PARIS III

User's Guide

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Introduction

PARIS III is a third generation Windows-based computer software to assist the design of solvents by estimating values of the solvent properties that characterize the static, dynamic, performance, and environmental behavior of the solvent. PARIS III works with single solvents or solvents with multiple components. PARIS III finds either a single chemical or a mixture that matches these estimated values within user-defined tolerances. PARIS III allows the user to search for replacement solvents with higher or lower values of any of these parameters to suit particular applications. Using PARIS III, one could, for example, design a chemical mixture that had an air toxicity index half the value of that in the currently used solvent while keeping other properties approximately constant or even improving them.

The static properties considered by PARIS III are molecular mass, molar volume, boiling point, vapor pressure, surface tension, and infinite dilution activity coefficients. The dynamic properties are viscosity and thermal conductivity. The performance requirement is the flash point. The environmental requirements are an air index and an overall environmental impact index. PARIS III screens solvents to ensure the replacements are only in liquid phase. Note that the user needs to know the composition of the solvent, but not the values for any of the properties since the program either has them in a database or has estimation methods for them.

PARIS III incorporates the PARIS III solvent database of chemical and physical properties with approximately 4000 chemicals. In addition, a suite of pure fluid and mixture property prediction routines is incorporated, including the UNIFAC group contribution and other well-established methods. To provide an indication of the potential environmental impact of a solvent formulation designed by PARIS III, a database of relative environmental impact scores has been created by drawing on government and non-government sources. Eight different categories of impact potential are considered:

Human Toxicity Potential by Ingestion
Human Toxicity Potential by Inhalation
Human Toxicity Potential by Dermal

Exposure
Aquatic Toxicity Potential
Global Warming Potential or **GWP**
Ozone Depletion Potential or **ODP**
Photochemical Oxidation Potential or **PCOP**
Acid Rain Potential or **Acidification Potential**

The user has wide latitude to weight the relative importance of these environmental effects to suit particular applications. All of these elements function under the guidance of a powerful solvent design algorithm to comprise a very versatile tool.

System Requirements

It is recommended that PARIS III be run on 32 bit or 64 bit Windows PC compatible computers with the Windows XP or Windows 7 operating system, and a minimum of 2.0 GB RAM and an Intel Xeon processor with a clock speed of 2.66 GHz or greater. Note that there are a number of algorithms in PARIS III that are computer resource intensive, so PARIS III will run faster on higher-end machines.

To use all the functionality of PARIS III, free hard disk space of about 10 GB is required.

Current Mixture Screen

Purpose and Description

On this screen, information about the current solvent mixture to be replaced is specified by the user. This information will be used by the program to replace the current solvent with a single chemical or a mixture of chemicals. The process of finding a replacement for a solvent using PARIS III begins with the user entering information about the current solvent's composition and the operating conditions at which the solvent is used. The operating temperature and pressure are used to determine the list of chemicals (from the complete list of chemicals in the PARIS III solvent database) in liquid phase at the specified conditions.

Buttons and Information

System Name
A name for the current solvent system is entered here. This name will be used to refer to the current system in the following screens.

Units: SI
If this option is selected, the SI system, whose three basic units are the meter (m), the kilogram (kg), and the second (s), will be used to display all the chemical properties. These will be used in internal calculations.

Unit: Common
If this option is selected, the most common units will be used to display each chemical property. The SI system will be used in internal calculations.

Units: US
If this option is selected, the American or FPS system, whose three basic units are the foot (ft), the pound (lb), and the second (s), will be used to display all the chemical properties. However, the SI system will be used in internal calculations.

Units: CGS
If this option is selected, the CGS system, which uses the centimeter (cm), gram (g) and the second (s), will be used to display all the chemical properties. However, the SI system will be used in internal calculations.

Temperature
The temperature at which the current system is used is specified here. Whatever units are selected, the default temperature of 25 °C is set.

Pressure
The pressure at which the current system is used is specified here. Whatever units are selected, the default pressure of 1.0 atm is set.

Chemical Display Options
To select the chemicals that are in the current solvent, the user has to select chemicals from the PARIS III solvent database. To facilitate searching and viewing, chemicals in the database can be viewed by searching for chemicals by name or by specifying chemicals by CAS number.

Search for Chemicals by Name
If this option is selected, the user can type the chemical name in the "Chemical Name Search" box. The program will automatically search through chemical names and bring up the closest matched chemical name in the "Chemicals" list box. The user can directly go to the "Chemicals" list box and select the chemical name. Any chemical within the database that has no chemical name on file is listed by CAS number.

Search for Chemicals by CAS Number
If the user knows the CAS number of their solvent, the user can search by supplying a CAS number (with the format *-xx-x). If this option is selected, the user enters the CAS number of the chemicals in their solvent system. The program will automatically search the CAS Numbers for you and bring up the closest matched CAS Number in the "Chemicals" list box. The user can directly go to the "Chemicals" list box and select the chemical by CAS Number.

Mixture list

Chemicals present in the current solvent system are to be specified here. Chemicals can be selected by clicking on the chemical in the Chemicals list and then clicking the > Add button to copy the chemical by name to the Mixture list. A maximum of four chemicals can be specified in one formulation.

Mixture Percentage Options

Wt% can be changed to Mol% by clicking on this button.

Option: Wt%

The user can enter the composition on a weight % basis or on a mole % basis. The weight % of a chemical in the current solvent system is specified here. If the total weight % of all the components in the Mixture list is not 100%, an error message is displayed when leaving this screen.

Option: Mol%

The user can enter the composition on a weight % basis or on a mole % basis. The mole % of a chemical in the current solvent system is specified here. If the total mole % of all the components in the Mixture list is not 100%, an error message is displayed when leaving this screen.

[Ref](#)

When this button is clicked, information on the properties of the chemical selected in the Chemicals list is displayed on a popup screen. The source for data displayed in the reference screen is the PARIS III solvent database.

Chemicals

The database of chemicals contains all the liquid chemicals included in the PARIS III solvent database. These chemicals can be selected as components of the current solvent system.

> Add

When this button is clicked, the selected chemical from the "Chemicals" list is added to the Mixture list. Duplicate entries are not allowed in the Mixture list.

< Remove

When this button is clicked, the selected chemical from the Mixture list is removed.

Impact Factors Screen

Purpose and Description

On this screen, impact factors for each potential environmental impact are specified by the user. In this step, the user assigns an impact factor to each of the environmental impact categories to suit their particular application. Higher impact factors should be placed on categories that are more important to the user. These factors are used in subsequent steps of the program to rank and select chemicals to be replacements. Eight categories of environmental impacts are included in PARIS III to estimate the potential environmental impact of a solvent system.

Buttons and Information

User Assigned Weights

The weight α_j for each of the eight categories expresses the importance of that impact category relative to the other impact categories. Initially, PARIS III assigns a default value of 5 to all of the weighting factors. This implies that all of the impact categories are equally important. The user can override the default values and assign a more appropriate weight. This allows the environmental impact to be customized to the environmental concerns of a particular facility. For example, if the chemical process facility is located in an area where air pollution is a serious concern, then the user may decide to raise the weighting factor for the Photochemical Oxidation Potential (PCOP) above its default value. If the process plant is discharging to a water body, then the user may choose to raise the value of the factor for Aquatic Toxicity Potential above its default value. If any one of the impact categories is deemed irrelevant for a particular design, the weight can be lowered to a value that is more representative of that concern, possibly a value of 0. For example, someone considering a process that operates in the middle of a desert may not be as concerned with the emission of chemicals that have Acid Rain Potential (ARP) and would accordingly decrease that weight.

The Environmental Impact categories are:

Human Toxicity Potential by Ingestion
Human Toxicity Potential by Inhalation
Human Toxicity Potential by Dermal Exposure
Aquatic Toxicity Potential
Global Warming Potential or GWP
Ozone Depletion Potential or ODP
Photochemical Oxidation Potential or PCOP
Acid Rain Potential or Acidification Potential

Default

Click on this button to use the default weight for all environmental impact categories.

User Assigned Weights - Up and Down Arrows

The Up and Down arrows are used to assign a weight from 0 to 10 for an environmental impact criterion. The higher the number is, the greater the importance given to that environmental impact category in finding replacements.

Chemicals

The names of the solvents in the original mixture are given in each row.

Wt%

In this column, the weight percentage of each solvent in the original mixture is given in each row. The total weight percentage of the solvents is given in the last row and should always be 100%.

Environmental Impact Categories

The normalized environmental impact value of each solvent is given under each respective category (e.g., Human Toxicity Potential by Ingestion, Human Toxicity Potential by Inhalation) and does not change.

Totals

Each value in the final column represents the total environmental impact contributed by each solvent in the mixture. These solvent impacts in the final column add up to give the total

environmental impact of the whole mixture that is shown in the bottom right corner of the table. This is the Environmental Index of the solvent mixture to be replaced.

Similar to the layout described above, each value in the bottom row represents the total environmental impact for each category of environmental impacts multiplied by impact factors set by the user. As before, a sum of the values across the bottom row is equal to the Environmental Index of the solvent mixture to be replaced.

Physical Properties Screen

Purpose and Description

The purpose of this screen is to show how the physical properties of possible solvent replacements compare to the properties of the original solvent mixture. This includes a listing of either single solvent replacements or mixture solvent replacements.

Buttons and Information

Property
These are the names of the physical and environmental properties for which data is displayed.

Tolerance (%)
The tolerance percentage is used to calculate the lower and upper bounds a replacement solvent property might have from the desired property of the original mixture. This tolerance percentage may be altered from the default values to modify the ranking of replacement solvents.

Lower
This is a lower bound for the replacement solvent's property.

Desired
This is the desired value of the replacement solvent's property. By default, it is the property value of the original solvent mixture, but may be changed.

Upper
This is an upper bound for the replacement solvent's property.

Replacement
This is the property value of the selected solvent replacement. Green values are within the bounds of the desired value, and red values are outside the bounds of the desired value.

Units
The set of property units chosen from the Current Mixture Screen will be displayed in this column.

Single/Mixture Solvent Replacements
In this listing, the names of possible replacement solvents are given and are ranked by those solvents whose properties are closest to the properties of the original solvent mixture. The integer number that appears before the solvent name is the total number of physical and chemical properties that are within bounds of the desired property value. Clicking on a solvent's name in this list will display the possible replacement solvent's properties in the replacement column.

Single/Mixture button
Once an analysis of possible solvent mixtures has been performed, the Mixture button will be available to view ranked solvent mixtures as possible replacements for the original solvent mixture. If the Mixture button is selected, a table will appear below the replacement list showing the weight percentage of each component in the solvent mixture selected

Activity Coefficients Screen

Purpose and Description

The purpose of this screen is to show how the chemical properties of possible solvent replacements compare to the chemical properties of the original solvent mixture. This includes a listing of either single solvent replacements or mixture solvent replacements.

Buttons and Information

Substance Name
These are the chemicals that act as solutes for infinite dilution activity coefficients.

Tolerance (%)
The tolerance percentage is used to calculate the lower and upper bounds a replacement solvent property might have from the desired property of the original mixture. This tolerance percentage may be altered from the default values to modify the ranking of replacement solvents.

Lower
This is a lower bound for the replacement solvent's property.

Desired
This is the desired value of the replacement solvent's property. By default, it is the property value of the original solvent mixture, but may be changed.

Upper
This is an upper bound for the replacement solvent's property.

Replacement
This is the property value of the selected solvent replacement. Green values are within bounds of the desired value, and red values are outside the bounds of the desired value.

Single/Mixture Solvent Replacements
In this listing, the names of possible replacement solvent are given which are ranked by those solvents with properties closest to those of the original solvent mixture. The integer number that appears before the solvent name is the total number of physical and chemical properties that are within bounds of the desired property value. Clicking on a solvent's name in this list will display the possible replacement solvent's properties in the replacement column.

Single/Mixture button
Once an analysis of possible solvent mixtures has been performed, the Mixture button will be available to view ranked solvent mixtures as possible replacements for the original solvent mixture. If the Mixture button is selected, a table will appear below the replacement list showing the weight percentage of each component in the solvent mixture selected.

Tolerance Scale Factor
By shifting this scale factor, all tolerances can be increased or decreased by the same factor. This changes all lower and upper bounds, and consequently how chemicals are ranked.

Solvent Mixtures Screen

Purpose and Description

The purpose of this screen is to perform a search to find out if the solvents selected may be mixed together in the right proportions to come close to imitating the properties of the original solvent mixture, but have less environmental impact. This is achieved by including in the search only solvents that are greener than the original solvent mixture, and mixing various proportions of these chosen solvents together until the total search has been completed.

Buttons and Information

Primary Solvent List

This is the ranked list of single solvents from the Physical Properties Screen and the Activity Coefficients Screen. They are to be used as the primary solvent of the mixture being investigated. Any number of solvents from this list may be selected and used in the mixture search.

Secondary Solvent List

This is the ranked list of single solvents from the Physical Properties Screen and the Activity Coefficients Screen. They are to be used as the secondary solvent of the mixture being investigated. Any number of solvents from this list may be selected and used in the mixture search.

Tertiary Solvent List

This is the ranked list of single solvents from the Physical Properties Screen and the Activity Coefficients Screen. They are to be used as the tertiary solvent of the mixture being investigated. Any number of solvents from this list may be selected and used in the mixture search.

Best Solvents

This chooses the 10 highest-ranking solvents to be used in the search.

All Green Solvents

This chooses all of the ranked solvents that are greener than the original solvent mixture to be used in the search.

Initial Solvents

This chooses all of the solvents from the original solvent mixture to be added to the list of solvents that are used in the search.

All Solvents

Sometimes it may be useful to add small portions of solvents that are not necessarily greener than the original solvent mixture into the solvent mixture search. Unchanged, this would add all solvents in the PARIS III solvent database into the search, but only a few should be highlighted and selected.

Mass Ratios

Only the selected mass proportions will be used in the solvent mixture search.

Find Mixtures

Once the solvents and mass ratios of the combinatorial search have been chosen, the search is started by choosing this option from the **Action** submenu on the **Main** menu bar.

Stop Mixtures

After the parameters of the combinatorial search have been chosen and the search has been started, the search can be stopped by choosing this option from the **Action** submenu on the **Main** menu bar. This will stop any further search and display only the best results that have been achieved so far.

Progress Bar

The progress bar on the bottom of the screen displays how the search is progressing.

Best Mixtures List

After the combinatorial search has been performed, the 250 best mixtures are ranked by how close the properties of this mixture are to the properties of the original solvent mixture. The integer number that appears before the mixture's name is the total number of physical and chemical properties that are within bounds of the desired property value. When a mixture is selected, the components and proportions are shown in the table below the Best Mixtures list. The values of the properties of this mixture are listed in the Replacement column on the Physical Properties Screen and the Activity Coefficients Screen.

Reference Information

Purpose and Description

This screen displays information about the selected chemical contained in the PARIS III solvent database.

Buttons and Information

Many formal pieces of information about the solvent selected, such as the chemical name, formula, CAS number, structure, and synonyms, are included. In addition, multiple static and thermodynamic properties of the solvent are included.

Press the OK button to close the window and return to the Current Mixture Screen.

Tutorial

From the PARIS III website, download and save the file ParisIII_w32.zip or ParisIII_w64.zip depending on whether you are using a Windows 32 bit or Windows 64 bit operating system. Using decompression software, unzip this file and create the ParisIII directory.

In the directory where ParisIII is unzipped, there should be a ParisIII file with an Eiffel tower icon. Click on this file. An initial PARIS III Window pops up with a picture of the Eiffel tower and several buttons. One button is the "Start" button. Click on this button. The main screen of PARIS III should open up with the "Current Mixture" screen selected.

The main screen of PARIS III has five tabs that may be selected to open various screens. These are the "Current Mixture" tab, the "Impact Factors" tab, the "Physical Properties" screen, the "Activity Coefficients" tab, and the "Solvent Mixtures" tab. In addition, there are four main menu options. The options are "File," "Edit," "Action," and "Help". From the Current Mixture Screen, choose the "File" main menu option.

A submenu drops down from the "File" option with many selections. Choose the "Open" option. A window pops up with a selection of files from the directory where PARIS III was started. Select the file "RollerWash.xml" and the file name should appear in the popup window. Then, click on the open button in the popup window. The popup window disappears and information from that file appears on the "Current Mixture" screen.

The "RollerWash.xml" file selected contains information about a common solvent mixture used to clean ink from the rollers of a printing machine that prints the labels of products being marketed. Unfortunately, this common solvent mixture has a bad effect on the environment when disposed of. The question examined by PARIS III is "Can a similar solvent mixture be found that cleans ink from the rollers, but is not as harmful to the environment when released?" The chemical components of the solvent mixture used are listed in the Mixture list on the bottom of the Current Mixture Screen.

When the "Impact Factors" tab is selected, the

Impact Factors Screen opens up with the impacts these components have on eight different categories of environmental impacts. The impact factors with a default value of 5 for each environmental category are listed across the top of the screen. These may be changed by the user to better reflect the environment where the replacement solvent mixture is to be used. But, leave these impact factors at their default values for now. The number appearing in the lower right corner is the Environment Index of the original solvent mixture to be replaced. Continue to the next screen by selecting the "Physical Properties" tab.

The Physical Properties Screen displays the properties of the original solvent mixture, mostly under the "Desired" column. The upper and lower bounds of how close the replacement solvent mixture should be to the desired property value are represented by the "Upper" and "Lower" columns. These upper and lower bounds are calculated by the default tolerance percentages listed under the "Tolerance (%)" column. These default values may be modified, but leave them the same for now. Note that, for safety, the desired Flash Point value of the original solvent mixture appears as a lower bound for replacement mixtures. Similarly, the Environmental Index and the Air Index of the original solvent mixture appear as an upper bound for the replacement mixtures to ensure that only greener solvents are considered as replacements.

On this screen, the Single Solvent Replacement box shows a ranked list of all solvents within the PARIS III solvent database that are greener than the original solvent mixture. These are ranked by how close their properties are to those of the original solvent mixture. The replacement properties that are within the bounds are shown in green, and the properties outside the bound are shown in red. The integer that appears in the list before the replacement name is a count of the total number of properties shown in red on this screen and on the Activity Coefficients Screen.

The next screen appears by selecting the "Activity Coefficients" tab. This screen is very similar in function to the previous screen except that infinite dilution activity coefficients are displayed here instead of physical properties. The solutes of the infinite dilution activity

coefficient are listed under the Substance Name column. Note the integer that appears before the name of the selected solvent replacement is the total number of the replacement properties that show in red on the two screens.

Selecting the final tab brings up the Solvent Mixtures Screen. The solvents that appear in the solvent lists are the same ranked list of solvents from the two previous screens. Initially, the primary solvents come up with the 10 best solvents selected. By clicking on the Secondary button, the secondary solvents are brought up, again with the 10 best solvents selected. Notice how a selected list of mass ratios was brought up. The search for solvent mixtures that could make good replacements is a combinatorial search among all the selected solvents and mass ratios. By clicking on the Action menu and selecting the "Find Mixtures" option, the search is started.

After the search, the 250 best-ranking replacements are shown in the Best Mixture list. Notice how the integer number that appears before the best mixture name has changed from a 7 on the previous single solvent replacement list to a 4 on the solvent mixture replacement list. This means that only four properties are outside of the bounds for all of the physical and chemical properties of the original solvent mixture. By clicking on the Tertiary button, and selecting the "Find Mixtures" option under the Action menu, the next mixture search is started. After this search, the best mixture has only three properties outside of bounds of the original solvent mixture.

We might improve the Best Mixtures list by selecting more solvents to be used in the search. Clicking on the Tertiary button again turns it off, but clicking on "All Green Solvents" under the Secondary button enhances the selection of solvents used as secondary solvents in the search. By selecting the "Find Mixtures" option under the Action menu, the search starts again with these solvents and mass ratios selected. This combinatorial search will take longer because of the greater number of combinations selected. Notice that after this search the best mixture has only two properties outside of bounds of the original.

By going back to the Activity Coefficients Screen, the infinite dilution activity coefficients

that are outside of the bounds of the original solvent mixture are shown in red. By going to the Physical Properties Screen, the properties are all shown to be within bounds. We can select various mixtures in the Solvent Replacement list and compare how the Environmental Index and the Air Index are reduced. The eighth solvent mixture down in the list reduces these indexes significantly, while keeping most of the properties within range.

With the eighth mixture selected, the Molecular Mass is outside of bounds. If it is not important that the replacement mixture's molecular mass is close to the molecular mass of original mixture, the tolerance percentage can be increased from 11.0 to 22.0. Then, clicking on the desired value changes the lower and upper bounds and brings the molecular mass within the bounds. Likewise, after proceeding to the Activity Coefficients Screen and changing the same mixture's tolerance for the solute diethyl ether from 30.0 to 43.0 and changing the tolerance for the solute water from 30.0 to 60.0, all properties are within bounds.

All of these changes can be seen by going back to the Solvent Mixtures Screen, clicking on the secondary button, and selecting the All Green Solvents button. By performing the search again, many possible solvent mixture replacements are found that are all within the bounds of the original solvent mixture. It only remains to go back to the Physical Properties Screen to compare and write down those solvent mixtures that reduce the environmental indexes the most. These are the less harmful solvent mixtures that may then be substituted in industrial processes for the original mixture to verify they make good solvent replacements.

Appendix 1: Definition of Properties and Chemical Terms

Molecular Weight – Is the sum of the atomic weights of all the atoms in a molecule.

Mole - The SI unit of amount of substance. It is equal to the amount of substance that contains as many elementary units as there are atoms in 0.012 kg of carbon-12. The elementary units in the PARIS III program are molecules.

Mole Fraction – This is the fraction of total moles that each component of a mixture has. The mole fraction of component A is given by: $x_A = n_A/N$, where n_A is the number of moles of A and N is the total number of moles of all components in the mixture.

Molar Volume - The volume occupied by one mole of a substance. The density is equal to 1.0 / (molar volume).

Weight Fraction – This is the fraction of total mass that each component of a mixture has.

Boiling Temperature - Is the temperature at which a pure chemical boils. In PARIS III, the boiling temperature of a mixture is set equal to the bubble temperature, which is the temperature at which gas bubbles form in the liquid.

Vapor Pressure - The pressure exerted when a solid or liquid is in equilibrium with its own vapor. The vapor pressure is a function of the substance and temperature.

Surface Tension - Due to molecular attractions, two fluids in contact exhibit tension. For example, a liquid with high surface tension will not readily mix with another liquid.

Viscosity - All fluids possess a definite resistance to change of form. This property, a sort of internal friction, is called viscosity.

Thermal Conductivity – This is the property of how easy it is for a material to conduct heat. It is given by the time rate of transfer of heat by conduction, per distance per difference of temperature.

Flash Point - The temperature at which the vapor above a volatile liquid forms a combustible mixture with air. At the flash point, the application of a naked flame gives a momentary flash rather than sustained combustion.

UNIFAC - Acronym for Universal Functional Activity Coefficient. It is a method for estimating the effect of non-idealities on mixtures from the contributions of the groups making up the molecules present in a mixture. This method is widely used.

Activity Coefficient – Is a factor that characterizes the non-ideality of a mixture. It depends on temperature, pressure, mixture composition, and the forces between the molecules. The activity coefficient for a chemical A at infinite dilution in a solvent or mixture is calculated by letting the mole fraction of the chemical A go to zero.

Infinite Dilution Activity Coefficient - The infinite dilution activity coefficient represents the molecular interactions between one molecule of each of the specified ten chemicals and the molecules in the solvent. Each of the ten chemicals is a prototype of a commonly used family of chemicals. The infinite dilution activity coefficient is used to match the molecular behavior of proposed replacements to that of the original solvent. This helps to ensure the replacement will perform as well as the original.

PARIS III Solvent Database - Organized by the U.S. Environmental Protection Agency and represents an effort dedicated to the compilation, measurement, and evaluation of physical property data for industrially important chemicals. The database contains physical, thermodynamic, and transport property data for about 4000 of the most commonly used chemicals. This compilation contains critically evaluated, internally consistent data.

Appendix 2: Definition of Environmental Indexes and Air Indexes

Eight environmental impact scores $\varphi_{i,j}$:

Human Toxicity Potential by Ingestion

Human Toxicity Potential by Inhalation

Human Toxicity Potential by Dermal

Exposure Aquatic Toxicity Potential

Global Warming Potential or **GWP**

Ozone Depletion Potential or **ODP**

Photochemical Oxidation Potential or **PCOP**

Acid Rain Potential or **Acidification Potential**

Normalized environmental impact score $\overline{\varphi_{i,j}}$:

Assuming that a score of 1 is average for all the chemicals, the normalized environmental impact scores are calculated from:

$$\overline{\varphi_{i,j}} = \frac{\varphi_{i,j}}{\frac{1}{N}\sum_{k=1}^{N}\varphi_{k,j}} \qquad (1)$$

Where $\overline{\varphi_{i,j}}$ is the normalized environmental impact score of chemical *i* for impact *j*, $\varphi_{i,j}$ is the environmental impact score of chemical *i* for impact *j*, and N is the total number of non-zero impacts for chemicals.

Environmental Index – Is the overall relative measure of the potential impact of a chemical or a mixture on human health and the environment. This includes all of the eight impact categories mentioned above. For a pure chemical *i*, it is calculated from:

$$\Psi_i = \sum_{j=1}^{8}\sigma_j\overline{\varphi_{i,j}} \qquad (2)$$

Where Ψ_i is the environmental index of

chemical *i*, and the summation is taken over the eight categories of impacts in PARIS III, α_j is the user-assigned weight of impact *j* independent of chemical *i*, and $\overline{\varphi_{i,j}}$ is the normalized impact score of chemical *i* for impact *j*, as calculated by equation (1).

For a mixture, a weight fraction averaged index is calculated from:

$$\Psi_M = \sum_i W_i\Psi_i = \sum_i W_i\sum_{j=1}^{8}\alpha_j\overline{\varphi_{i,j}} \qquad (3)$$

Where Ψ_M is the mixture environmental index for mixture M, W_i is the weight fraction of chemical *i* in the mixture, and the summation is taken over all chemicals present in the mixture.

Air Index - Overall relative measure of the potential impact of a chemical or a mixture mediated through the air on human health and the environment. The air index is calculated by multiplying the environmental index of each chemical by its fugacity in the liquid phase. The fugacity gives an estimate of the tendency of a chemical to vaporize. For a pure chemical, the air index is given by

$$\Psi_i^{air} = \frac{P_i^v\Psi_i}{P} \qquad (4)$$

Where P_i^v is the vapor pressure of component *i*, Ψ_i is the environmental index of component chemical i as given by equation (2), and P is the pressure at which the solvent is being used.

For a solvent consisting of a mixture of component chemicals, the mixture air index is given by

$$\Psi_M^{air} = \frac{\sum x_i\gamma_i P_i^v\Psi_i M_i}{P\sum_j x_j M_j} \qquad (5)$$

Where x_i is the mole fraction of chemical

component i, γ_i is the activity coefficient of chemical component i, P_i^v is the vapor pressure of chemical component i, Ψ_i is the environmental index of component chemical i as given by equation (2) , M_i is the molecular mass of component chemical i, and P is the pressure at which the solvent is being used.

The Environmental Impact Categories are defined as follows:

Human Toxicity Potential by Ingestion

Human Toxicity Potential by Ingestion is approximated by the value of the lethal dose through ingestion that would kill 50% of a sample population of rats, which is known as the oral rat LD_{50}. This is a popular indicator for evaluating the toxicity of chemicals. The LD_{50} is generally reported in units of (mg of chemical/kg of rat). In this system, a higher LD_{50} value represents a less toxic chemical. Thus, to align these impact values with the other impact values, the scores were obtained by inverting the LD_{50} values.

$$\varphi_{i,j} = \frac{1}{(LD_{50})_i}$$

Use of the equation allowed for proportional relationships to be maintained. For example, a chemical with an LD_{50} of 200 mg/kg, producing a $\varphi_{i,j} = 0.005$, is considered to be twice as harmful as a chemical with an LD_{50} of 400 mg/kg, producing a $\varphi_{i,j} = 0.0025$.

These values were obtained from the following sources: Lewis (1996), HSDB, RTECS.

Limitations: The major limitation in this category is that the LD_{50} values could not be found for every chemical in the database. Instead, many values were estimated using molecular methods such as Quantitative

Structural Activity Relationships (QSAR). Only acute effects are represented in this category.

Human Toxicity Potential by Inhalation

Human Toxicity Potential by Inhalation is approximated by using 8-hour threshold limit values (TLV) as recommended by OSHA, ACGIH, or NIOSH. This was considered an adequate measuring stick for comparison of chemicals that would pose a threat to human health through inhalation and dermal exposure routes. These agencies have evaluated the chemicals of significant concern. Recall, only a relative comparison within categories is needed for this methodology. For the same reasons as before, these values were inverted to maintain the proper relationships within the database. The units for the TLV s are mg/m^3.

$$\varphi_{i,j} = \frac{1}{(TLV)_i}$$

There are six chemicals in the database (benzidine, ethyleneimine, p-aminodiphenyl, bis(chloromethyl) ether, chloromethyl methyl ether, beta-propiolactone) that are considered to be carcinogenic and have no acceptable level of exposure. These chemicals have been arbitrarily assigned a TLV that is 0.01*TLV of beryllium, which is the smallest TLV in the database. These carcinogenic chemicals will have a toxicity value that is at least 100 times greater than any other chemical in the database. However, these carcinogenic chemicals were not included in the calculation of the average score $\varphi_{i,j}$ of all non-zero values in this category.

These values were obtained from the following sources: OSHA (1998), ACGIH (1999), and NIOSH.

Limitations: As suggested by the above agencies, these values provide an estimation of the relative toxicity potential of chemicals through routes other than ingestion as suggested by the above agencies.

Human Toxicity Potential by Dermal Exposure

Human Toxicity Potential by Dermal Exposure is approximated by the value of the lethal dose through dermal exposure that would kill 50% of a sample population of rabbits, which is known as the dermal rabbit LD_{50}. This is a popular indicator for evaluating the dermal toxicity of chemicals. This LD_{50} is generally reported in units of mg of chemical/kg rabbit. In this system, a higher LD_{50} value represents a less toxic chemical. Thus, to align these impact values with the other impact values, the scores were obtained by inverting the LD_{50} values.

$$\varphi_{i,j} = \frac{1}{(LD_{50})_i}$$

Use of the equation allowed for proportional relationships to be maintained. For example, a chemical with an LD_{50} of 200 mg/kg, producing a $\varphi_{i,j} = 0.005$, is considered to be twice as harmful as a chemical with an LD_{50} of 400 mg/kg, producing a $\varphi_{i,j} = 0.0025$.

As before, these values were obtained from the following sources: Lewis (1996), HSDB, RTECS.

Limitations: The major limitation of this category is that the LD_{50} values could not be found for every chemical in the database. Instead, many values were estimated using molecular methods such as QSAR. Only acute effects are represented in this category.

Aquatic Toxicity Potential

Aquatic **T**oxicity **P**otential (ATP) is estimated by using toxicological data for a single, representative species of fish, *Pimephales promelas* (fathead minnows). This species was chosen again because of its acceptance as a universal aquatic indicator and because of the prevalence of data about it. The data for this assay come in the form of an LC_{50}, a lethal concentration that causes death in 50% of the test specimens. Similarly, the scores for this category were calculated by the following

$$\varphi_{i,j} = \frac{1}{(LC_{50})_i}$$

The data used in this database specifically comes from 96-hour LC_{50} experiments. The units of the LC_{50} are mg/L.

These values were obtained from the following sources: AQUIRE, Prager (1995), ECOSAR, Verschueren (1996), HSDB, and Mackay (1992).

Limitations: A single species of fish was chosen to represent the entire aquatic community, which includes other types of biota. Again, LC$_{50}$ values for a significant portion of the chemicals in the database were not available and had to be estimated by molecular models. Only acute effects are represented in this category.

Global Warming Potential

Global **W**arming **P**otential (GWP) is determined by comparing the amount of infrared radiation a unit mass of a chemical can absorb in 100 years as compared to the amount of infrared radiation a unit mass of carbon dioxide can absorb over the same time span. This takes into account the decay of the chemicals in the atmosphere over this time span as well.

This relative amount is used as the score φ_{ij} of chemical *i* for GWP impact. These values were obtained from Houghton et al. (1992) and Heijungs et al. (1992). These amounts take into account the decomposition of the chemicals in the atmosphere.

Limitations: These values have only been tabulated for a few simple gases and a limited amount halogenated hydrocarbons. However, the chemicals of primary concern regarding global warming have been captured in the analysis of this impact category. The decomposition products are not included as sources for GWP.

Ozone Depletion Potential

Ozone **D**epletion **P**otential (ODP) is

determined by comparing the rate at which a unit mass of a chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. In general, for a chemical to have an ODP, it must contain a chlorine or bromine atom. The ODP takes into account the decomposition of the chemicals in the atmosphere.

This relative value was used as the score φ_{ij} of the chemical i for ODP impact. These values were obtained from World Meteorological Organization (1991) and Heijungs et al. (1992).

Limitations: These values have only been tabulated for a limited amount of halogenated hydrocarbons. However, the chemicals of primary concern have been captured in the analysis of this impact category. The decomposition products are not included as sources for ODP.

Photochemical Oxidation Potential

Photo**c**hemical **O**xidation **P**otential (PCOP) is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical (OH^-) to the rate at which a unit mass of ethylene reacts with OH^-. These values have been determined for many low and medium molecular weight hydrocarbons.

This relative amount is used as the score φ_{ij} of chemical i for PCOP impact. These values were obtained from UNECE (1991) and Heijungs et al. (1992).

Limitations: The values used in this impact category were determined through analysis performed in Europe and may not adequately represent the concern in the United States.

Acid Rain Potential

Acidification or **A**cid **R**ain **P**otential (ARP) is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2.

This relative amount is used as the score φ_{ij} of chemical i for ARP impact. These values were obtained from Heijungs et al. (1992).

Limitations: Values are calculated for a limited number of chemicals of primary concern regarding acid rain.

Abbreviations

ACGIH - The American Conference of Governmental Industrial Hygienists

AQUIRE - Aquatic Toxicity Information Retrieval Database

ECOSAR - Ecological Structure Activity Relationships

HSDB - Hazardous Substance Database, NIH

NIH - The National Institute of Health

NIOSH - The National Institute for Occupational Safety and Health

OSHA - The Occupational Safety and Health Administration

RTECS - Registry of Toxic Effects of Chemical Substances

UNECE - United Nations Economic Commission for Europe

Literature Cited

Cabezas, H., P.F. Harten, and M.R. Green, "Designing Greener Solvents," Chemical Engineering, Vol. 107, No. 3, 109 (2000).

Li, M., P.F. Harten, and H. Cabezas, "Experiences in Designing Solvents for the Environment," Industrial and Engineering Chemistry Research, 41, 5867 (2002).

Verschueren K (1996): Handbook of Environmental Data on Organic Chemicals. 3rd ed. NY, NY: Van Nostrand Reinhold (1996).

Heijungs, R., J.B. Guinée, G. Huppes, R.M. Lankreijer, H.A. Udo de Haes, A. Wegener Sleeswijk, A.M.M. Ansems, P.G. Eggels, R. van Duin & H.P. de Goede, 1992: *Environmental Life Cycle Assessment of products. Guide and Backgrounds.* Centre of Environmental Science (CML), Leiden University, Leiden.

Houghton, Callender & Varney, *Climate Change 1992. The supplementary report to the IPCC scientific assessment*, Cambridge University Press, Cambridge, UK, 1992.

Lewis, R.J. Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1-3. New York, NY: Van Nostrand Reinhold, 1996. p.1088.

Mackay D., Shiu W. Y., & Ma K.C. 1992 *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals*. Volume II: Polynuclear aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans. Lewis Publishers. Boca Raton, Florida. pp. 1-367. In: IPCS.

Prager, J.C., 1995, Environmental contaminant reference databook - Volume I: Van Nostrand Reinhold, New York, 1,240 p.