Green Chemistry

Environmental risk-based ranking of solvents using the combination of a multimedia model and multi-criteria decision analysis†

Marek Tobiszewski,*[a] Jacek Namieśnik[a] and Francisco Pena-Pereira[b]

A novel procedure for assessing the environmental risk related to solvent emissions has been developed. The assessment of risk was based on detailed hazard and exposure investigations. The potential exposure related to different environmental phases was calculated using a basic multimedia model, which gives the percentage distribution of solvent in environmental compartments as a result. Specific hazards – toxicological, environmental persistence or photochemical ozone creation data have been assigned to each compartment. The environmental distribution of solvents gives the weights applied in the multicriteria decision analysis, which was applied to obtain the full ranking of solvents. The results show that alcohols and esters can be considered as low environmental risk solvents, whereas chlorinated solvents or aromatic hydrocarbons are the most problematic. The assessment procedure holds promise for solvent selection during process design as well as in finding alternatives to hazardous solvents used in existing processes.

Introduction

The introduction of the green chemistry concept[1] has changed the perception of chemical-related risks from exposure management to hazard management. Risk management in chemical practice can be performed in two ways as can be seen from the eqn (1):[2]

$$\text{Risk} = \text{Hazard} \times \text{Exposure} \qquad (1)$$

In this sense, the risk assessment of chemical application or emission should take into account both factors – hazard, as well as exposure.

There are several different approaches used to assess the "greenness" of solvents applied in chemical practice. Solvent selection guides, mainly developed in the pharmaceutical industry, allow one to obtain the first view on a solvents' environmental, health and process safety issues.[3–5] There are "greenness" screening procedures, based on the environmental, health and safety (EHS) aspects of solvents.[6] Life-cycle assessment (LCA) allows one to perform a comprehensive

*[a]Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology (GUT), 11/12 G. Narutowicza St., 80-233 Gdańsk, Poland.
E-mail: marektobiszewski@wp.pl*
[b]Department of Analytical and Food Chemistry, Faculty of Chemistry, University of Vigo, Campus As Lagoas - Marcosende s/n, 36310 Vigo, Spain
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c6gc03424a

assessment from the stage of solvent production to disposal practices.[7] The combination of EHS and LCA approaches allow one to assess the environmental impact of solvents and find which ones should be incinerated or treated *via* distillation.[8] However, as far as we are aware, a procedure for purely assessing the environmental risks associated to solvent emissions has not been reported before. In fact, certain aspects associated to the use of organic solvents (and not only their effect in environmental compartments) are commonly considered to classify solvents in terms of their greenness and, as a result, solvents that show non-negligible environmental and hazard issues have been assigned with the "green label" due to their convenient handling or disposal. An environmental risk evaluation approach is particularly applicable when the use of a solvent involves their intentional environmental release (*e.g.*, metal surfaces degreasing and application as cleaning agents or paints constituents). Currently, industrial applications of solvents include their recovery and recycling. However, accidental solvent releases of different scales cannot be neglected, even if the solvents are applied in closed systems.

Multi-criteria decision analysis (MCDA) is an approach that supports the decision making process when complex problems need to be solved. It is particularly useful when several possible alternatives are considered, described by contradictory assessment criteria. MCDA has been intensively used in environmental sciences,[9] including to support the choice of processes that fit the principles of green chemistry in the best way.[10] It has been used to select sustainable route for biodiesel

Table 1 The input criteria for multicriteria decision analysis together with the assignment of their weight category

Criterion	Description	Weight category
Inhalation LC$_{50}$	The concentration of the solvent vapour in the air that kills half of the rodent population when exposed for 4 h. The data for rats were selected over the data obtained for other rodents	Air
POCP	The potential to form a tropospheric ozone in relation to ethane (POCP for ethane = 100)	Air
Fish LC$_{50}$	The concentration of solvent in water that kills half of the fish population over a period of 96 h. Data for *fathead minnow* was selected when available	Water
log BCF	The logarithm of the bioconcentration factor	Water
Biodegradability $t_{1/2}$	The time needed for the initial solvent concentration to drop by half because of microorganism activity	Water, soil and sediment
Oral LD$_{50}$	The amount of solvent that kills half of the rodent population when administered orally. Expressed as the mass of solvent per kg of rodent body mass. Data for rats was selected when available	Water, soil and sediment
IARC cancer class	The IARC cancer class was translated into numerical values in the following way: Group 1 (human carcinogen) – 10; Group 2A (probable human carcinogen) – 8; Group 2B (possible human carcinogen) – 7; Groups 3 and 4 (not classifiable and probable human non-carcinogen, respectively) – 0	Air, water, soil and sediment
Other specific effects	Each of the effects – mutagenicity, teratogenicity, reproductive effects, neurotoxicity or other chronic effects is given one point	Air, water, soil and sediment

production,[11] find safe alternatives for personal care products[12] or evaluate the sustainability of chemical syntheses.[13] From the several MCDA tools, the technique for order of preference by similarity to ideal solution (TOPSIS)[14] was selected as one of the simplest in its algorithm. The result of TOPSIS analysis is the ranking of alternatives and each alternative is described with a numerical value, commonly known as similarity to ideal solution. The TOPSIS algorithm indicates the best alternative; however, as it is only a decision support tool, the final decision is always made by the decision maker. Apart from being a decision making support tool, TOPSIS is used for the assessment of products[15] or processes.[16] It also allows one to implement other than the strictly "greenness" criteria to the decision making or assessment procedure.[17] As the application of weights may be considered a weak point of MCDA analysis, it is strongly required to find a systematic approach for reasonable weights application.

Based on the fugacity concept,[18] there have been four different levels of calculations developed, which can be applied for the description of environmental fate of chemicals.[19] Level I mass balance model calculations include the assumptions of steady state conditions, closed system and no degradation of the chemical as well as its equilibrium distribution in the environment. Level II calculations are performed for steady-state conditions and equilibrium distribution of chemical in the environment with the assumption that the chemical undergoes degradation processes. Both Level III and Level IV calculations are performed for non-equilibrium conditions with degradation and intermediate transfer. The difference lies in steady state and unsteady state assumption for Level III and Level IV, respectively.[20] These models have been successfully applied to assess the environmental fate of chemicals in the evaluative environments of various types,[21] including the assessment of a solvents' environmental fate for the selection of more benign ones.[22]

The aim of the study is to perform the ranking of commonly applied solvents in terms of the risks related with their emission to the environment. In the presented approach, only environmental risks were considered, and risks related to solvent handling (*i.e.* flammability), occupational exposure or disposal practices (*i.e.* formation of azeotropes that disturb distillation) were neglected. Moreover, the environmental impact during the solvent production stage was neglected. The other aim was to present a general view on the solvents' distribution in the evaluative environment.

Experimental

Dataset

The dataset consists of 78 organic solvents described by physicochemical, toxicological and environmental persistence data. The solvents from a previous study[23] that could be fully characterized in terms of these criteria (see Table 1) were included in the dataset. These solvents originate from different chemical classes, namely hydrocarbons ($n = 16$), alcohols ($n = 20$), ethers ($n = 4$), aldehydes ($n = 4$), ketones ($n = 8$), organic acids ($n = 6$), esters ($n = 7$), chlorinated solvents ($n = 8$), terpenes ($n = 4$) and acetonitrile. They were described by their physicochemical properties obtained mainly from the Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals[24] and Material Safety Data Sheets (MSDS). The physicochemical properties data were needed to calculate the distribution of the solvents in the environment. The second dataset consisted of toxicological and environmental persistence data as described in Table 1. All the toxicological and biodegradability data were extracted from MSDS, whereas the photochemical ozone creation potentials (POCPs) were extracted from the literature.[25–27] The cancer class of each solvent was taken from the International Agency for Research on Cancer website.[28] These criteria reflect the term "hazard" in eqn (1).

The availability of the data used for the sustainability assessment was one of the procedural problems. In our pre-

vious study we applied assessments within confidence levels.[23] This means that a high confidence level assessment involved fewer solvents, but they were comprehensively characterized. Lower confidence level assessments included large amounts of solvents, but they were characterized with fewer criteria. Another approach was to substitute the missing values with estimates. Herein, the data for a nearest neighbour – solvent that is present in the same chemical class and is nearest homologue, mean value for chemical class or missing value calculation with usually simple model are applied to replace missing values. The assessment result for the solvents that were characterized with the estimated data should be treated with a lower level of confidence.[29]

Assigning the inhalation LC_{50} and POCP to air weight category and fish LC_{50}, oral LD_{50}, biodegradability together with the log BCF to water weight category seems to be evident; however, it is necessary to clarify why the biodegradability half-life and oral LD_{50} criteria were assigned to the soil weight category. Biodegradation of the chemicals takes place much faster in soil and sediments than in water. Connection of the oral LD_{50} with soils and sediments was also justified – chemicals that sorb in soil and sediments can be taken up by plants and can potentially sorb on food. In addition, the risks of soil digestion itself are described in the literature.[30] The IARC cancer class and other specific effects are assigned to all categories of weight as the risk of cancer, mutagenic, teratogenic and neurotoxic effects may be connected with the occurrence of solvent in all environmental compartments. Only solvents that could be entirely characterized (there was no missing data) were included in the study. The full raw dataset is in presented in the ESI.†

As it will be stated in the "Modified TOPSIS analysis" section below, all criteria should fit the preference function "the lower, the better". The inhalation LC_{50}, fish LC_{50} and oral LD_{50} are characterized by "the higher, the better" preference function because less toxic chemicals have high numerical values for these criteria. Therefore, the data transformation was performed by dividing 1000 by the original values. In this way the required preference function was fulfilled.

Level I mass balance model

Level I was selected as it is the simplest of the models. The model should only be as complex as it is required to give answers to the asked questions. The Level II–IV models give information that is not needed for the application of appropriate weights in the TOPSIS ranking.

The equilibrium distribution of a fixed quantity of non-degrading chemical in a closed environment was calculated in a Level I simulation. It was assumed that no degradation processes occur that can lead to a decrease in the emitted chemical concentration. The environmental compartment that receives the emission was not important since the chemical is instantaneously distributed until the system reaches equilibrium.[31] This assumption appears to be very important, as solvents can be emitted to soil, water and air. The input data to the Level I simulation were the compound's molar mass, water

solubility, vapour pressure, log KOW and melting point and the temperature for which the data are valid. As a result of the Level I simulation, the partition coefficients, system fugacity and concentrations together with the percentage distribution in each environmental compartment were obtained. The percentage of solvent distribution in the environment reflects the term "exposure" in eqn (1).

Apart from the physicochemical parameters of an investigated chemical, it is important to define the volumes of the environmental compartments. Different evaluative environments have been defined to model the real environment. The evaluative environments consist of homogenous phases of constant composition and simplify the real environment; however, the chemicals are expected to behave very similarly in both the real and evaluative environments. To perform this study, a regional 100 000 km² evaluative environment was selected because it was of relatively large dimensions and has been successfully applied before.[32] The volumes of the respective compartments are presented in Fig. 1. For simplification of the model, no suspended sediments and fish were considered as compartments; their volumes were set to zero. These two processes are expected to be marginal as solvents do not sorb on suspended matter[33] and do not bioaccumulate to an extent as persistent organic pollutants.[34]

Modified TOPSIS analysis

TOPSIS was developed by Hwang and Yoon in 1981.[35] The general scheme of TOPSIS application can be summarized in a few steps. Firstly, the problem to be solved should be stated. In this case it was the assessment of environmental risk connected with the emission of solvents into the environment or the selection of an environmentally benign one. The next steps are finding the alternatives (here 78 solvents) and criteria (herein, they are described in Table 1) that allow the selection of the best alternative. Then, it is needed to define the preference functions for each of the criteria, usually as "the lower,
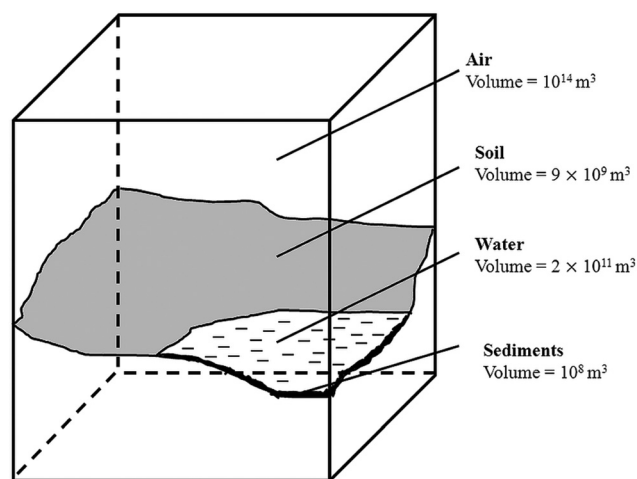

Fig. 1 The volumes of the compartments in the evaluated environment.

the better" or "the higher, the better". Weights are then assigned to set the relative importance of the criteria. This point is usually very tricky, as it is user-dependent and the final ranking strongly depends on the numerical values of the weights (the relative importance of the criteria). Herein, the weights are the result of the Level I multimedia model, and therefore they are not user-dependent and they are methodologically well justified. Then, the TOPSIS algorithm was applied, which is relatively straightforward and may be presented in a few simple eqn (2)–(8) as follows:

First, the normalized decision matrix was determined. The normalized value r_{xy} was calculated as follows:

$$r_{xy} = x_{xy} \div \sqrt{\sum_{x=1}^{m} x_{xy}^2} \quad x = 1, 2, \ldots, m \text{ and } y = 1, 2, \ldots, n \quad (2)$$

where x_{xy} and r_{xy} are original and normalized score of the decision matrix, respectively.

Next, determination of the weighted normalized decision matrix was carried out. The weighted normalized values v_{xy} are calculated as follows:

$$v_{xy} = r_{xy} \times w_{xy} \quad x = 1, 2, \ldots, m \text{ and } y = 1, 2, \ldots, n \quad (3)$$

where w_{xy} is the weight of the criterion and $\sum_{y=1}^{n} w_{xy} = 1$. In this place, a modification of the original TOPSIS algorithm was introduced. In the original TOPSIS, weights w_y are applied to each criterion. The introduced modification to apply different weights w_y was methodologically justified, and is described as the "Level I mass balance model" section. The solvent distribution in the environment results from the application of the Level I model. However, the introduced TOPSIS modification requires the preference functions to be none other than "the lower, the better" function.

In the next step, determination of the positive ideal solution (A^*) and negative ideal solution (A^-) was performed.

$$A^* = \left\{ \left(\max_x v_{xy} \mid y \in C_b \right), \left(\min_x v_{xy} \mid y \in C_c \right) \right\}$$
$$= \{ v_y^* \mid y = 1, 2, \ldots, m \} \quad (4)$$

Positive ideal solution

$$A^- = \left\{ \left(\min_x v_{xy} \mid y \in C_b \right), \left(\max_x v_{xy} \mid y \in C_c \right) \right\}$$
$$= \{ v_y^- \mid y = 1, 2, \ldots, m \} \quad (5)$$

Negative ideal solution

Then, the separation measures using the m-dimensional Euclidean distance were determined. The separation measures of each alternative from the positive ideal solution and the negative ideal solution, respectively, were calculated as follows:

$$S_x^* = \sqrt{\sum_{y=1}^{m} (v_{xy} - v_y^*)^2} \quad y = 1, 2, \ldots, m \quad (6)$$

$$S_x^- = \sqrt{\sum_{y=1}^{m} (v_{xy} - v_y^-)^2} \quad y = 1, 2, \ldots, m \quad (7)$$

In the last step, determination of the relative closeness to the ideal solution was carried out. The relative closeness of the alternative A_x with respect to A^* is defined as follows:

$$C_x^* = \frac{S_x^-}{S_x^* + S_x^-}, \quad x = 1, 2, \ldots, m \ \& \ 0 < C_x^* < 1 \quad (8)$$

The alternative with C_x^* closest to 1 indicates the best preference and can be selected.

Results and discussion

Multimedia model results

The results obtained from applying the Level I model to *tert*-butyl alcohol, as an example, are presented in Fig. 2. This compound partitions to all four compartments of the evaluative environment, with the majority being present in water (72.5%) and a significant amount is present in air (27.4%). This result appears to be reasonable due to the following reasons: (1) *tert*-butyl alcohol is polar, and therefore it should be present in water; (2) it is volatile, and hence it is expected to occur in the atmospheric air. An output of the Level I analysis, needed in the further step of the presented approach, is the possible exposure to this chemical in 72.5% coming from the water compartment; 27.4% of the exposure is related to the air compartment and the remaining fraction with the soil and sediment compartments.

Such results were obtained for all the solvents investigated and are presented in Table 2. According to the model, hydrocarbons partition mainly to air, with the heavier aliphatic ones being present in soil and aromatic ones being noticeable in
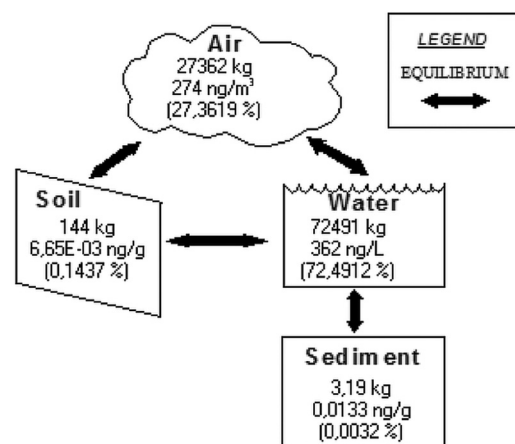

Fig. 2 The simplified distribution diagram for *tert*-butyl alcohol in a four-compartment environment. The amount of emission was assumed to be 100 000 kg.

Table 2 The results of the Level I model application expressed as the percentage of solvent distributed in every environmental compartment

Group	Solvent	CAS number	Air [%]	Water [%]	Soil [%]	Sediment [%]
Hydrocarbons	Pentane	109-66-0	99.99	0.00	0.01	0.00
	Hexane	110-54-3	99.97	0.00	0.03	0.00
	Cyclohexane	110-82-7	99.89	0.03	0.08	0.00
	Heptane	142-82-5	99.95	0.00	0.05	0.00
	Octane	111-65-9	99.73	0.00	0.26	0.01
	Isooctane	540-84-1	99.96	0.00	0.04	0.00
	Nonane	111-84-2	99.61	0.00	0.38	0.01
	Decane	124-18-5	74.11	0.03	25.30	0.56
	Undecane	1120-21-4	73.64	0.00	25.78	0.58
	Dodecane	112-40-3	40.44	0.00	58.26	1.30
	Benzene	71-43-2	98.67	0.85	0.47	0.01
	Toluene	108-88-3	98.99	0.74	0.26	0.01
	o-Xylene	95-47-6	96.99	1.37	1.60	0.04
	m-Xylene	108-38-3	97.72	0.94	1.31	0.03
	p-Xylene	106-42-3	97.97	0.91	1.10	0.02
	Styrene	100-42-5	96.99	1.58	1.40	0.03
Alcohols	Methanol	67-56-1	9.83	90.15	0.02	0.00
	Ethanol	64-17-5	6.59	93.37	0.04	0.00
	1-Propanol	71-23-8	10.73	89.13	0.14	0.00
	Isopropanol	67-63-0	14.62	85.29	0.09	0.00
	1-Butanol	71-36-3	15.25	84.17	0.57	0.01
	Isobutanol	67-63-0	46.97	52.97	0.06	0.00
	sec-Butyl alcohol	78-92-2	14.06	85.61	0.32	0.01
	tert-Butyl alcohol	76-65-0	27.36	72.49	0.14	0.01
	1-Pentanol	71-41-0	20.00	77.77	2.18	0.05
	1-Hexanol	111-27-3	21.57	71.49	6.79	0.15
	1-Heptanol	111-70-6	18.65	59.80	21.08	0.47
	1-Octanol	111-87-5	21.58	41.16	36.45	0.81
	1-Nonanol	143-08-8	7.67	5.28	85.15	1.90
	Allyl alcohol	107-18-6	9.94	89.94	0.12	0.00
	Benzyl alcohol	100-51-6	0.84	98.04	1.09	0.03
	Glycerol	56-81-5	0.00	100.00	0.00	0.00
	Phenol	108-95-2	2.97	94.33	2.64	0.06
	o-Cresol	95-45-7	4.37	88.02	7.44	0.17
	m-Cresol	108-39-4	2.14	90.40	7.30	0.16
	p-Cresol	106-44-5	2.24	90.61	6.99	0.16
Ethers	Diethyl ether	60-29-7	93.66	6.30	0.04	0.00
	Methyl – tert butyl ether	1634-04-4	91.99	7.95	0.06	0.00
	Furan	110-00-9	99.08	0.90	0.02	0.00
	Tetrahydrofuran	109-99-9	35.83	64.00	0.17	0.00
Aldehydes	Ethanal	75-07-0	80.53	19.42	0.05	0.00
	1-Propanal	123-38-6	62.18	37.69	0.13	0.00
	1-Butanal	123-72-8	85.14	14.76	0.10	0.00
	Furfural	98-08-1	6.05	93.74	0.21	0.00
Ketones	Acetone	67-64-1	61.54	38.44	0.02	0.00
	2-Butanone	78-93-3	42.02	57.88	0.10	0.00
	2-Pentanone	107-87-9	43.92	55.70	0.37	0.01
	3-Pentanone	96-22-0	48.84	50.79	0.36	0.01
	Methyl isobutyl ketone	108-10-1	73.06	26.37	0.56	0.01
	2-Hexanone	591-78-6	37.57	61.10	1.30	0.03
	2-Heptanone	110-43-0	68.89	28.63	2.42	0.06
	Cyclohexanone	108-94-1	11.89	87.60	0.50	0.01
Terpenes	ᴅ-Limonene	5989-27-5	97.82	0.08	2.05	0.05
	p-Cymene	99-87-6	95.41	0.44	4.06	0.09
	α-Pinene	80-56-8	99.31	0.03	0.65	0.01
	β-Pinene	127-91-3	98.25	0.08	1.63	0.04
Organic acids	Formic acid	64-18-6	0.48	99.49	0.03	0.00
	Acetic acid	64-19-7	5.07	94.89	0.04	0.00
	Butyric acid	107-92-6	2.70	96.76	0.53	0.01
	Isobutyric acid	79-31-2	6.21	93.05	0.72	0.02
	Valeric acid	109-52-4	1.65	96.21	2.09	0.05
	Hexanoic acid	142-62-1	0.95	92.11	6.79	0.15
Esters	Ethyl acetate	141-78-6	73.51	26.36	0.13	0.00
	Ethyl acrylate	140-88-5	91.10	8.74	0.16	0.00
	Butyl lactate	138-22-7	1.47	97.86	0.66	0.01
	Ethyl lactate	97-64-3	1.27	98.67	0.06	0.00
	Methyl formate	107-31-3	90.11	9.89	0.00	0.00
	Methyl acetate	79-20-9	88.60	11.38	0.02	0.00
	Methyl laurate	111-82-0	0.00	0.36	97.48	2.16

Table 2 (Contd.)

Group	Solvent	CAS number	Air [%]	Water [%]	Soil [%]	Sediment [%]
Chlorinated	Dichloromethane	75-09-2	97.51	2.45	0.04	0.00
	Chloroform	67-66-3	98.66	1.25	0.09	0.00
	Carbon tetrachloride	56-23-5	99.76	0.17	0.07	0.00
	Trichloroethene	79-01-6	99.32	0.56	0.12	0.00
	Tetrachloroethene	127-18-4	99.58	0.31	0.11	0.00
	1,2-Dichloroethane	107-06-2	96.03	3.87	0.10	0.00
	1,3-Dichloropropene	542-75-6	97.16	2.65	0.19	0.00
	Hexachlorobutadiene	87-68-3	90.46	0.17	9.17	0.20
Other	Acetonitrile	75-05-8	41.02	58.96	0.02	0.00

water and soil. Alcohols are present mainly in water, but a discernible fraction is present in the air and in the soil in case of heavy aliphatic alcohols. Ethers, terpenes and chlorinated solvents are mainly present in the atmospheric air, as are aldehydes; however, in this case a significant fraction partitions to the water compartment. Organic acids and esters partition mainly to water and the environmental behaviour of ketones is variable. Thus it can be concluded that they partition between air and water in the approximate proportion of half by half.

Ranking of solvents

Based on the weights (the percentage of distribution) described in Table 2, an environmental risk ranking of the solvents was created using the TOPSIS procedure. By introducing these weights, a very strong relative importance to the hazard criteria was given. As an example, water-related hazards for hexane are ignored as it does not partition to water, and the significant hazards connected with the emission of this compound are related with the air compartment. The full ranking obtained in this way is presented in Table 3.

Some of the solvents present in the ranking are recognised as green in numerous references. Those solvents that have been reported as being green are highlighted in grey in Table 3.[36,37] Remarkably, 1-propanol was ranked first even though it has not been considered as a green solvent, presumably due to its high impact during the stage of petrochemical production.[38] The results of this study show that 1-propanol can be considered as a green solvent concerning its environmental risks after emission. Thus, finding more sustainable synthetic pathways for the production of 1-propanol would make this solvent ideal as a replacement for conventional hazardous solvents. The second most preferable organic solvent was ethanol, being assessed as a green solvent by the pharmaceutical solvent selection guides.[39] Ethanol partitions mainly to water, and therefore the hazards related to this environmental compartment are relevant in its case. It has a very low log BCF, it is non-toxic to fish and is readily biodegradable. It has been used as a green alternative in extraction processes[40] and as a mobile phase in liquid chromatography.[41] The third rank was gained by 1-butanol, another green, acceptable solvent. The fourth rank was obtained by *tert*-butyl alcohol, a solvent widely accepted as green. It was ranked lower than ethanol because of its higher toxicity towards fish and higher inhalation toxicity; in the case of this solvent, the partitioning to air compartment plays a more important role

(27.4%) when compared to ethanol (6.6%). Acetone, placed at five in the ranking, is referred as a green alternative, along with ethanol, and is used as a green mobile phase constituent in liquid chromatography.[42] The next two ranking locations are scored by acetic and formic acids. Their parameters do not differ much since formic acid is more toxic, but more readily biodegradable and is characterized by a lower POCP. Acetic acid and formic acid are ranked high as relatively green solvents. The pharmaceutical solvent selection guide states that the utilization of these solvents was acceptable in terms of their environmental aspects.[39] However, their poor assessment score in the "health" criteria makes their overall score as "problematic".

Another solvent widely recognized as green is glycerol. It is obtained from plant oils with its price depending on the purity grade and is considered to be a renewable resource.[43] In fact, it is a by-product of biodiesel production from triglycerides as a raw material,[44] but this process yield is not high. It possesses a series of desired properties as a solvent and its main drawback is its high viscosity.[45] It is relatively non-toxic *via* oral exposure.[46] Application of Level I fugacity model shows that it partitions to water only. The important factors are toxicity towards fish, bioconcentration factor, biodegradability and oral LD_{50}. For all of these criteria, glycerol performs well even though there are solvents that are characterized with better values for all of the assessment criteria. This is the reason for glycerol being present at the 14th position in the ranking among other green solvents.

In general terms, methyl and ethyl esters are ranked high. They undergo fast biodegradation, do not undergo bioconcentration, and show low or moderate toxicity towards fish and rodents when administered orally or *via* inhalation. However, ethyl acrylate (rank 69) is marked as a potential carcinogen. It is also characterized by a relatively high inhalation toxicity. Ethyl lactate (rank 29) was investigated in more detail as a potential green solvent due to its favourable properties, apart from previously mentioned ones, such as low price and being approved to be used in food products.[47] The application of this solvent in industry can be challenging due to its high viscosity and resulting poor mass transfer parameters.[48]

A very interesting result is the low position of all terpenes in the rankings. β-Pinene, α-pinene, *p*-cymene and D-limonene are ranked 53, 57, 60 and 72, respectively. The results of the Level I model show that terpenes partition mainly to atmospheric air. Their POCP values are particularly high and their

Table 3 Environmental risk ranking of solvents. High rank solvents are characterized by low environmental risk. Solvents commonly recognized as green are highlighted in grey

Rank	Chemical group	Solvent	Molar mass [g]	CAS number	Similarity to ideal solution score
1	Alcohol	1-Propanol	60	71-23-8	0.9545
2	Alcohol	Ethanol	46	64-17-5	0.9300
3	Alcohol	1-Butanol	74	71-36-3	0.9213
4	Alcohol	tert-Butyl alcohol	74	76-65-0	0.9183
5	Ketone	Acetone	58	67-64-1	0.9166
6	Organic acid	Acetic acid	60	64-19-7	0.9118
7	Organic acid	Formic acid	46	64-18-6	0.9118
8	Ester	Methyl laurate	214	111-82-0	0.9112
9	Ester	Methyl formate	60	107-31-3	0.9083
10	Ester	Methyl acetate	74	79-20-9	0.9054
11	Hydrocarbon	Dodecane	170	112-40-3	0.8919
12	Ester	Ethyl acetate	88	141-78-6	0.8868
13	Organic acid	Isobutyric acid	88	79-31-2	0.8867
14	Alcohol	Glycerol	92	56-81-5	0.8861
15	Ether	Methyl tert-butyl ether	88	1634-04-4	0.8855
16	Alcohol	1-Pentanol	88	71-41-0	0.8836
17	Alcohol	Benzyl alcohol	108	100-51-6	0.8812
18	Alcohol	1-Hexanol	102	111-27-3	0.8788
19	Ether	Tetrahydrofuran	72	109-99-9	0.8779
20	Alcohol	1-Heptanol	116	111-70-6	0.8721
21	Ketone	3-Pentanone	86	96-22-0	0.8714
22	Organic acid	Hexanoic acid	116	142-62-1	0.8705
23	Hydrocarbon	Decane	142	124-18-5	0.8703
24	Organic acid	Butyric acid	88	107-92-6	0.8702
25	Ketone	Cyclohexanone	98	108-94-1	0.8702
26	Organic acid	Valeric acid	102	109-52-4	0.8700
27	Alcohol	Isopropanol	60	67-63-0	0.8698
28	Ester	Butyl lactate	146	138-22-7	0.8697
29	Ester	Ethyl lactate	188	97-64-3	0.8694
30	Alcohol	1-Octanol	130	111-87-5	0.8689
31	Other	Acetonitrile	41	75-05-8	0.8687
32	Hydrocarbon	Undecane	156	1120-21-4	0.8677
33	Alcohol	Methanol	32	67-56-1	0.8644
34	Aldehyde	1-Propanal	58	123-38-6	0.8636
35	Aldehyde	1-Butanal	72	123-72-8	0.8608
36	Aldehyde	Furfural	96	98-08-1	0.8586
37	Alcohol	1-Nonanol	144	143-08-8	0.8583
38	Alcohol	Isobutanol	74	67-63-0	0.8525
39	Hydrocarbon	Pentane	72	109-66-0	0.8475
40	Ketone	2-Hexanone	100	591-78-6	0.8456
41	Hydrocarbon	Nonane	128	111-84-2	0.8427
42	Ketone	2-Heptanone	114	110-43-0	0.8400
43	Hydrocarbon	Isooctane	114	540-84-1	0.8342
44	Hydrocarbon	Octane	114	111-65-9	0.8330
45	Alcohol	sec-Butyl alcohol	74	78-92-2	0.8285
46	Ketone	2-Butanone	72	78-93-3	0.8208
47	Ether	Diethyl ether	74	60-29-7	0.8168
48	Alcohol	p-Cresol	108	106-44-5	0.8090
49	Alcohol	o-Cresol	108	95-45-7	0.8081
50	Alcohol	Allyl alcohol	58	107-18-6	0.8073
51	Hydrocarbon	Heptane	100	142-82-5	0.8021
52	Hydrocarbon	Cyclohexane	84	110-82-7	0.7892
53	Terpene	β-Pinene	136	127-91-3	0.7815
54	Alcohol	Phenol	94	108-95-2	0.7789
55	Hydrocarbon	m-Xylene	106	108-38-3	0.7594
56	Alcohol	m-Cresol	108	108-39-4	0.7558
57	Terpene	α-Pinene	136	80-56-8	0.7475
58	Ketone	2-Pentanone	86	107-87-9	0.7362
59	Hydrocarbon	Toluene	92	108-88-3	0.7344
60	Terpene	p-Cymene	134	99-87-6	0.7252
61	Chlorinated	Dichloromethane	85	75-09-2	0.7150
62	Hydrocarbon	p-Xylene	106	106-42-3	0.7072
63	Hydrocarbon	Hexane	86	110-54-3	0.7057
64	Chlorinated	1,2-Dichloroethane	99	107-06-2	0.6954
65	Ketone	Methyl isobutyl ketone	100	108-10-1	0.6939
66	Chlorinated	1,3-Dichloropropene	111	542-75-6	0.6922
67	Chlorinated	Dichloroform	119	67-66-3	0.6862

Table 3 (Contd.)

Rank	Chemical group	Solvent	Molar mass [g]	CAS number	Similarity to ideal solution score
68	Chlorinated	Tetrachloroethene	166	127-18-4	0.6841
69	Ester	Ethyl acrylate	100	140-88-5	0.6787
70	Hydrocarbon	Styrene	104	100-42-5	0.6786
71	Hydrocarbon	o-Xylene	106	95-47-6	0.6715
72	Terpene	D-Limonene	136	5989-27-5	0.6641
73	Aldehyde	Ethanal	44	75-07-0	0.6572
74	Chlorinated	Carbon tetrachloride	154	56-23-5	0.6424
75	Chlorinated	Trichloroethene	131	79-01-6	0.6291
76	Hydrocarbon	Benzene	78	71-43-2	0.6098
77	Ether	Furan	68	110-00-9	0.4755
78	Chlorinated	Hexachlorobutadiene	261	87-68-3	0.4044

inhalation toxicities are at moderate levels. The POCP value for D-limonene even defines the anti-ideal solution; it indicates that it is the highest in the entire dataset. However, terpenes are considered to be green solvents as stated in numerous reports and there is reasoning behind this statement. For example, D-limonene can be obtained from citrus oils, and therefore it is a bio-based solvent, obtained often from food industry waste, and it is biodegradable.[49] It is characterized by low oral toxicity and it performs well when it substitutes traditionally used organic solvents such as hexane[50] or toluene.[51] Similarly, α-pinene is a solvent obtained from a bio-based and renewable resource, conifer waste.[52] The results of the present study show that the environmental risk associated with the emission of terpenes is considerable in relation to the other solvents, and thus it has to be taken into consideration when selecting terpenes as the solvent in various processes.

Solvents that are carcinogens, potential or possible carcinogens, toxic or causing other effects are located in the lower part of the ranking. Without any discussion, hexachlorobutadiene, trichloroethene and other chlorinated solvents, benzene, styrene and xylenes have to be treated as undesirable solvents.

It is worth noting that the present assessment methodology does not include the data used for full LCA methodology, does not include safety data and partially covers health data used in EHS based approach. Despite these facts, the obtained results are generally in good agreement with the results reported by other solvent assessment tools.[37] Some deviations are related to the environmental risk assessment of terpenes, although these discrepancies are methodologically well justified by our approach.

As our assessment methodology does not include any information that influences the sustainability of solvents during pre-emission stages, application of an additional assessment tool is required. It might be detailed in the LCA that includes origin of feedstock used to solvent production, manufacturing purposes and safety issues in assessment protocol.

Conclusions

The presented study provides a novel approach to assess the environmental risk related to solvent emissions. The results of

Level I modelling give an overview of solvent distribution in the environmental compartments and can be used at the initial stage of solvent assessment. This model also supplies methodologically justified weights to the MCDA. Ranking with the MCDA analysis results shows the relative environmental risks of the emitted solvents. The least environmentally problematic are short chain alcohols, esters, and some carboxylic acids. The solvents that pose some serious threats to the environment are chlorinated solvents, aromatic hydrocarbons and, quite surprisingly, terpenes.

The proposed assessment procedure can give some other results if a different evaluative environment is considered. The proposed approach may be applied for case studies, when solvents are selected for application in specific locations. To fit the case study, different criteria reflecting the hazards can be applied as input data in the assessment procedure and different results can be obtained.

The assessment procedure is focused on the environmental risks related to solvent emissions. Therefore, this tool is favourable when the application of the solvent is related to its release to the environment. On the other hand, as only the environmental aspect is considered, the procedure can be treated as a screening tool and when used for full assessment it has to be supported by LCA.

Acknowledgements

References

1 P. T. Anastas and J. Warner, *Green Chemistry Theory and practice*, Oxford University Press, Oxford, 1998.
2 M. Poliakoff, J. M. Fitzpatrick, T. R. Farren and P. T. Anastas, *Science*, 2002, **297**, 807–810.
3 R. K. Henderson, C. Jimenez-Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Binks and A. D. Curzons, *Green Chem.*, 2011, **13**, 854–862.

4   D. Prat, O. Pardigon, H.-W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. Ruisseau, P. Cruciani and P. Hosek, *Org. Process Res. Dev.*, 2013, **17**, 1517–1525.

5   K. K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, *Green Chem.*, 2008, **10**, 31–36.

6   S. Hellweg, U. Fischer, M. Scheringer and K. Hungerbühler, *Green Chem.*, 2004, **6**, 418–427.

7   A. Amelio, G. Genduso, S. Vreysen, P. Luis and B. Van der Bruggen, *Green Chem.*, 2014, **16**, 3045–3063.

8   C. Capello, U. Fischer and K. Hungerbühler, *Green Chem.*, 2007, **9**, 927–934.

9   I. B. Huang, J. Keisler and I. Linkov, *Sci. Total Environ.*, 2011, **409**, 3578–3594.

10 M. Tobiszewski and A. Orłowski, *J. Chromatogr., A*, 2015, **1387**, 116–122.

11 D. Kralisch, C. Staffel, D. Ott, S. Bensaid, G. Saracco, P. Bellantoni and P. Loeb, *Green Chem.*, 2013, **15**, 463–477.

12 P. Gramatica, S. Cassani and A. Sangion, *Green Chem.*, 2016, **18**, 4393–4406.

13 P.-M. Jacob, P. Yamin, C. Perez-Storey, M. Hopgood and A. A. Lapkin, *Green Chem.*, DOI: 10.1039/c6gc02482c.

14 M. Behzadian, S. K. Otaghsara, M. Yazdani and J. Ignatius, *Expert Syst. Appl.*, 2012, **39**, 13051–13069.

15 G. Sakthivel, M. Ilangkumaran and A. Gaikwad, *Ain Shams Eng. J.*, 2015, **6**, 239–256.

16 H. Al-Hazmi, J. Namieśnik and M. Tobiszewski, *Curr. Anal. Chem.*, 2016, **12**, 261–267.

17 P. Bigus, J. Namieśnik and M. Tobiszewski, *J. Chromatogr., A*, 2016, **1446**, 21–26.

18 D. Mackay and S. Paterson, *Environ. Sci. Technol.*, 1982, **16**, 654A–660A.

19 D. Mackay, *Multimedia Environmental Models The Fugacity Approach*, CRC Press LLC, USA, 2001.

20 D. Mackay, A. Di Guardo, S. Paterson and C. E. Cowan, *Environ. Toxicol. Chem.*, 1996, **15**, 1627–1637.

21 D. Mackay, A. Di Guardo, S. Paterson, G. Kicsi, C. E. Cowan and D. M. Kane, *Environ. Toxicol. Chem.*, 1996, **15**, 1638–1648.

22 S. Gama, D. Mackay and J. A. Arnot, *Green Chem.*, 2012, **14**, 1094–1102.

23 M. Tobiszewski, S. Tsakovski, V. Simeonov, J. Namieśnik and F. Pena-Pereira, *Green Chem.*, 2015, **17**, 4773–4785.

24 D. Mackay, W. Y. Shiu, K.-C. Ma and S. C. Lee, *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, Taylor & Francis, Boca Raton, USA, 2006.

25 Y. Andersson-Sköld, P. Grennfelt and K. Pleijel, *J. Air Waste Manage. Assoc.*, 1992, **42**, 1152–1158.

26 W. Wu, B. Zhao, S. Wang and J. Hao, *J. Environ. Sci.*, DOI: 10.1016/j.jes.2016.03.025.

27 J. Altenstedt and K. Pleijel, *J. Air Waste Manage. Assoc.*, 2000, **50**, 1023–1036.

28 International Agency for Cancer Research, website http://www.iarc.fr (visited 27.09.2016).

29 C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879–3890.

30 E. Calabrese, R. Barnes and E. J. Stanek, *Regul. Toxicol. Pharmacol.*, 1989, **10**, 123–137.

31 The Canadian Centre for Environmental Modelling and Chemistry Level I Model Version 2.11 - August 1999. http://www.trentu.ca/academic/aminss/envmodel/models/VBL1.html (visited 27.09.2016).

32 D. Mackay, A. Di Guardo, S. Paterson and C. E. Cowan, *Environ. Toxicol. Chem.*, 1996, **15**, 1627–1637.

33 W.-H. Chen, W.-B. Yang, C.-S. Yuan, J.-C. Yang and Q.-L. Zhao, *Chemosphere*, 2014, **103**, 92–98.

34 C. Fan, Y.-c. Chen, H.-w. Ma and G.-s. Wang, *J. Hazard. Mater.*, 2010, **182**, 778–786.

35 C. L. Hwang and K. P. Yoon, *Multiple attribute decision making: Methods and applications*, Springer-Verlag, New York, 1981.

36 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.

37 F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. R. McElroy and J. Sherwood, *Sustainable Chem. Processes*, 2016, **4**, 1–24.

38 C. Capello, U. Fischer and K. Hungerbühler, *Green Chem.*, 2007, **9**, 927–934.

39 D. Prat, J. Hayler and A. Wells, *Green Chem.*, 2014, **16**, 4546–4551.

40 R. Cardoso de Oliveira, S. T. Davantel de Barros and M. Luiz Gimenes, *J. Food Eng.*, 2013, **117**, 458–463.

41 Y. Shen, B. Chen and T. A. van Beek, *Green Chem.*, 2015, **17**, 4073–4081.

42 C. S. Funari, R. L. Carneiro, M. M. Khandagale, A. J. Cavalheiro and E. F. Hilder, *J. Sep. Sci.*, 2015, **38**, 1458–1465.

43 Y. Gu and F. Jérôme, *Green Chem.*, 2010, **12**, 1127–1138.

44 A. E. Díaz-Álvarez, J. Francos, P. Crochet and V. Cadierno, *Curr. Green Chem.*, 2014, **1**, 51–65.

45 J. I. García, H. García-Marín and E. Pires, *Green Chem.*, 2014, **16**, 1007–1033.

46 A. Wolfson, C. Dlugy and Y. Shotland, *Environ. Chem. Lett.*, 2007, **5**, 67–71.

47 S. Aparicio and R. Alcalde, *Green Chem.*, 2009, **11**, 65–78.

48 Y. L. Kua, S. Gan, A. Morris and H. K. Ng, *Sustainable Chem. Pharm.*, 2016, **4**, 21–31.

49 Y. Zhu, Z. Chen, Y. Yang, P. Cai, J. Chen, Y. Li, W. Yang, J. Peng and Y. Cao, *Org. Electron.*, 2015, **23**, 193–198.

50 M. Virot, V. Tomao, C. Ginies, F. Visinoni and F. Chemat, *J. Chromatogr., A*, 2008, **1196–1197**, 147–152.

51 S. Veillet, V. Tomao, K. Ruiz and F. Chemat, *Anal. Chim. Acta*, 2010, **674**, 49–52.

52 S. Bertouche, V. Tomao, K. Ruiz, A. Hellal, C. Boutekedjiret and F. Chemat, *Food Chem.*, 2012, **134**, 602–605.