SOLVENT EMISSION, TRANSPORT AND TRANSFORMATION IN THE ENVIRONMENT

(ECO-)TOXIC EFFECTS ARE A MANIFESTATION OF MOLECULAR STRUCTURE

- Pyridine (hepatotoxic)
- CCl_4 (hepatotoxic, renal damage)
- Benzene (carcinogenic)
- Hexane (neurotoxic)

Vertrel XF	AEL 200 ppm	8 hour TWA
trans-1,2-dichloroethylene	TLV 200 ppm	8 hour TWA
Cyclopentane	TLV 600 ppm	8 hour TWA

Green Chemistry & Green Engineering: Inherently Safer Chemistry

Risk = Hazard x Exposure

- Anastas, P.T. and Warner, J.C.. "Green Chemistry: Theory and Practice". Oxford University Press, 2000.
- Anastas, P.T., and Zimmerman, J.B., "Design through the Twelve Principles of Green Engineering", Env. Sci. and Tech., 37, 5, 95 – 101, 2003.

◆ NASA and the Center for Green Chemistry and Green Engineering at Yale have launched a collaborative project with the following objective:

To provide engineering review, analysis, study and reporting of potential chemical alternatives for environmentally friendly oxygen systems and component cleaning that will replace existing Class II Ozone Depleting Chemicals (ODC's).

◆ Recently, IUCT launched ***SOLVSAFE***, a cooperative research project aimed at developing safer solvent alternatives to classical solvents for metal degreasing, paints and varnishes, crop protection formulations and the manufacture of fine chemicals:

Efficacy of Function *vs* Chemical Function (F)

$$F = \Sigma f_{\text{efficacy}} + \Sigma f_{\text{health}} + \Sigma f_{\text{environment}} + \Sigma f_{\text{economy}}$$

◆ A characteristic feature of complex chemical systems is that the ***F***s are complicated nonlinear functions of the ***S***s. The equations linking function and structure should then admit, under certain conditions, several solutions (rather than just the one optimal solution). Often, the relationship between structure and function is unknowable due to a lack of fundamental understanding of the chemical system.

$$\boldsymbol{F}(\boldsymbol{S}_{n+1}) = h\,[\boldsymbol{F}(\boldsymbol{S}_n), \boldsymbol{S}_n, \lambda]$$

- Therefore, to search for maximum chemical function, the green chemist is forced to generate a chemical space as much diverse as possible. The more structural diversity the more chances to achieve the desired chemical function. We assume this equation:

$$\boldsymbol{F} = \alpha\,[div\boldsymbol{S}]^{\beta}$$

THE SIMILARITY OF FUNCTION PARADOX

GOALS WHEN SEARCHING SOLVENT ALTERNATIVES

1. Reduce or eliminate both (eco-)toxicity and environmental impact

    Means significant change in molecular structure (dissimilarity) according to the *similar property principle*

2. Maintain or improve efficacy of function

    Means keeping molecular structure close to the original chemical entity (similarity)

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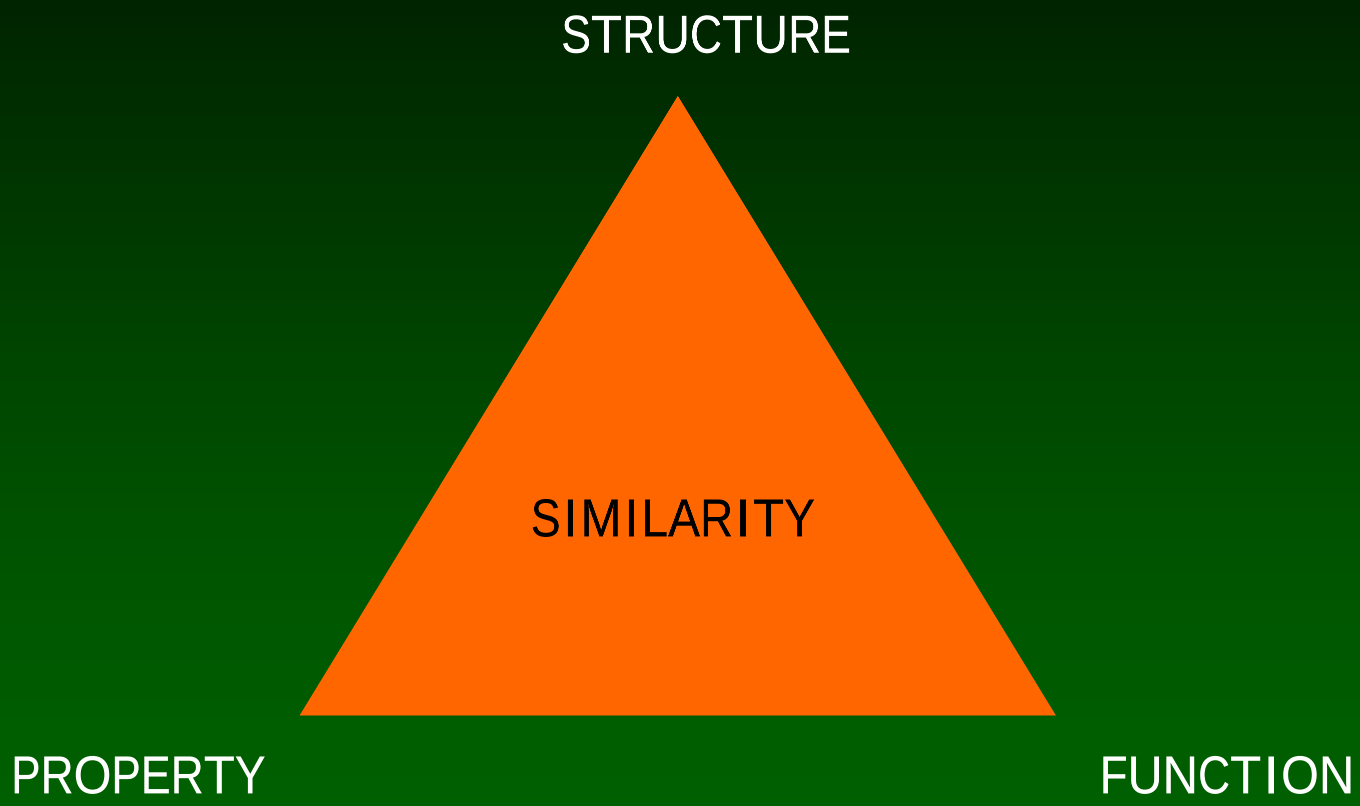
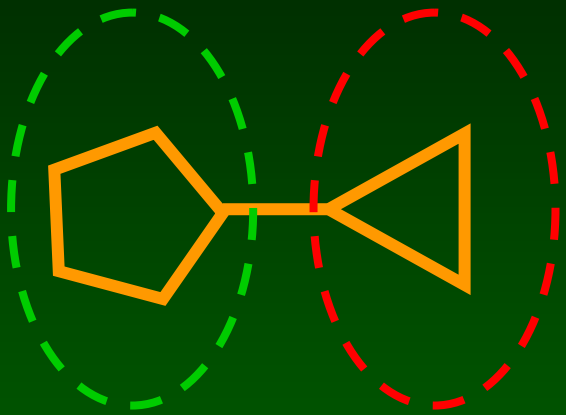


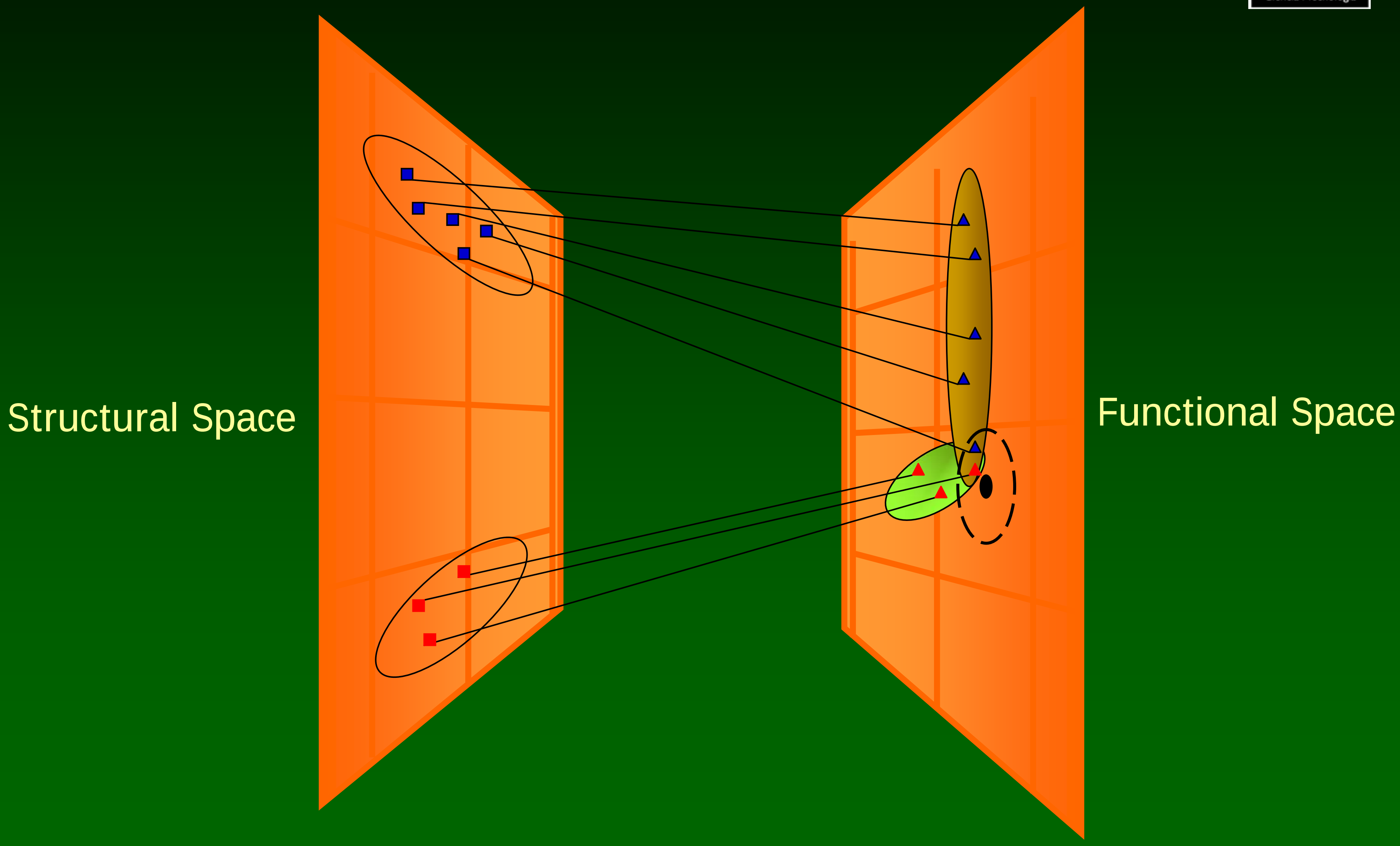
Chemical Function and Green Design

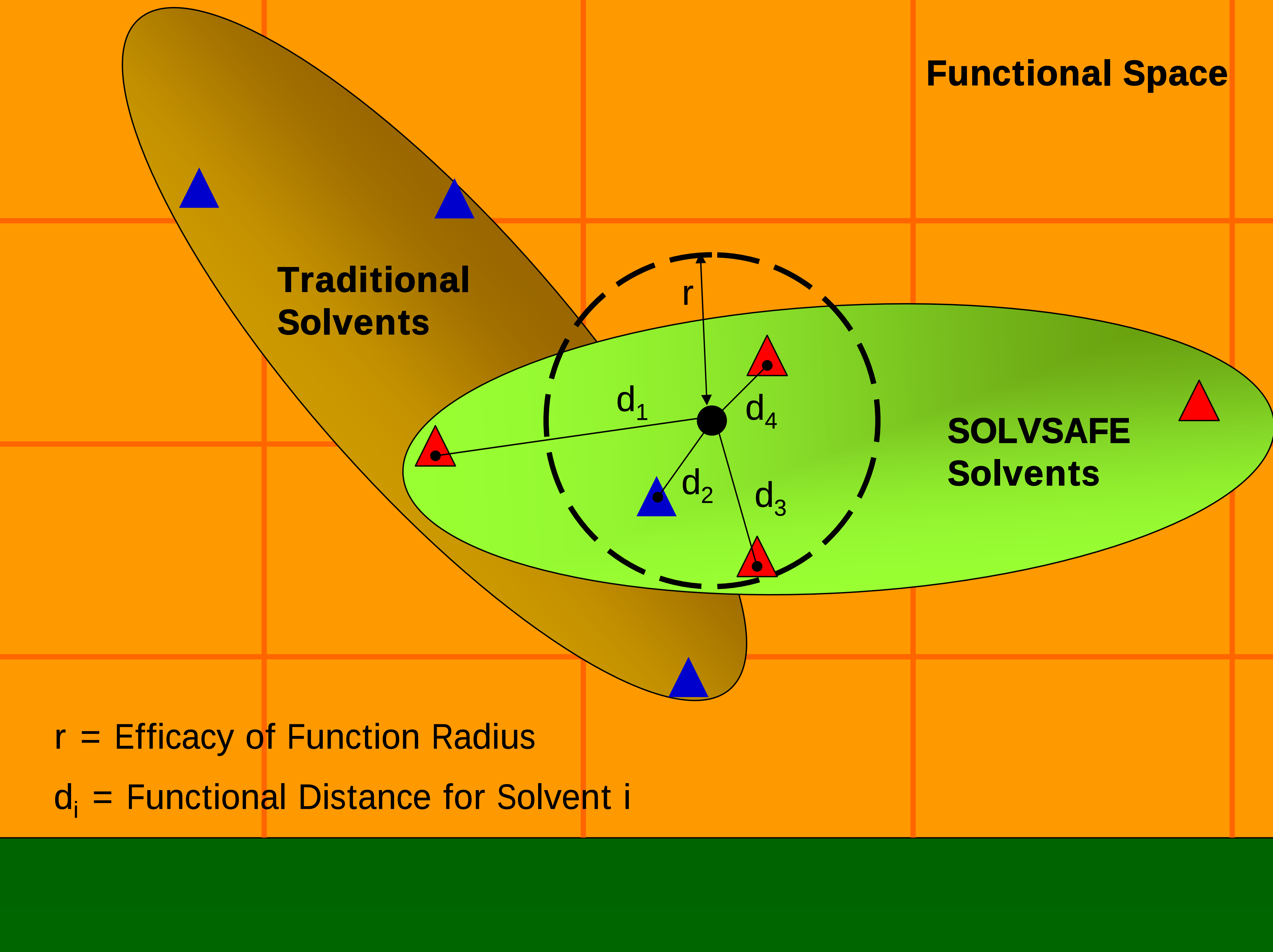
- Platform Fragment
- Basic Chemical Properties and Function
- Synthetic Accesibility
- Product Cost



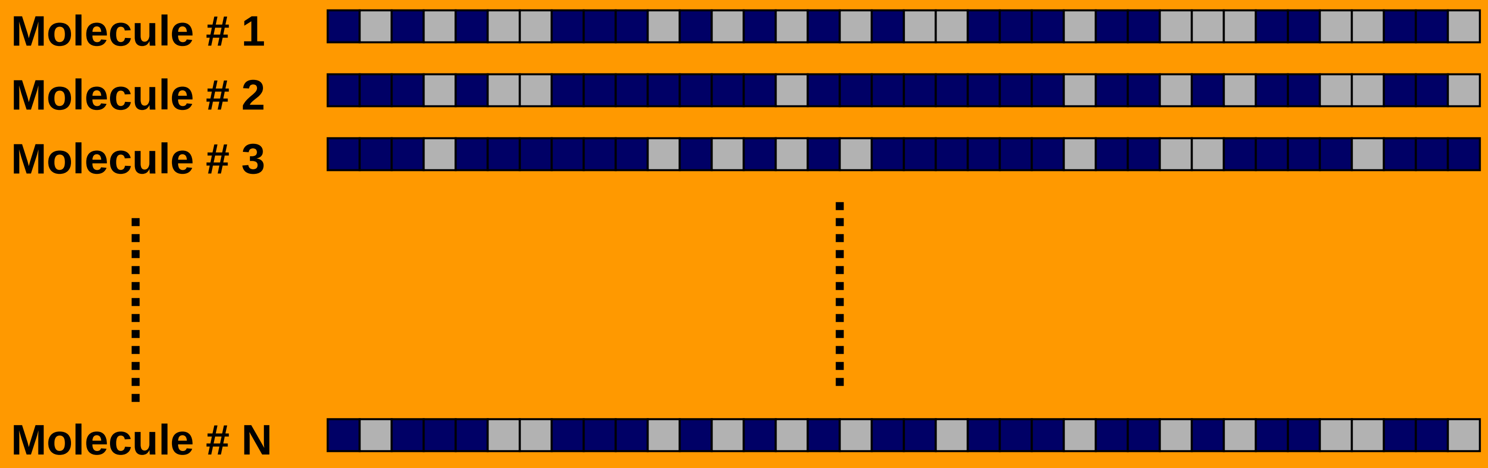
- Variable Fragment
- Source of Chemical Diversity
- Functional Fitness
- Product Cost

$$F = F_{\bullet} + F_{\bullet}$$


Structural Space
Functional Space


Functional Space
Traditional Solvents
SOLVSAFE Solvents
r
d1
d2
d3
d4
r = Efficacy of Function Radius
di = Functional Distance for Solvent i

Bit Strings



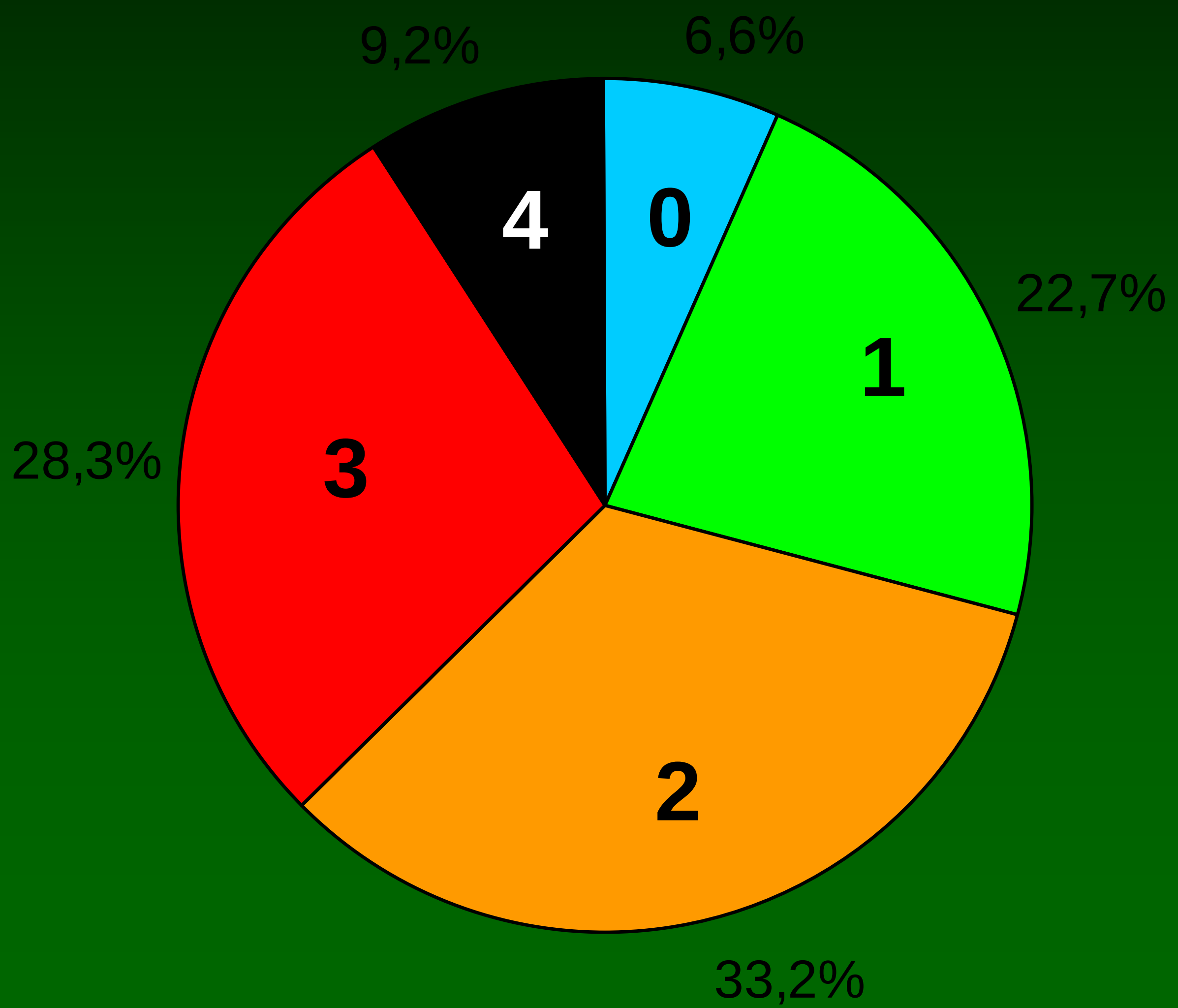
SOLVSAFE Design Strategy

- Design of Solvent Virtual Library
- Prediction of health hazardous characteristics.
- Prediction of efficacy of function.
- Synthesis.
- Characterization of physico-chemical properties.
- Experimental test of efficacy.
- Experimental measurement of toxicity.
- Validation of industrial processing and/or formulation.

Health Hazard Categories

Risk Level	Acute Health Hazards	Chronic Health Hazards
0	Harmless by experience (H2O, sugar, paraffin and similar).	
1	Irritant to eyes, skin and respiratory system. Ssubstances causing skin dryness or lung damage when swallowed.	Otherwise chronically affecting substances.
2	Harmful to health by inhalation, in contact with skin and if swallowed. Substances which may accumulte in breast milk. Substances causing burns and serious damage to eyes. Non toxic gases or vapors that may cause suffocation by air displacement.	Substances toxic to reproduction of category 3 which may cause impaired fertility and harm to the unborned child.
3	Toxic by inhalation, in contact with skin and if swallowed. Highly corrosive causing severe burns. Skin and respiratory tract sensitising substances	Substances toxic to reproduction of category 1 or 2. Carcinogenic and mutagenic substances of category 3. Substances with danger of cumulative effects.
4	Very toxic by inhalation, in contact with skin and if swallowed.	Carcinogenic and mutagenic substances of categories 1 or 2 causing cancer and heritable genetic damage.

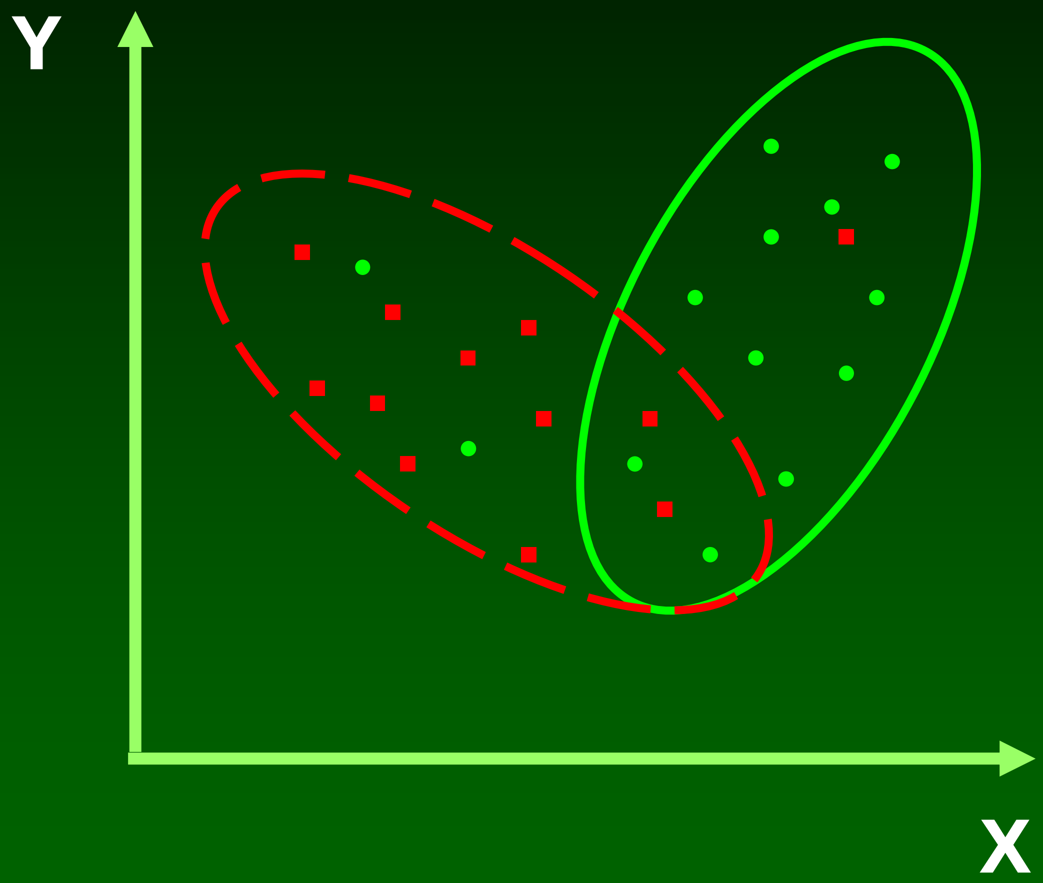
Population of Health Hazard Categories



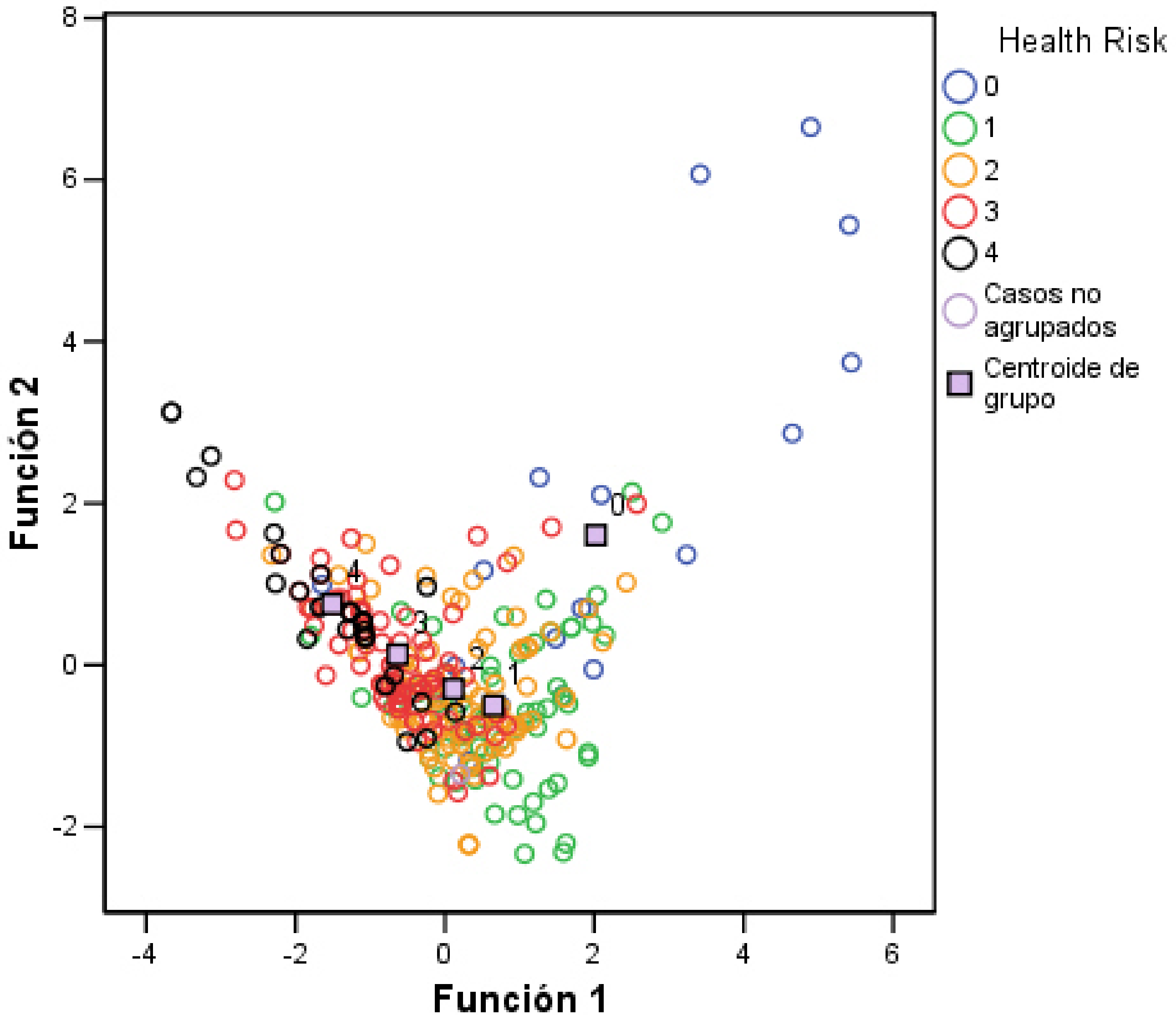
Model for Health Hazard Prediction

- Categorize molecules in health hazard risk levels.
- Training dataset of 300 molecules of known toxicity with molecular weights ranging from 18 to 426.
- Predictor variables based on molecular constitutional, topological and connectivity descriptors.
- Validation and test of predictive model.
- Estimation of risk level for SOLVSAFE solvents.

Basic Intuition of the Model



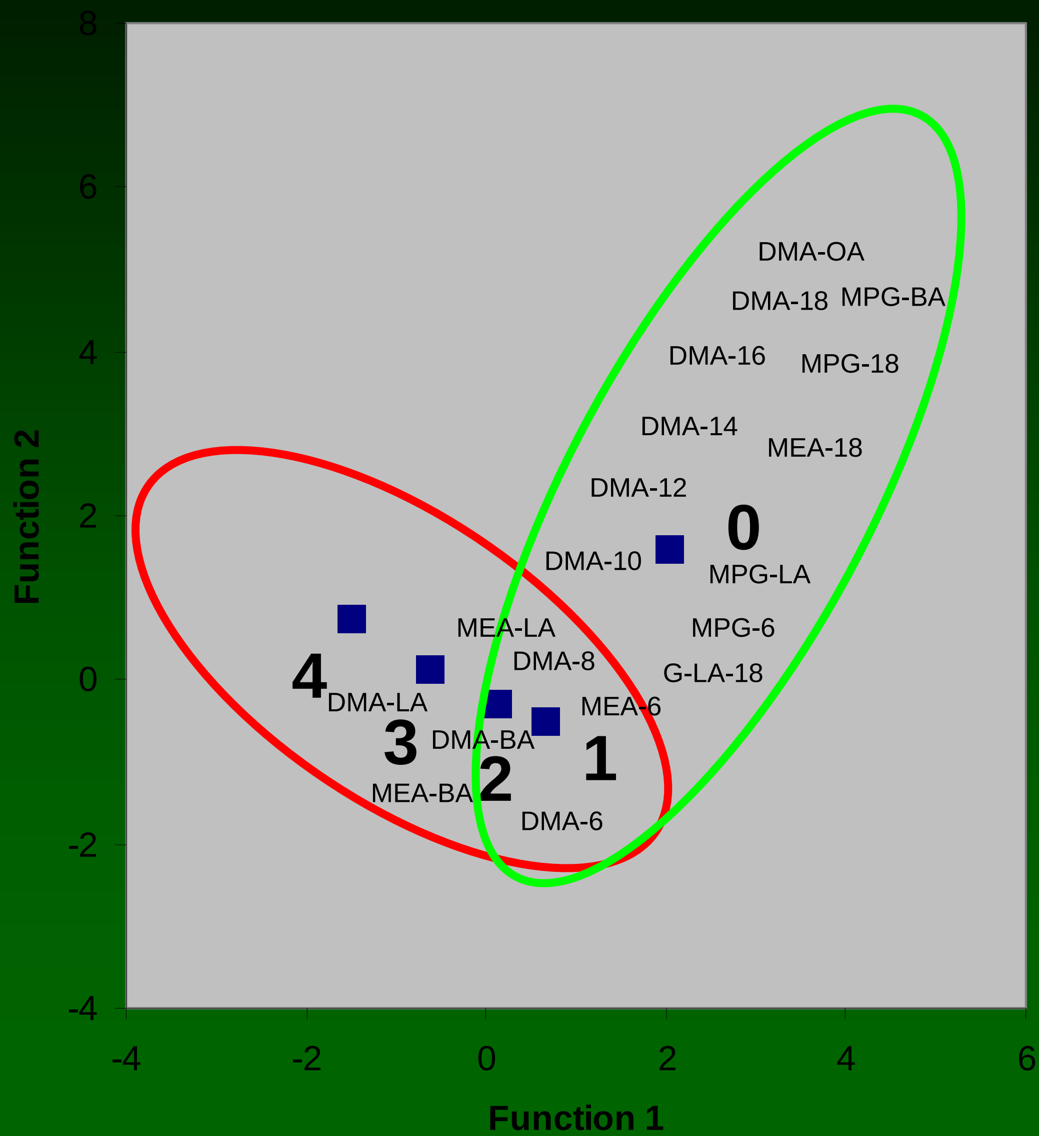
The ellipses show two possible decision boundaries. The green circles inside the red (dashed) ellipse are misclassified with low probability. The red squares inside the green ellipse are misclassified with low probability. Red squares and green circles in the intersection are misclassified with high probability.



Health Risk
0
1
2
3
4
Casos no agrupados
Centroide de grupo
Función 2
Función 1
8
6
4
2
0
-2
-4
-2
0
2
4
6

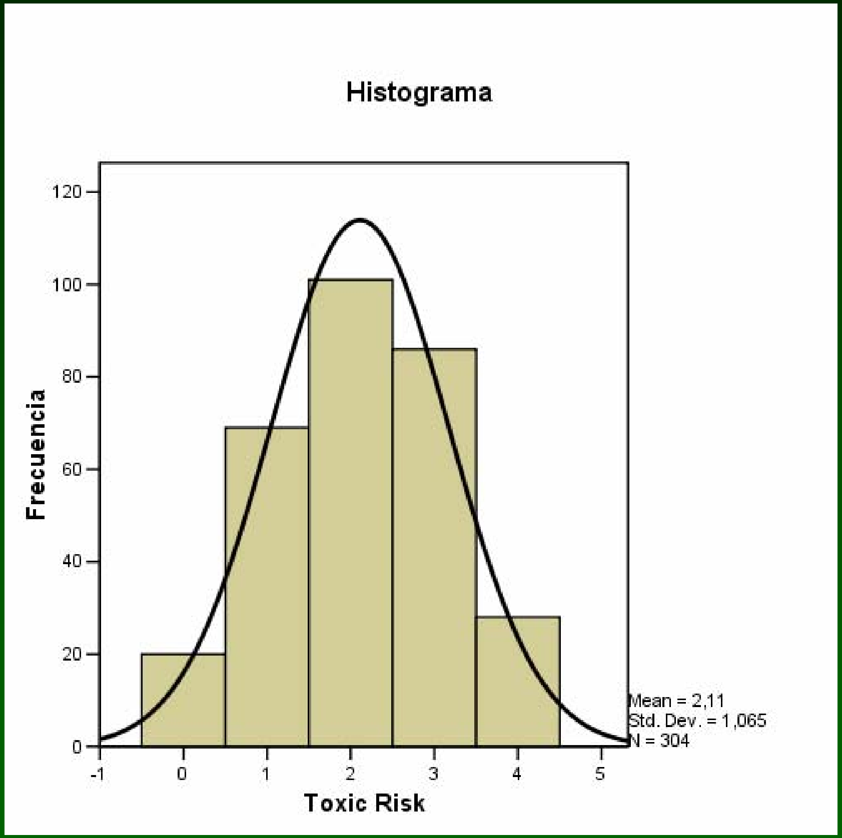
	Percentage of correct classifications	
Method	Non-toxic	Toxic
LDA	69	83
NEURAL NETWORK	58	100

Health Risk

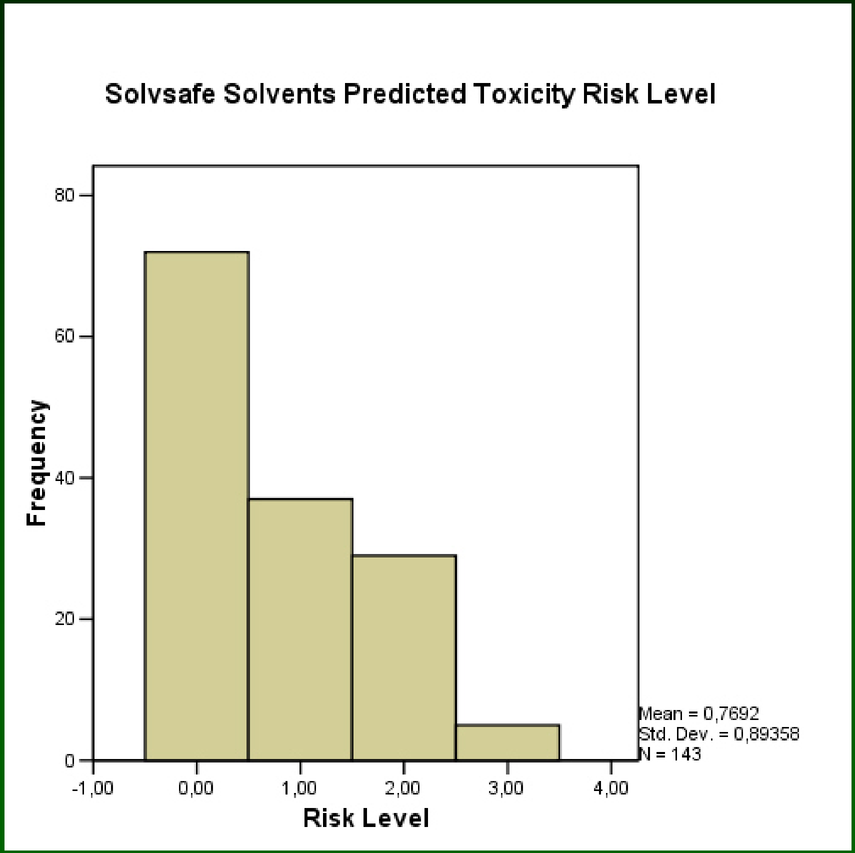


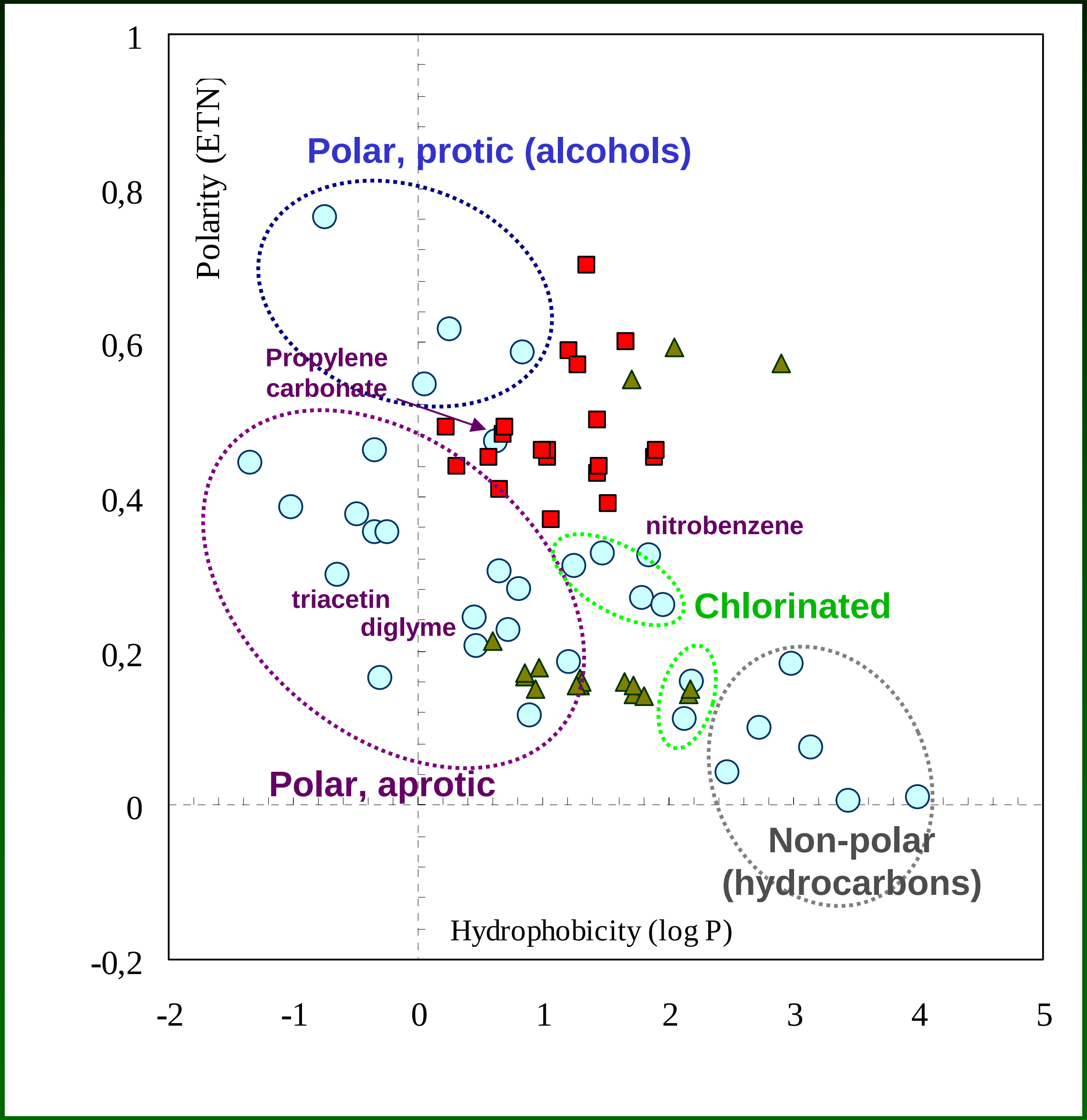
8
6
4
2
0
-2
-4
Function 2
-4
-2
0
2
4
6
Function 1
DMA-OA
DMA-18
MPG-BA
DMA-16
MPG-18
DMA-14
MEA-18
DMA-12
0
DMA-10
MPG-LA
MEA-LA
MPG-6
DMA-8
G-LA-18
4
DMA-LA
MEA-6
3
DMA-BA
1
2
MEA-BA
DMA-6

Traditional Solvents



SOLVSAFE

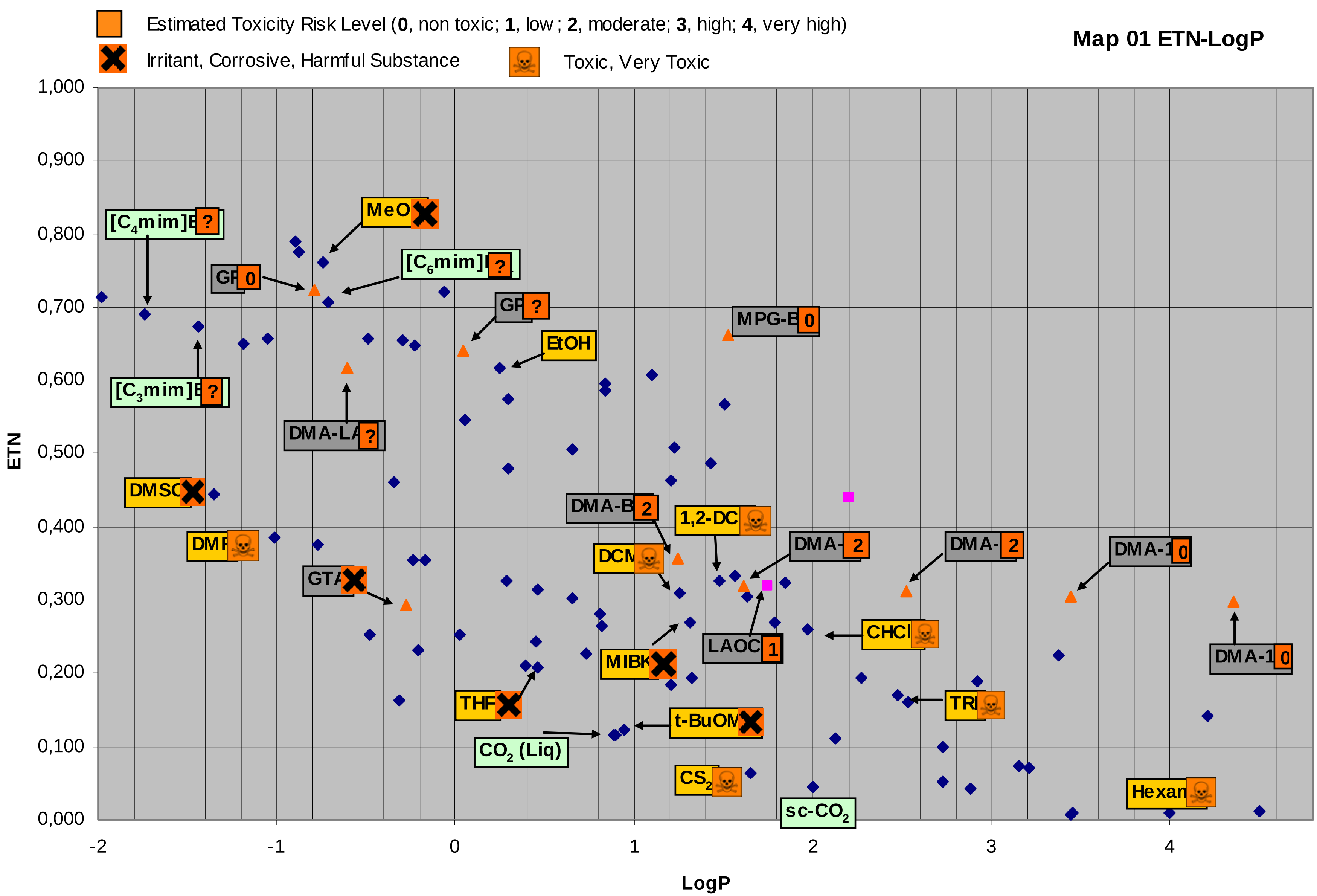




Glycerol diethers

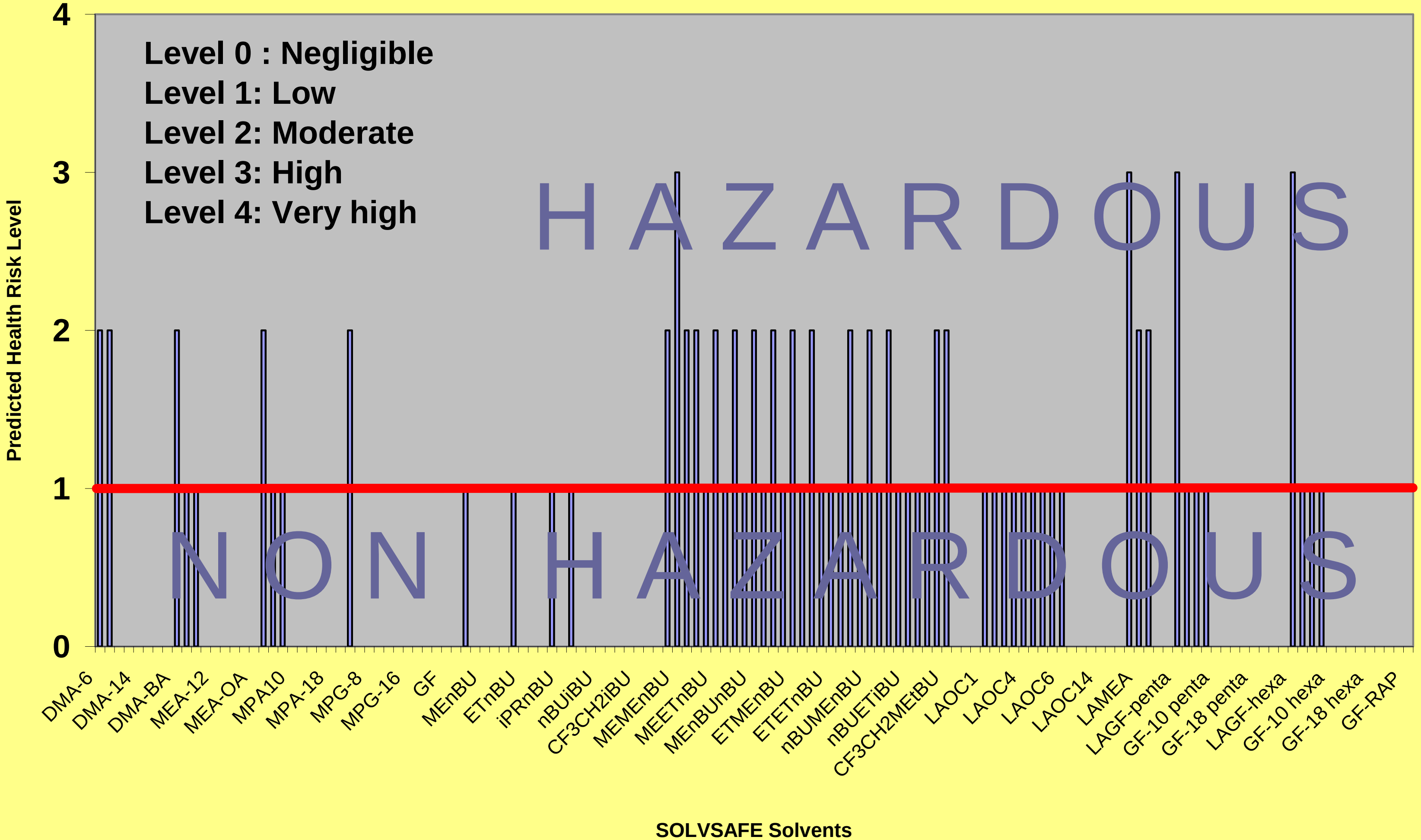
Glycerol triethers

1 - DMSO
2 - DMF
3 - Methanol
4 - Triacetin
5 - Acetonitrile
6 - 1,4-dioxane
7 - Acetone
8 - i-Propanol
9 - Propanol
10 - Diglyme
11 - THF
12 - Pyridine
13 - Ethyl acetate
14 - Cyclohexanone
15 - Butanol
16 - Diethyl ether
17 - Diethyl Carbonate
18 - Dichlorometane
19 - 1,2-dichloroetane
20 - 1,1,-dichloroetane
21 - Nitrobenzene
22 - Chloroform
23 - Benzene
24 -Toluene
25 - Bromobenzene
26 - p-Xylene
27 - Cyclohexane
28 - n-Hexane

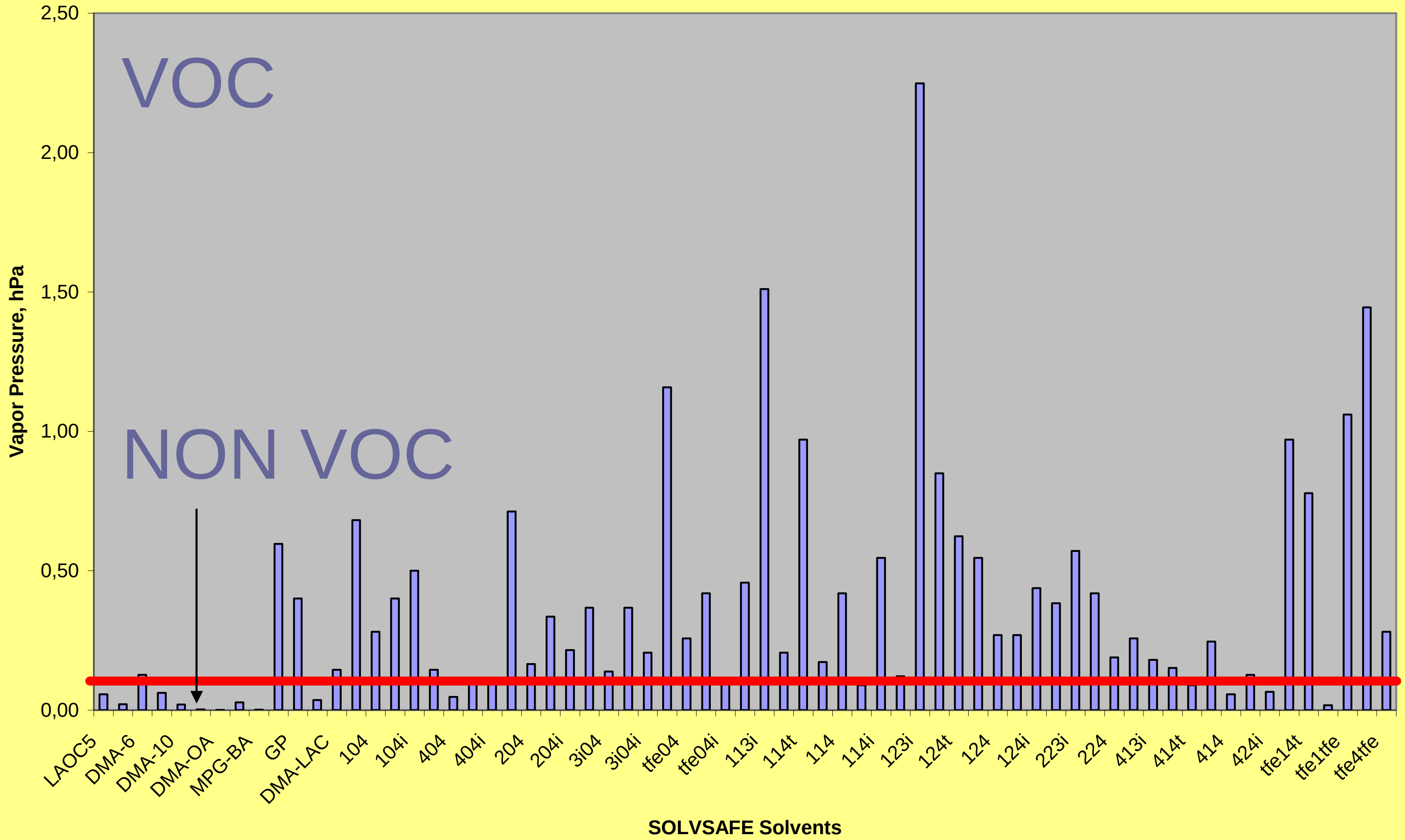


Estimated Toxicity Risk Level (0, non toxic; 1, low ; 2, moderate; 3, high; 4, very high)
Irritant, Corrosive, Harmful Substance
Toxic, Very Toxic
Map 01 ETN-LogP
ETN
LogP
[C4mim]B ?
MeO
GP 0
[C6mim]I ?
GP ?
EtOH
MPG-B 0
[C3mim]B ?
DMA-LA ?
DMSO
DMF
GTA
DMA-B 2
1,2-DC
DCM
DMA- 2
DMA- 2
DMA-1 0
DMA-1 0
CHCl
LAOC 1
MIBK
THF
t-BuOM
TRI
CO2 (Liq)
CS2
sc-CO2
Hexan

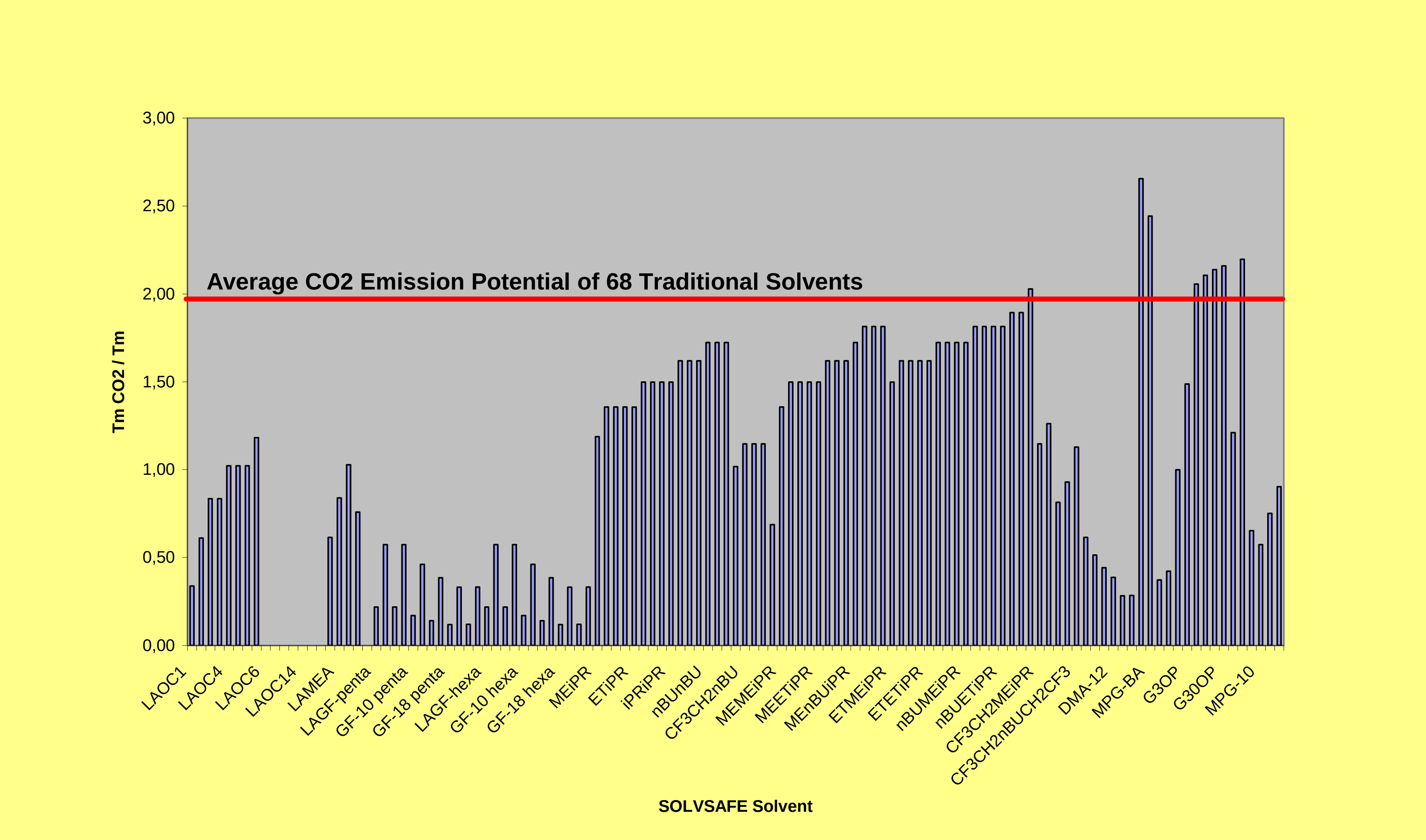
Predicted Health Risk Level



Vapor Pressure of SOLVSAFE Solvents



CO_2 Emission Potential of SOLVSAFE Solvents

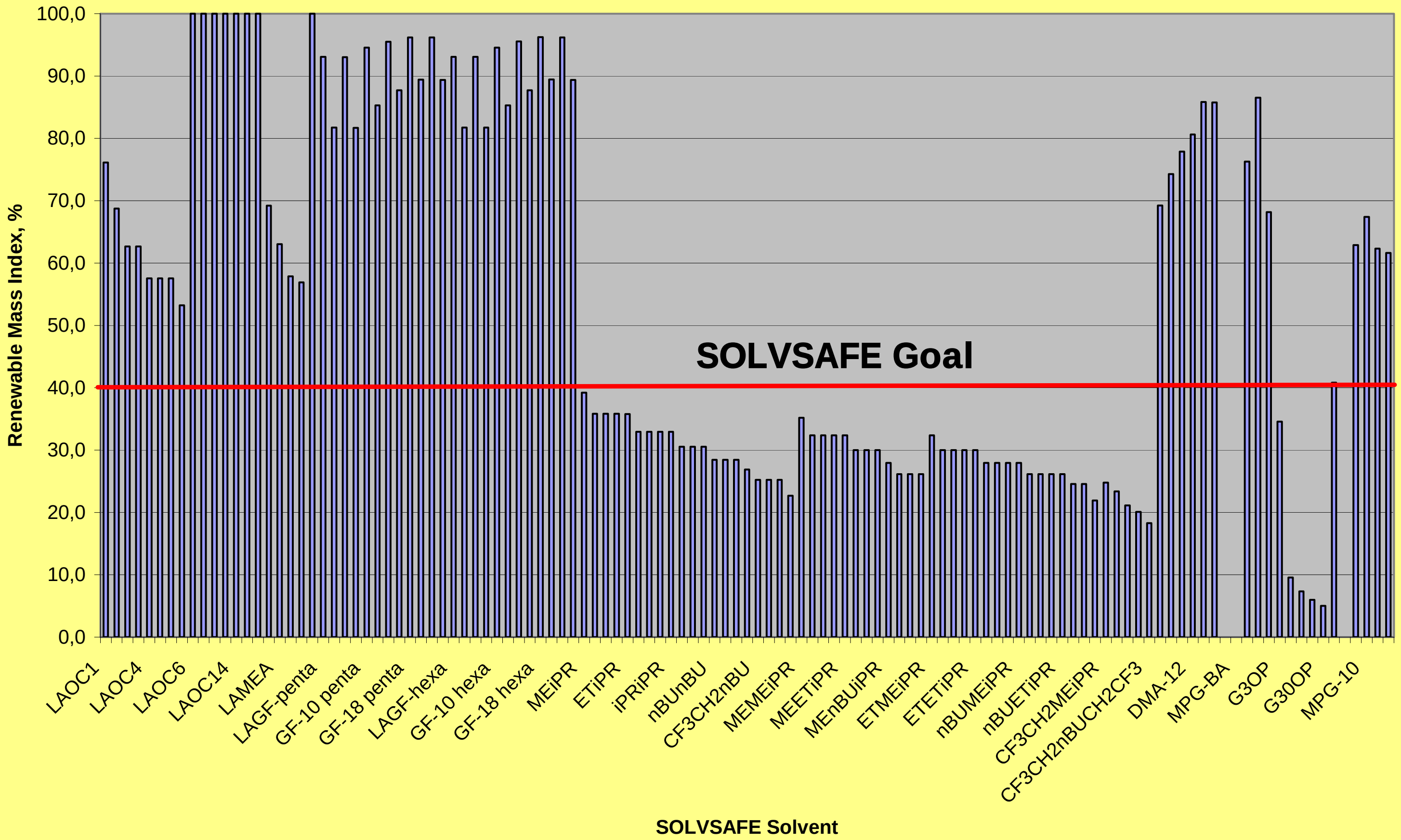


CO_2 Emission Potential

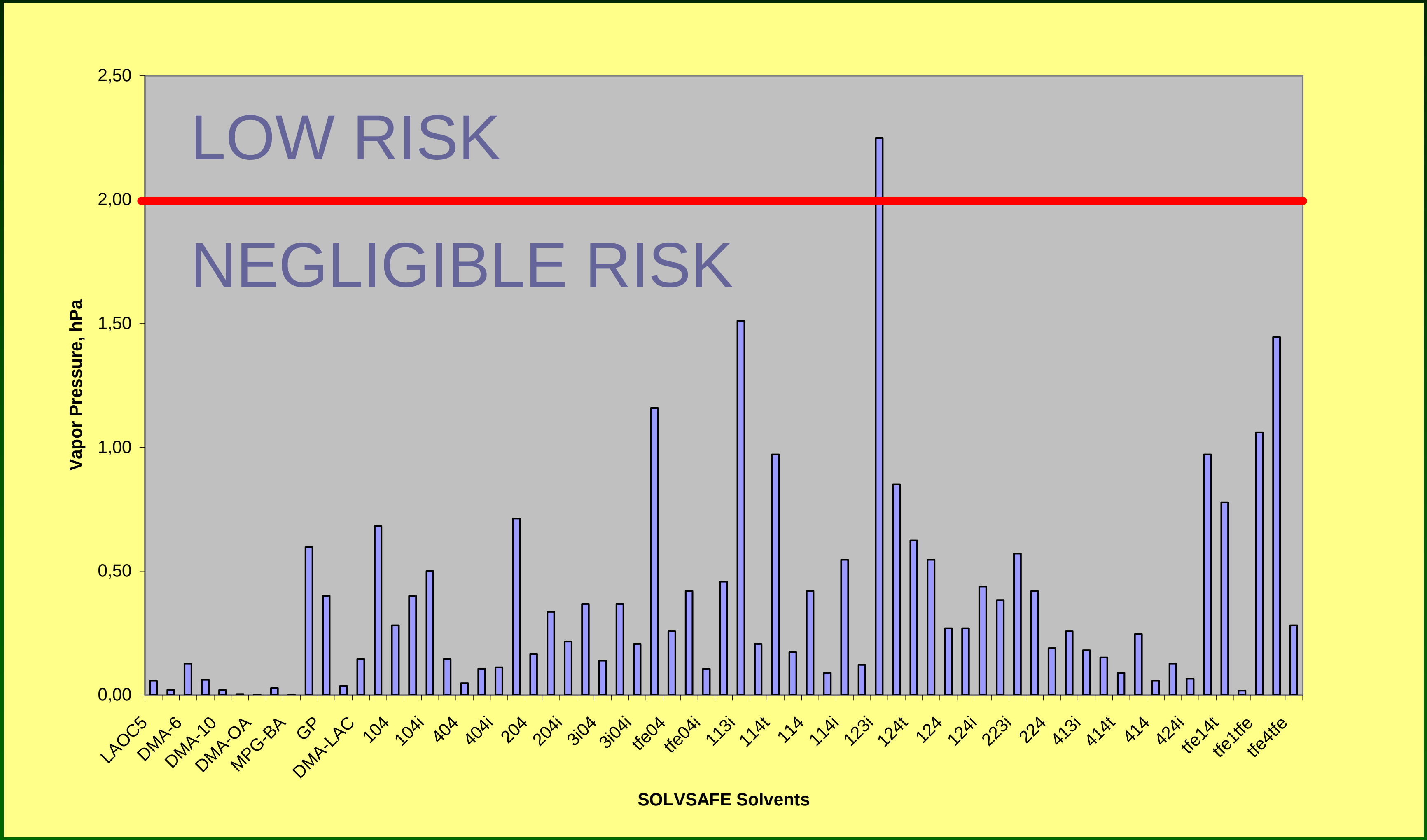
Mass of CO_2 emitted to the atmosphere upon complete oxidation (incineration, ultimate biodegradation, tropospheric oxidation, etc.) per unit mass of solvent.

$$\text{Solvent } CO_2 \text{ Emission Potential} = \frac{\text{Tm } CO_2}{\text{Tm Solvent}}$$

RMI of SOLVSAFE Solvents



Occupational Exposure Risk of SOLVSAFE Solvents



Metal degreasing

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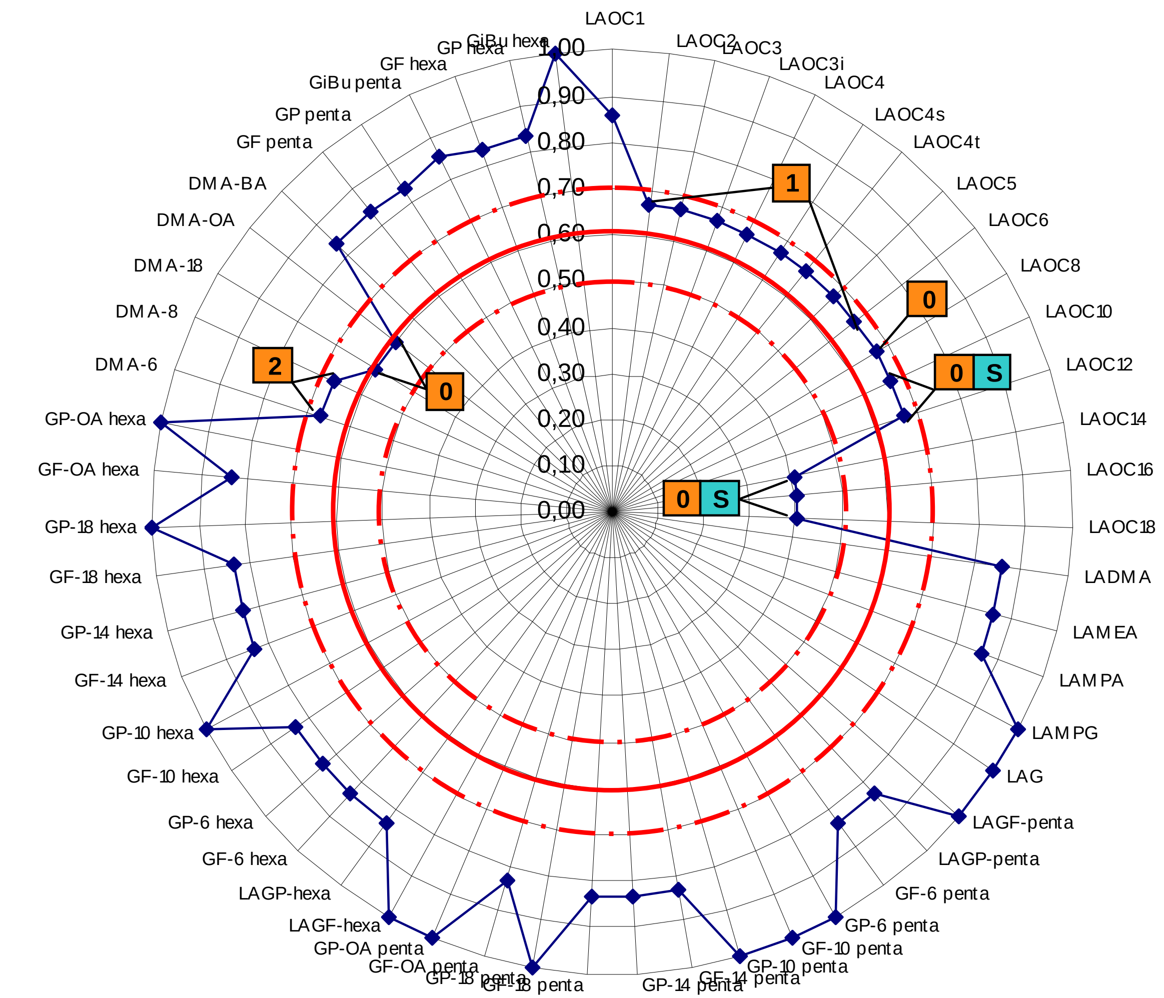
Challenges

- Approximately 15% of solvent use in Europe involves metal degreasing.
- The traditional industrial standard is trichloroethylene, a suspected carcinogenic substance.
- Aqueous based alternatives are not satisfactory.

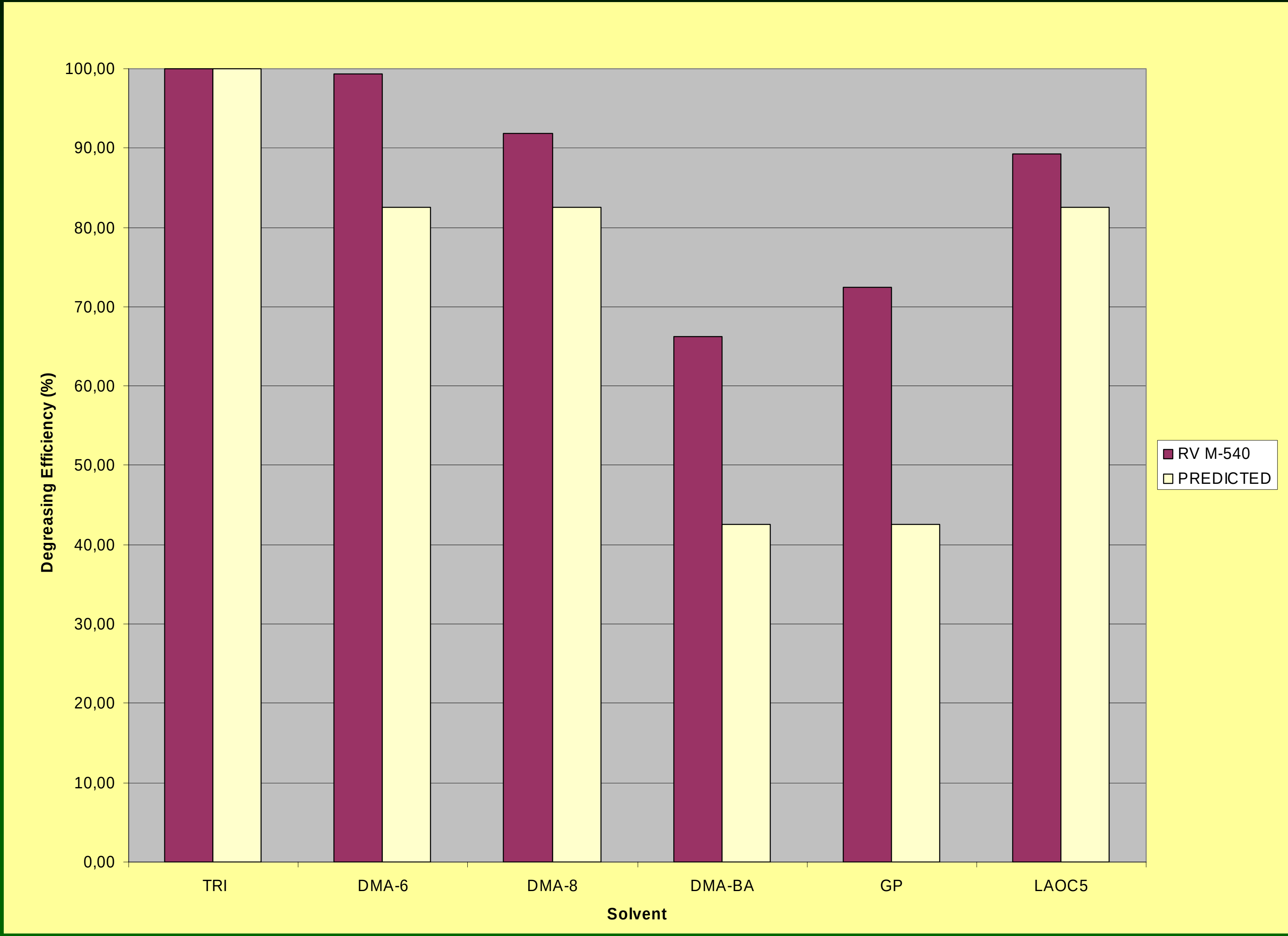
Efficacy of Function Prediction

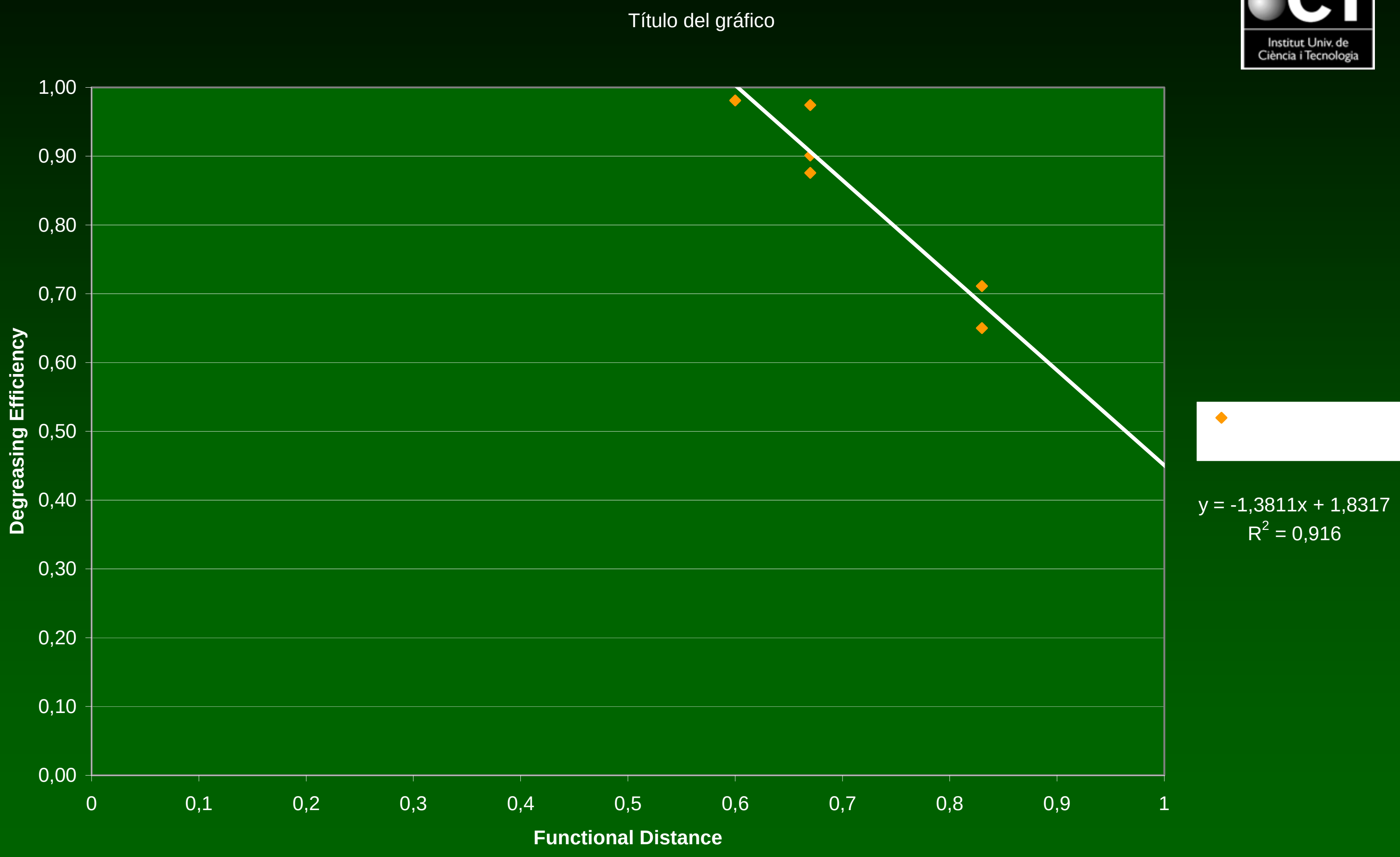


55 Solvent Candidates Predicted

(%)	Efficient	Efficient or very active	Active	Non-active
Non-toxic	5	24	36	20
Toxic	0	4	7	4

Experimental *vs* Predicted





Título del gráfico
1,00
0,90
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
Degreasing Efficiency
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
Functional Distance
y = -1,3811x + 1,8317
R2 = 0,916

Metal degreasing

Achievements

“Two solvents found to display excellent removal efficiencies for metal protectors at ambient temperature.

The low volatility of solvents assure a low VOC emission and make them suitable for immersion or spray open systems.

The design strategy involves the recovery of both solvent and rinsing water.”

- Dr. Julie Zimmerman. Center for Green Chemistry and Green Engineering at Yale.

- Mr. John Herrington. ITB, Inc. NASA TEERM Point of Contact.