A Comparison of Partial Order Technique with Three Methods of Multi-Criteria Analysis for Ranking of Chemical Substances

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An alternative to the often cumbersome and time-consuming risk assessments of chemical substances could be more reliable and advanced priority setting methods. An elaboration of the simple scoring methods is provided by Hasse Diagram Technique (HDT) and/or Multi-Criteria Analysis (MCA). The present study provides an in depth evaluation of HDT relative to three MCA techniques. The new and main methodological step in the comparison is the use of probability concepts based on mathematical tools such as linear extensions of partially ordered sets and Monte Carlo simulations. A data set consisting of 12 High Production Volume Chemicals (HPVCs) is used for illustration. It is a paradigm in this investigation to claim that the need of external input (often subjective weightings of criteria) should be minimized and that the transparency should be maximized in any multicriteria prioritisation. The study illustrates that the Hasse diagram technique (HDT) needs least external input, is most transparent and is least subjective. However, HDT has some weaknesses if there are criteria which exclude each other. Then weighting is needed. Multi-Criteria Analysis (i.e. Utility Function approach, PROMETHEE and concordance analysis) can deal with such mutual exclusions because their formalisms to quantify preferences allow participation e.g. weighting of criteria. Consequently MCA include more subjectivity and loose transparency. The recommendation which arises from this study is that the first step in decision making is to run HDT and as the second step possibly is to run one of the MCA algorithms.

I. INTRODUCTION

Many chemical substances have adverse effects on human health and the environment. This has, for example, motivated the European Union to decide that the risk from chemicals on the European market should be assessed and their use successively regulated if necessary.[1] For this purpose a technical guidance document (TGD)[2] was developed together with a supportive software package, EUSES.[3] Unfortunately, the risk assessment procedure as described in the TGD is rather cumbersome and time-consuming. At present, due to the relative complexity of the models involved and, consequently, the lack of data, only a rather limited number of risk assessments have been adopted (see for an actual status: http://ecb.ei.jrc.it). Considering, the 100106 existing chemical substances registered in Europe,[4] an efficient alternative to the present risk assessment procedure is needed.

An alternative to the risk assessments could be more reliable priority setting methods. This is in accordance with the precautionary principle in the sense that regulation is to be made before scientific evidence is fully established.[5] The precautionary principle thus bypasses the risk assessment as illustrated in Figure 1. This could be combined with a shift in the responsibility for producing full risk assessments from the government institutions to the chemical industry as suggested by the European Commission.[6]

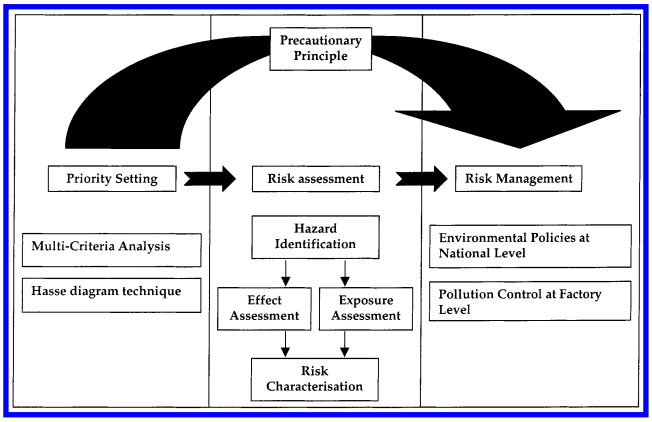

Figure 1. The natural order of priority setting, risk assessment and risk management and the coupling of priority setting and risk management using the precautionary principle.

Besides sophisticated multivariate statistics, which is useful in preprocessing data (i.e. cluster analysis or reduction of the dimensionality) priority setting has from a methodological point of view been rather simplistic.

At present the European Commission relies on a simple scoring method, the European Union Risk Ranking Method

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(EURAM), for preliminary priority setting.[7] This method is based on a level I multimedia fugacity model.[8] The development and use of scoring methods have been extensive. Besides EURAM, well-known examples are COMMPS,[9] CHEMS-1,[10] ASTER[11] and the GUS-index.[12]

If the priority setting phase is assumed to play a prominent role it is wise to use more advanced or at least investigate the possibilities of various algorithms. An alternative to the simple scoring methods can be provided by Hasse Diagram Technique (HDT)[13] and/or Multi-Criteria Analyses (MCA). An in depth investigation and comparison of these methodologies is therefore of interest.

A comparison of HDT with a scoring method, CHEMS-1, has previously been presented,[14] and significant discrepancies due to the weighting of descriptors and lack of data were revealed. Further, there were discrepancies in the importance of carcinogenicity as a descriptor. In CHEMS-1 it turned out that carcinogenicity did not have a major influence on the ranking results, whereas in HDT it had.

In this paper HDT is evaluated relative to three MCA techniques (Utility Function,[15] PROMETHEE[16,17] and Concordance Analysis[18]). The evaluation is performed in order to find common regularities and to give recommendations on when it may be suitable to use HDT and when an input extensive MCA is to be preferred.

One of the MCA methodologies, the Utility Function, covers the general principle of scoring methods. The conclusion from the comparison of HDT with the Utility Function can therefore to some degree be transferred to the scoring methods mentioned above. The Utility Function is sometimes also referred to as the Index Function or the Quality Function.

When priority setting methods are compared or evaluated the following two criteria should be kept in mind:

- *Subjectivity/Transparency.* Political or subjective considerations should only be involved when strictly necessary. Further, the transparency of a methodology is often inversely related to the degree of subjective consideration involved.
- *Precision.* The result needs to be precise enough to allow useful decisions.

Advanced techniques will be applied to examine HDT relative to the three MCA methods. The new and main methodological step in the comparison is to use probability concepts based on mathematical tools such as linear extensions of partial ordered sets and Monte Carlo simulations. Finally, a first step in the identification of a general mathematical scheme to evaluate the ranking methods is considered.

A data set consisting of 12 High Production Volume Chemicals (HPVC) is used for illustration.[19]

II. SURVEY OF THE RANKING METHODS

II.1. Hasse Diagram Technique. Hasse Diagram Technique (HDT) is based on partial order theory.[13,20,21,22] The HDT appears as a simple method, which a priori includes "$\leq$" as only mathematical relation. If a series of substances is considered, *X*, which can be described by a row of descriptors, *Q*, then a given substance, x_1, is characterized by the descriptors $q_j(x_1)$. Another substance, x_2, is characterized by the descriptors $q_j(x_2)$ and so on. In HDT the set *Q* is called an information base. The substances, x_1 and x_2, can subsequently be compared through comparison of the individual descriptors. The substance x_1 will be ranked higher than substance x_2 ($x_2 \leq x_1$) if all descriptors for x_1 are higher than or equal to the corresponding descriptors for x_2. In mathematical terms this can be expressed as: $x_2 \leq x_1$ if $q_j(x_2) \leq q_j(x_1)$ for all j. Obviously, if all descriptors for x_1 are equal to the corresponding descriptors for x_2, i.e., $q_j(x_2) = q_j(x_1)$ for all j, the two substances will have identical rank and will be considered as equivalent, $x_1 \sim x_2$. (For more details concerning equivalence, see ref 20). It further follows that if $x_2 \leq x_1$ and $x_3 \leq x_2$ then $x_3 \leq x_1$. If two substances cannot be given a mutual order relative to each other, they are said to be incomparable.

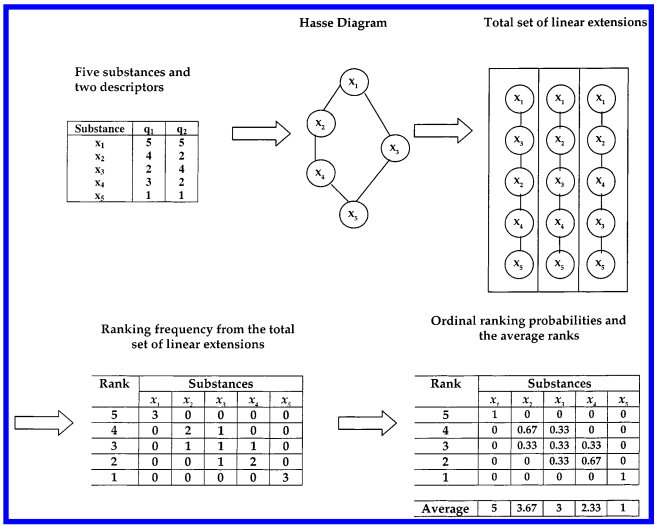

Figure 2. A Hasse diagram for five substances based on two descriptors (the so-called decision matrix, and all linear extensions). The ordinal ranking probability is found as the frequency of the occurrence of a rank for a given substance.

The HDT assumes neither linearity nor any numerical relationship among descriptors and is further defined as a so-called nonmetric method. Only the relative designation "high" and "low" of the descriptors is of importance. To illustrate the principle a simple Hasse diagram is constructed for five substances $x_1,x_2,..,x_5$ using two descriptors in Figure 2.

A linear extension is a total order, where all comparabilities of the partial order are reproduced.[13,23] Because incomparabilities may appear in the partial order, several linear extensions are possible from one partial order. If all possible linear extensions are found, a ranking probability can be calculated. The number of linear extensions where a selected substance has obtained a specific rank relative to the total number of linear extensions is equal to the "ordinal ranking probability". In Figure 2 it is illustrated that the substance x_1 is related to the highest rank since, x_1, obviously is placed above all other substances in all the linear extensions. On the other hand, the substance x_3 is equally related to three ranking levels. For the substance x_3 the ordinal ranking probability for rank no. 5 is equal to 0 and for rank no. 4 it is 0.33 etc.

When all possible linear extensions are found it is also possible to calculate the average ranks of the substances in a partially ordered set.[24,25] The average rank is simply the average of the ranks in all the linear extensions. Note: This procedure implies that the ranks derived from linear extensions get a metric. That means (in simple, non mathematical

words) that rank numbers can be added and be multiplied with scalars. Therefore the notation "ordinal ranking probability" is introduced. Using Figure 2 as an example, the average rank of the substance x_2 is 3.667. For the substance x_3 the average rank is 3. Therefore in the linear rank, x_2 will be given a higher rank than x_3. In the example given in Figure 2 the most probable sequence of ranks is $x_1 > x_2 > x_3 > x_4 > x_5$.

II.2. Utility Function Approach.[15] In contrast to HDT, when using the Utility Function, each descriptor is given a weight indicating the relative importance of that particular descriptor. Considering the descriptors used in this paper, it is thus necessary to decide if, for example, the bioaccumulation expressed by log K_{ow} is more or less important than acute toxicity for fish expressed by LC50. Weighting of the descriptors is a way to take into account additional external judgments. It can be seen as a formalism to introduce the participation principle in the ranking procedure. This is interesting since the participation principle seems to play a more and more important role in modern environmental policy-making. The outcome of the Utility Function approach is a quantity Γ for each substance, which is a numerical aggregation of descriptors, often simply their weighted sum. Based on the value of $\Gamma(x)$ the corresponding ordinal rank of x is derived. This means the set of substances is totally ordered by the values of Γ. A more specific description is given in Appendix I.

II.3. PROMETHEE.[16,17] The *P*reference *R*anking *O*rganisation *METH*od for *E*nrichment *E*valuations (PROMETHEE) was developed as a tool in operational research.[16,17] It has found broad application in the field of decision-making. However in environmental sciences application of PROMETHEE seems at present to be limited (see for example ref 26 for evaluation of environmental management strategies,[27] for application in LCA,[28] in problems of biodiversity or[29] for general evaluations of landscapes).

In contrast to the Utility Function approach the various descriptors of each substances are not aggregated. However a preference function will be constructed based on the mutual comparison of any two substances. The preference function needs—as in the utility function approach—weights and an information about the significance of numerical differences between the descriptor values of two substances, here called Δq^0. The outcome of PROMETHEE is usually divided into two parts: By PROMETHEE I a dominance, $d\pi$ and a subdominance indicator, $sd\pi$, is found. The dominance indicator describes how much a substance is preferred over all other, whereas the subdominance indicator describes how much all other substances are preferred over some specific substance. In PROMETHEE II just the difference is formed $\Gamma = d\pi - sd\pi$. By the quantity Γ the substances can be ranked, i.e., a total order is formed. For details, see Appendix II.

Before moving on to the Concordance Analysis (section II.4), it should be mentioned that a decision support system based on fuzzy sets similar to PROMETHEE was introduced by Munda.[30] The analysis of this system, called NAIADE, is, however, outside the scope of the present study.

II.4. Concordance Analysis.[18] The use of the Concordance Analysis has been introduced as a priority setting system for chemicals by Opperhuizen and Hutzinger.[18] The most important difference between the Concordance Analysis and PROMETHEE, the Utility Function approach and HDT is the introduction of a reference substance and the system of parameters by which preferences with respect to that reference substance are formulated. The system of formulating preferences and vetos by many parameters is further developed in the decision support systems ELECTRE[31] and ORESTE.[15] However according to our knowledge, up to now especially ORESTE has not found a broad application in environmental sciences.

The main idea of the Concordance Analysis is to derive two indices, the Concordance and the Discordance index. The Concordance index measures how much a substance is preferred to the reference substance, whereas the Discordance index quantifies how much a substance is less acceptable compared to the reference substance. The rank of substances can be found by the difference of both indices.

In our application we follow the main ideas of introducing the reference substance and of formulating two indices for each substance. However we selected as concordance index that one which measures the degree of being worse and as discordance index that one of being better than the reference substance. For details see Appendix III.

II.5. Order Preserving Mapping. In the present paper our sets consist of a series of substances, *X*, and a row of descriptors, *Q*. The series of substances, *X*, remain constant in the various manipulations, whereas the row of descriptors, *Q*, might differ $(Q_1,Q_2,..,Q_n)$, for example by different methods to transform and aggregate the descriptors. The comparison of the (partially ordered) sets with each other (i.e. (X,Q_1), (X,Q_2),..(X,Q_n)) can in mathematical terms be phrased as maps, φ_{nm}, which are to be characterized due to their ability of order preserving, order embedding or order isomorphisms (identical orders)[23] or at least by the similarity between, e.g. (X,Q_1) and (X,Q_2):

$$(X,Q_1) \xrightarrow{\varphi_{12}} (X,Q_2) \tag{1}$$

A mathematical map is thus a general expression for a relationship between sets. In the present paper the sets of interest exhibit a structure, i.e., the structure of an order. We are thus interested in determining if a map is order preserving or not. In other words, do we obtain the same order relations with two different ranking methods? If a map is order preserving it means that if $x_1 \leq x_2$ in the first set, (X, Q_1), then the relation $x_1 \leq x_2$ will also be found in second set, (X, Q_2). If an order preserving map can be found between two total orders, obviously, the comparison is trivial. On the other hand it does provide valuable information if, for example, a partial order of one method can be related to the order of another method through an order preserving map. In that sense a specific linear extension is the image of an order preserving map.

All ranking methodology comes after a series of manipulations to some kind of order, mostly a total order. However, each manipulation can also be considered as a mapping of one set into another.

III. DATA

Data for 12 HPVC are found in the IUCLID database.[19] Four characteristic properties (descriptors of molecular/environmental properties) are used to describe the environmental impact of the pesticides. The production volume (PV)

Table 1. Data on Production Volume (PV), Acute Toxicity for Fish (LC50), the *n*-Octanol−Water Partitioning Coefficient (log K_{ow}) and Biodegradation (BD) for 12 Pesticides

CAS no.	EINECS no.	abbr	name	PV[a]	LC 50 (mg/L)	log K_{ow}	BD (%/day)
100−00−5	202−809−6	CNB	1-chloro-4-nitrobenzene	4	1.5	2.6	0.2
100−01−6	202−810−1	4NA	4-nitroaniline	2	35	1.4	0
100−02−7	202−811−7	4NP	4-nitrophenol	1	7	1.9	0.1
1912−24−9	217−617−8	ATR	atrazin	2	4.3	2.5	0.5
999−81−5	213−666−4	CHL	chlormequat chlorid	2	80	−2.2	1
333−41−5	206−373−8	DIA	diazinon	1	2.6	3.3	0
60−51−5	200−480−3	DIM	dimethoate	2	7.5	0.7	0
26761−40−0	247−977−1	LIN	ethofumesate	1	11	2.7	0.4
1071−83−6	213−997−4	GLY	glyphosate	2	52	0.002	0.3
34123−59−6	251−835−4	ISO	isoproturon	2	3	2.5	30
121−75−5	204−497−7	MAL	malathion	3	0.04	2.7	100
137−26−8	205−286−2	THI	thiram	2	0.3	1.7	0

[a] 1 = 5.000−10.000 tons/year, 2 = 10.000−50.000 tons/year, 3 = 50.000−100.000 tons/year and 4 = 100.000−500.000 tons/year.

is used as an indicator of the exposure and the acute toxicity to fish (LC50) is used as an indicator of the toxicity. The partitioning coefficient between *n*-octanol and water (log K_{ow}) is used as an indicator for the ability to accumulate in biota or in targets such as sediments, suspended matter and soil particles. Finally, the biodegradation (BD) indicates the persistence of the substance in the environment. In the case that more than one numerical value for a given descriptor is available the most conservative value is chosen assuming a "worst case scenario". This was especially the case for the biodegradation and to a certain extent also for log K_{ow}. We did not further evaluate the data quality since the numbers are merely used to illustrate the methodology and not to estimate exactly which of the 12 HPVC have the highest environmental impact. Further, we do not intend to go into an elaborated discussion on the actual choice of descriptors. The pesticides, their CAS (CAS: Chemical Abstracts Service) no., EINECS (EINECS: European Inventory of Existing Chemical Substances) no., the abbreviations used in figures and tables and the descriptors are given in Table 1. The data in Table 1 thus form the decision matrix, which is the basis for both HDT and the MCAs.

When using HDT the descriptors must have the same orientation. Thus, if a high value for one descriptor indicates a high environmental impact, such as is the case with log K_{ow}, high values for all descriptors must indicate a high environmental impact. Since a low acute toxicity for fish (LC50) increases the environmental impact the LC50 values have been multiplied with minus one to ensure that the substances with the lowest values will be ranked highest. This is also the case for the biodegradation.

IV. THE HASSE DIAGRAM

Figure 3 shows the Hasse diagram for the 12 substances included in this investigation. The description of the graphical presentation of a partial order can be found in several publications (see for example ref 32), nevertheless some remarks may be valuable: Let there be an order relation between two substances x_1 and x_2: $x_1 \leq x_2$. Then x_2 is located in the drawing plane above x_1 and both are connected by a line. In doing this there is still some freedom to locate the substances. Thus, it is convenient to arrange the substances in levels and to avoid crossings of the lines (details, see ref 13). Beyond this purely graphical arrangement, the assignment to levels can be seen as another

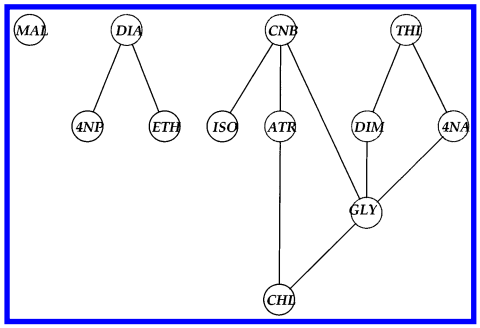

Figure 3. The Hasse diagram based on the data separated into six equidistant classes derived from data of Table 1.

example of order-preserving map, which leads to a simple evaluation scheme.[33] The identification of levels has in several studies been one of the most important conclusions that could be obtained from the Hasse diagram (e.g. ref 14).

The Hasse diagram in Figure 3 is arranged into four levels. In the highest level (corresponding to the highest environmental impact) there are four substances (malathion (MAL), linuron (LIN), 1-chloro-4-nitrobenzene (CNB) and thiram (THI)) and in the lowest there is only one substances (chlormequat chlorid (CHL)). In the present data set there is a relative high number of incomparable chemicals. This is not surprising since the number of incomparabilities is often dependent on the number of substances relative to the number of descriptors, which are not rank-correlated. In the present study four descriptors for twelve substances are used. This is a relative high number of descriptors for the (relative low) number of substances.[34]

The Hasse diagram (Figure 3) reveals two groups of substances and an isolated substance. The largest group includes eight and the small group includes three substances. The substances in the small group are characterized as having small production volumes and relative high log K_{ow} values. The large group shows the reverse trend. The production volume and log K_{ow} are denoted "antagonistic" indicators because they are capable of separating the Hasse diagram in two groups so-called hierarchies according to Halfon and Reggiani.[22] Malathion (MAL) is an isolated substance because it has the lowest LC50 and at the same time the fastest biodegradation.

Using all linear extensions the probability distribution of ranks for each substance can be found. Table 2 gives the ordinal probability for the individual substances to occupy a certain rank. The ranking probabilities are spread out in

Table 2. Probability Distribution of Ranks When Using All Linear Extensions (HDT)

substance/rank	12	11	10	9	8	7	6	5	4	3	2	1
CNB	0.285	0.228	0.177	0.132	0.092	0.055	0.025	0.007	0	0	0	0
4NA	0	0.059	0.107	0.141	0.161	0.163	0.147	0.116	0.074	0.031	0	0
4NP	0	0.023	0.043	0.061	0.077	0.091	0.102	0.111	0.118	0.123	0.125	0.125
ATR	0	0.031	0.059	0.084	0.106	0.123	0.136	0.141	0.135	0.114	0.072	0
CHL	0	0	0	0	0	0	0.002	0.011	0.042	0.118	0.273	0.553
DIA	0.250	0.205	0.164	0.127	0.095	0.068	0.045	0.027	0.014	0.005	0	0
DIM	0	0.059	0.107	0.141	0.161	0.163	0.147	0.116	0.074	0.031	0	0
ETH	0	0.023	0.043	0.061	0.077	0.091	0.102	0.111	0.118	0.123	0.125	0.125
GLY	0	0	0	0	0.010	0.041	0.094	0.162	0.228	0.259	0.207	0
ISO	0	0.026	0.049	0.068	0.085	0.098	0.107	0.112	0.114	0.114	0.114	0.114
MAL	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083
THI	0.382	0.263	0.169	0.100	0.053	0.024	0.008	0.002	0	0	0	0

Table 3. Most Probable Rank Obtained by Using All Linear Extensions (HDT) and the Rankings Obtained When Using the Utility Function, PROMETHEE, and the Concordance Methods with Equal Weightings ($g_j = 0.25$)

rank	HDT all linear extensions	av rank	the Utility Function	Γ	PROMETHEE	Γ	Concordance Analysis	Γ
12	THI	10.71	CNB	0.963	CNB	29.40	CNB	1.000
11	CNB	10.71	ATR	0.782	ATR	10.95	4NA	0.708
10	DIA	9.75	THI	0.760	THI	7.91	ATR	0.708
9	4NA	7.28	DIA	0.742	DIA	7.02	DIM	0.708
8	DIM	7.28	ISO	0.713	ISO	2.73	ISO	0.708
7	MAL	6.50	DIM	0.692	DIM	−0.01	THI	0.708
6	ATR	5.93	ETH	0.687	ETH	−0.10	4NP	0.625
5	ISO	5.09	4NP	0.664	MAL	−0.63	DIA	0.625
4	4NP	4.88	MAL	0.639	4NP	−3.32	ETH	0.625
3	ETH	4.88	4NA	0.638	4NA	−4.95	MAL	0.625
2	GLY	3.84	GLY	0.520	GLY	−16.24	GLY	0.208
1	CHL	1.69	CHL	0.331	CHL	−32.75	CHL	0.125

the interval of possible ranking positions. Clearly the probabilities of isolated objects, like malathion (MAL) (compare Figure 3), will be spread equally out over the whole interval providing an average rank of 6.5. The highest probability for a position is only 0.553 for chlormequat chlorid (CHL) on rank no. 1. The average rank is presented in the HDT-column in Table 3.

V. RESULTS OF MULTI-CRITERIA ANALYSIS

The Utility Function. If it is possible to determine the relative importance of the descriptors and thus ascribe specific weights an exact ranking can be obtained. However, to illustrate the methodological differences, the rank using equal weights ($g_j = 0.25$) is calculated (Table 3, column "The Utility Function"). Compared with the rank obtained when using the HDT average rank, the most significant differences are atrazin (ATR) that changes from position no. 6 to no. 11 and 4-nitroaniline (4NA) that changes from position no. 9 to 3. The change in position of 4-nitroaniline (4NA) can probably be ascribed to the rather low LC50. When using a metric method, such as the Utility Function, the actual numbers obviously influence the result more than when using a nonmetric method, such as HDT. Thus, if a substance, like 4-nitroaniline (4NA) has a descriptor with a very low value, the ranking result may vary significantly. Note that there are other examples of inversion like 4-nitrophenol (4NP) and malathion (MAL): They switch their positions, when the ranking by HDT is compared with that of the Utility Function.

If a set of weights is chosen it will result in one definite rank. If another set of weights is selected another rank will occur. To illustrate the range of possible ranks the influence of the weights is estimated by a Monte Carlo Simulation. In the Monte Carlo Simulation random weights (from 0 to 1) are repetitively chosen and the utility, Γ, for each substance and the linear rank is calculated (number of runs = 10000). The average utility, $\Gamma_{average}$, is calculated, and based on the linear ranks the ranking probabilities are calculated and given in Table 4a. Comparing the ranking probabilities for the Utility Function with the ordinal ranking probabilities found by HDT it appears that the probabilities for the Utility Function are less spread out and clearly higher. As an illustrative example the probability for 1-chloro-4-nitrobenzene (CNB) on rank no. 12 is as high as 0.944. Figure 4 illustrates how the ordinal HDT ranking probabilities are more spread out than those for the Utility Function. It can thus be seen that the nonmetric approach (HDT) generally supplies more ranking possibilities than the variation of weights. Considering order preserving maps it has been proved that the partially ordered set (X, Q) from HDT is related by an order preserving map to the total ordered set (X, {Γ}) of the Utility Function.[13] Therefore: If any two substances x, y are comparable in HDT, e.g. $x < y$, then they must be comparable in the Utility Function approach (compare Appendix I, eq A1) $\Gamma(x) < \Gamma(y)$, independently which weights are selected. Given specific weights one of the possible linear extensions will represent the ranking due to Γ. Because of the metric nature of the Utility Function many different sets of weights may mapped onto the same linear extension, which explains the different distributions found by HDT and Utility Function approach, respectively.

PROMETHEE. The Γ-values derived from PROMETHEE and the ranks deduced from them are shown in Table 3 (third column "PROMETHEE"). The calculation was performed

Table 4. Distributions of Ranking Probabilities When Using a Monte Carlo Simulation on the Weights for a) the Utility Function, b) PROMETHEE, and c) the Concordance Analysis

substance/rank	12	11	10	9	8	7	6	5	4	3	2	1
						a. Utility Function						
CNB	0.944	0.055	0.001	0	0	0	0	0	0	0	0	0
4NA	0	0	0	0.023	0.064	0.064	0.109	0.139	0.288	0.312	0	0
4NP	0	0	0	0	0.017	0.165	0.156	0.244	0.212	0.151	0.044	0.012
ATR	0	0.424	0.477	0.086	0.012	0.001	0	0	0	0	0	0
CHL	0	0	0	0	0	0	0.008	0.003	0.011	0.010	0.093	0.876
DIA	0.055	0.176	0.137	0.188	0.112	0.149	0.106	0.046	0.021	0.009	0	0
DIM	0	0	0	0.164	0.118	0.150	0.187	0.200	0.152	0.030	0	0
ETH	0	0	0.007	0.091	0.150	0.123	0.233	0.179	0.140	0.054	0.018	0.004
GLY	0	0	0	0	0	0.023	0.013	0.030	0.038	0.225	0.671	0
ISO	0	0	0.015	0.145	0.341	0.179	0.118	0.115	0.057	0.022	0.009	0
MAL	0	0.196	0.038	0.042	0.022	0.065	0.051	0.042	0.082	0.187	0.165	0.109
THI	0.001	0.148	0.325	0.261	0.163	0.081	0.021	0.001	0	0	0	0
						b. PROMETHEE						
CNB	0.929	0.070	0	0	0	0	0	0	0	0	0	0
4NA	0	0	0	0.021	0.067	0.068	0.113	0.171	0.242	0.319	0	0
4NP	0	0	0	0	0.015	0.148	0.126	0.229	0.206	0.195	0.059	0.021
ATR	0	0.368	0.510	0.107	0.014	0.001	0	0	0	0	0	0
CHL	0	0	0	0	0	0	0.010	0.005	0.014	0.016	0.074	0.880
DIA	0.070	0.191	0.146	0.176	0.109	0.128	0.095	0.049	0.022	0.015	0	0
DIM	0	0	0	0.136	0.127	0.127	0.197	0.190	0.181	0.040	0	0
ETH	0	0	0.008	0.104	0.144	0.103	0.231	0.164	0.140	0.070	0.029	0.007
GLY	0	0	0	0	0	0.028	0.014	0.034	0.053	0.164	0.707	0
ISO	0	0	0.017	0.109	0.320	0.231	0.117	0.102	0.063	0.026	0.015	0
MAL	0	0.230	0.052	0.067	0.034	0.062	0.060	0.054	0.079	0.154	0.115	0.092
THI	0.001	0.141	0.266	0.280	0.169	0.105	0.036	0.002	0	0	0	0
						c. Concordance Analysis						
CNB	1.000	0	0	0	0	0	0	0	0	0	0	0
4NA	0	0.615	0.385	0	0	0	0	0	0	0	0	0
4NP	0	0	0	0	0	0	0.503	0.480	0.004	0.014	0	0
ATR	0	0	0.615	0.385	0	0	0	0	0	0	0	0
CHL	0	0	0	0	0	0	0.005	0.013	0	0.004	0.081	0.897
DIA	0	0	0	0	0	0	0	0.503	0.480	0.004	0.014	0
DIM	0	0	0	0.615	0.385	0	0	0	0	0	0	0
ETH	0	0	0	0	0	0	0	0	0.503	0.480	0.004	0.014
GLY	0	0	0	0	0	0	0	0.005	0.013	0.100	0.865	0.018
ISO	0	0	0	0	0.615	0.385	0	0	0	0	0	0
MAL	0	0.385	0	0	0	0	0.107	0	0.001	0.399	0.037	0.071
THI	0	0	0	0	0	0.615	0.385	0	0	0	0	0

using equal weights ($g_j = 0.25$), like for the Utility Function and $\Delta q^0_j = 0.5 * \text{std}(q_j)$ (std(q_j): standard deviation of q_j). Compared with the ranking based on the Utility Function no significant changes in positions are observed, only malathion (MAL) and 4-nitrophenol (4NP) changes position. As for the Utility Function, the weights of the descriptors play a crucial role for the ranking of the substances in PROMETHEE. The possible rankings which can be obtained due to the variation of the weights are again illustrated by a Monte Carlo Simulation using random weights. The simulation result is shown in Table 4b (number of runs = 10000). Comparing the ranking probabilities for PROMETHEE with the ordinal probabilities found by HDT then the ranking probabilities are less spread out and clearly higher. As an example the probability for 1-chloro-4-nitrobenzene (CNB) on rank no. 12 is as high as 0.929. Compared with the Utility Function the pattern seems similar.

In contrast to the Utility Function, Γ_i derived from PROMETHEE further depends on how the preference functions f_j are formulated (see Appendix II). If delta zero Δq^0 is small PROMETHEE becomes independent of the metric values, since the preference function will only take the value 0 or 1. On the other hand, if delta zero, Δq^0, is large the metric value of the descriptors becomes more important. For the following calculations Δq^0_j was set to n*std(q_j), with n varying. Table 5a shows how the average ranking from the Monte Carlo simulation changes as n increases from 0.1 to 0.9. The quantity μ indicates the number of substances that change position when n is changed by 0.1. Thus, changing n from 0.5 to 0.6 two substances change position, i.e., dimethoate (DIM) and Ethofumesate (LIN). Comparing the ranking obtained when $n = 0.1$ with the ranking obtained when $n = 0.8$ malathion (MAL) change position from no. 4 to no. 7. Using the PROMETHEE methodology, it is thus important to clarify how the choice of Δq^0-values influences the result.

Two partially ordered sets can be defined within PROMETHEE: $(X, Q_{PROMETHEEI})$ and $(X, Q_{PROMETHEEII})$, where $Q_{PROMETHEEI} = \{d\pi, sd\pi\}$ and $Q_{PROMETHEE\ II} = \{\Gamma\}$. The first partial order can be defined as follows: $x_1 > x_2 :\Leftrightarrow d\pi_1 > d\pi_2$ and $sd\pi_1 < sd\pi_2$ (PROMETHEE I). The corresponding Hasse diagram (based on $d\pi$ and $sd\pi$) usually contains more comparabilities than that based directly on the descriptors themselves. The remaining incomparabilities in PROMETHEE I are due to severe conflicts among attributes, which are still not resolved by the selection of weights and the preference functions, f_j.

It is difficult to characterize the map between HDT and PROMETHEE II in full generality. For HDT and PROMETHEE I, first attempts, analyzing a very simple Hasse

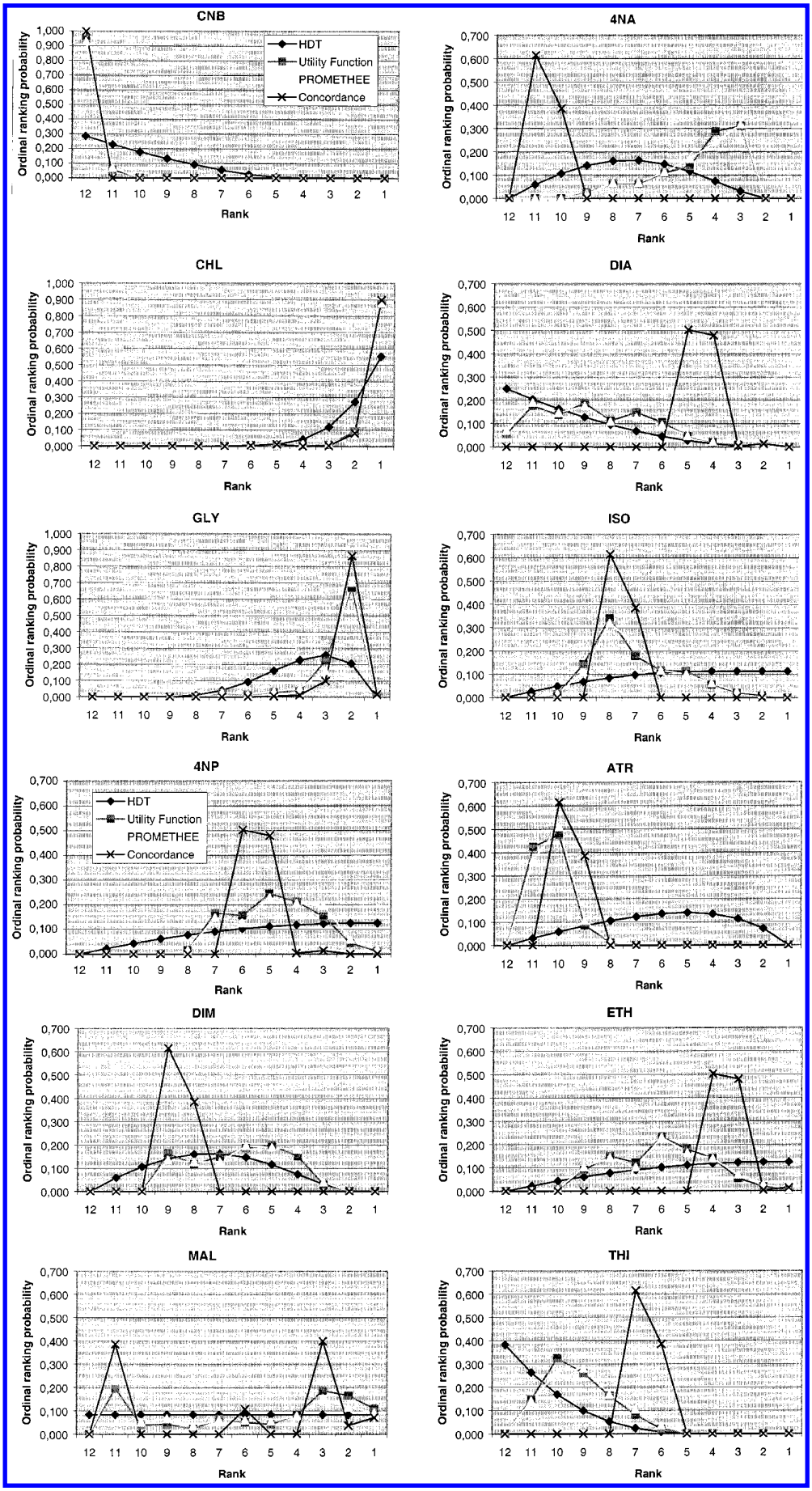

Figure 4. The distribution of the probability of ranks. Note the different scales.

Table 5. Change in Order When a) Delta Zero and b) the Descriptors for the Reference Element Increases

rank/n	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
				a. Monte Carlo Simulation: Delta Zero					
12	CNB	CNB	CNB	CNB	CNB	CNB	CNB	CNB	CNB
11	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR	ATR
10	THI	THI	THI	THI	THI	THI	THI	THI	THI
9	DIA	DIA	DIA	DIA	DIA	DIA	DIA	DIA	DIA
8	ISO	ISO	ISO	ISO	ISO	ISO	ISO	ISO	ISO
7	DIM	DIM	DIM	DIM	DIM	ETH	ETH	MAL	MAL
6	ETH	ETH	ETH	ETH	ETH	DIM	MAL	ETH	DIM
5	4NP	MAL	MAL	MAL	MAL	MAL	DIM	DIM	ETH
4	MAL	4NP	4NP	4NP	4NP	4NP	4NP	4NP	4NP
3	4NH	4NH	4NH	4NH	4NH	4NH	4NH	4NH	4NH
2	GLY	GLY	GLY	GLY	GLY	GLY	GLY	GLY	GLY
1	CHL	CHL	CHL	CHL	CHL	CHL	CHL	CHL	CHL
μ	2	0	0	0	2	2	2	2	
				b. Monte Carlo Simulation: Reference Substance					
12	CNB	CNB	CNB	CNB	CNB	CNB	CNB	CNB	CNB
11	4NA	4NA	4NA	4NA	4NA	ATR	ATR	ATR	DIA
10	ATR	ATR	ATR	ATR	ATR	ISO	THI	DIA	ATR
9	DIM	DIM	DIM	DIM	DIM	THI	4NP	ETH	DIM
8	GLY	GLY	GLY	ISO	ISO	4NP	DIA	DIM	THI
7	ISO	ISO	ISO	THI	THI	DIA	ETH	ISO	4NP
6	THI	THI	THI	4NP	4NP	ETH	DIM	THI	4NA
5	4NP	4NP	4NP	DIA	DIA	MAL	ISO	4NP	GLY
4	DIA	DIA	DIA	ETH	ETH	4NA	MAL	MAL	ISO
3	ETH	ETH	ETH	MAL	MAL	DIM	4NA	4NA	CHL
2	MAL	MAL	MAL	GLY	GLY	GLY	GLY	GLY	MAL
1	CHL	CHL	CHL	CHL	CHL	CHL	CHL	CHL	ETH
μ	0	0	1	0	2	3	2	8	

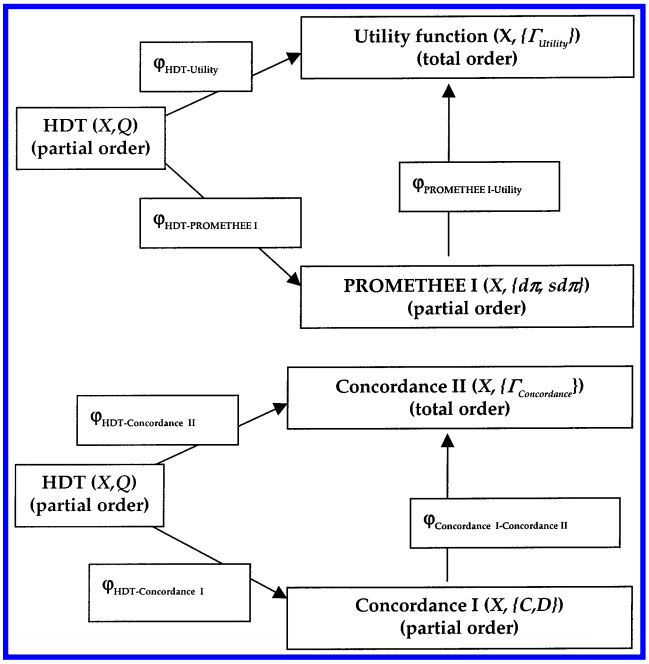

Figure 5. Mathematical maps between a) HDT, the Utility Function and PROMETHEE I and b) HDT, Concordance I and Concordance II. The map between HDT and the Utility Function approach is order preserving.

diagram, lead to the conclusion that comparabilities found in HDT will be reproduced in PROMETHEE I. Therefore there probably is an order preserving map

$$(X, Q) \xrightarrow{\varphi_{HDT-PROMETHEE\ I}} (X, Q_{PROMETHEE\ I})$$

(cf. Figure 5). The characterization of maps (whether order preserving) between HDT and PROMETHEE remains a topic for further studies.

In relation to the Utility Function, $\varphi_{HDT-Utility}$ is an order preserving map and in the case that $\varphi_{HDT-PROMETHEE\ I}$ also is order preserving, the noninvestigated map $\varphi_{PROMETHEE\ I-Utility}$ will be order preserving as well (Figure 5a).

Concordance Analysis. Using equal weights ($g_j = 0.25$) and defining the descriptors of a fictive reference substance as $[v_j(q_{jmax}) - v_j(q_{jmin})]/2$, ($v_j$ being normalization functions (see Appendix III)) the results are shown in Table 3 column "Concordance Analysis" and in Table 4c. It is difficult to compare this ranking with the other rankings since 4-nitroaniline (4NA), atrazin (ATR), dimethoate (DIM), isoproturon (ISO) and thiram (THI) are ranked equally as are 4-nitrophenol (4NP), diazinon (DIA), Ethofumesate (LIN) and malathion (MAL).

The Concordance Analysis does not have the opportunity to differentiate the final ranking result much because it only sums the weights (which are all 0.25) of the substances above the reference and subtracts the weighted difference to the descriptor, which is the lowest with respect to the reference substance. Examining the results one can conclude that the Concordance Analysis has some similarities with a simple multiplication of the descriptors. Thus, if one descriptor is very small relative to the reference element it will influence the overall ranking remarkably. This kind of ranking methodologies is to be preferred if all descriptors must be high, for example, to observe an environmental impact. The method is especially suitable if a well-defined reference substance is established. It is possible to imagine that a full risk assessment has been performed and a substance is found to be unwanted. Then all chemicals ranked above this substance can classified as unwanted.

Like the Utility Function and PROMETHEE the Concordance Analysis needs information on weights. Performing a Monte Carlo Simulation using random weights reveals that the influence from the choice of weights is irregular

compared to the influence of the weights of the Utility Function or of PROMETHEE (cf. Table 4c).

Further, the number of possible ranks is rather limited. Additionally in the Concordance Analysis the choice of a reference substance also influences the ranking. To observe the influence of the reference substance a fictive reference substance is defined as n times ($v_j(q_{jmax}) - v_j(q_{jmin})$). While using equal weights (0.25) n is changed in steps from 0.1 to 0.9. The changes in the rank position are observed in Table 5b, the number of changes, μ, is counted each time n increase with 0.1. The reference substance appears to have a very high influence on the ranking. When using equal weights an increase in the reference substance leads to a larger differentiation. This result indicates that in the Concordance Analysis one should be even more careful in the selection of the reference substance than in PROMETHEE in the selection of delta zero, Δq^0.

As for PROMETHEE the Concordance Analysis comes to the final total order by two steps. In the first step a partial order will be established by D and C ("Concordance I"):

$$x_1 > x_2 \text{ if } C(x_1) > C(x_2) \text{ and } D(x_1) < D(x_2) \qquad (2)$$

As explained by eq A10 a total order is found by balancing C and D (Concordance II). Thus a system of three maps could be studied (cf. Figure 5b).

If only relations to the reference substance are examined, the result is easily obtained. A substance $x_1 > x_{ref}$ in HDT will have a Concordance set equal to the information base, Q and an empty Discordance set. Therefore $D(x_1) = 0$ and $C(x_1) = 1$ using normalized weights. If another substance x_2 is studied with the same relation to the reference substance then, independent of the kind of relation x_1 and x_2 have in HDT, they will be equivalent. If, however, the substances both appear to be have the relation $x_1 \leq x_{ref}$ and $x_2 \leq x_{ref}$, then $C(x_1) = C(x_2) = 0$ and a discrimination is found only by $D(x_1) \neq D(x_2)$. Therefore the kind of mapping to be examined depends obviously on the position of x_{ref}. A more detailed analysis of the order preserving maps is necessary and will be the subject of further studies.

VI. DISCUSSION

The Generality of and Additional Information Obtained from HDT. The range of possible ranks for the Monte Carlo version of the MCA methods are all within the range of the minimum and maximum limits as defined by the Hasse diagram (cf. Figure 3 and Table 4a−c). In general the distribution of the ranking probabilities is narrower and the probabilities are higher for the MCAs. HDT can thus be characterized as being the most general and due to the neglection of weights the least subjective method. Figure 4 illustrates this showing the probability distribution of the ranks. The Concordance Analysis often results in a ranking distribution with a clear maximum. This is, however, not always the maximum that is identified using the other methods. In the present study, this is especially clear for 4-nitroaniline (4NA) and diazinon (DIA).

Evaluating the findings one should consider three cases.

- Case C: There is coincidence of HDT with all other three methods, i.e., the ranking is approximately the same when applying the different methods.
- Case W: There are different results, between HDT and the other three methods, and the other three methods coincide rather well, i.e., HDT delivers a rank for a substance, which differs from that of the other methods. Utility Function approach, PROMETHEE and Concordance Analysis deliver approximately the same ranks.
- Case S: There is no coincidence between HDT and the other three MCAs; however, among the MCAs there are also conflicting results, i.e., each of the four methods deliver another rank for a substance.

Table 6. Classification of the 12 Substances with Respect to the Cases C,[a] S,[b] and W[c]

cases	substances[d]	remarks
C	CNB, CHL, (DIA), GLY, (DIM)	more or less the same ranking results
S	4NA, (DIA), (DIM), ETH, THI	different rankings at all
W	ISO, 4NP, ATR, MAL	HDT differs from the results of the others

[a] Coincidence among all four methods. [b] The rank of a substance depends on the method and therefore on the formalisms to include participation. HDT, as a method based purely on the data matrix seems to be on the safe side. [c] "Worst" case, discrepancies arise because of the different approaches (nonmetric (HDT) vs metric (the other three methods)). [d] Substance identifiers in parentheses mean that the classification may not be convincing; such substances may also be listed in different classes.

In case C, the general *c*oincidence, there is no further discussion needed. In principle the result of ranking does not depend on weights and other subjective information.

In case S, the result depends on the algorithm used, on weights, on the use of preference functions or on the reference substances; discrepancies to HDT are due to the specific choices within the MCAs. Therefore in the case of uncertainties in the selection of weights, reference substances, preference functions, it seems that HDT is transparent displaying the ranking interval. (HDT may be on the *s*afe side in priority setting exercises.)

Case W: This is the *w*orst case to be interpreted. In general terms it can be stated that this situation arises when a metric algorithm (Utility Function approach, PROMETHEE, Concordance Analysis) is to be compared with a nonmetric (HDT) one. It can be expected that isolated substances or substances only loosely connected with the others in the Hasse diagram will be candidates for the case W, because then the ranking depends severely on how participation is included (for example by weightings). If the number of comparable compounds is counted (for example ATR has 2, DIM 3, MAL 0 THI 4 comparable compounds, etc.) then the case W is found for substances with a low number of connections to others, whereas cases C and S are associated with substances having a higher number of connections. Note that this is still a hypothesis, and further research is needed to confirm this. Table 6 discloses the single compounds belonging to the three cases C, S and W, respectively.

If the three cases are identified, how do we come to decisions?

Case C: This does not lead to a problem at all, because the results are coincident. Then HDT is most convenient, because it does not need to find weights, reference substances, etc.

Case S: HDT will display an extra ranking. So what to do? Once again, HDT shows that obviously the ranking result

depends on the kind how preferences are formulated. Therefore—if a decision is needed—HDT warns that the actual decision is severely depending on the algorithmic realization due to the three methods (Utility Function approach, PROMETHEE, Concordance Analysis).

Case W: In that case the numerical values of the attributes allow a rather unique decision by MCA. The discrepancy with HDT arises from a high amount of incomparabilities. Therefore the selection of weights can but must not strongly influence the results.

Summarizing: Most of the results in Table 6 are reflected in the tables. In case C a limited uncertainty is observed for both the HDT and the MCA. In case S the ranking uncertainty is large for the MCA, while case W is related to substances where the uncertainty of the rankings done by HDT are large and where the those of the MCA are small.

Besides the linear extension the Hasse diagram can provide additional information not captured in the MCAs. The Hasse diagram divides the substances into classes based on levels. Further, through structure analysis various branches or groups of substances can be identified having specific characteristics. Additionally, the Hasse diagram provides the possibility of estimating the quantitative importance of the descriptors. By removing them one at a time the changes in the Hasse diagram indicate the influence from that particular descriptor. Thus if the removal of a descriptor induces a large number of changes it means that it is important for the structure of the Hasse diagram and in general for most ranking functions. When removing (i) the production volume (PV) the number of changes is 9, (ii) the acute toxicity to fish (LC50) the number is 2, (iii) log K_{ow} the number is 9 and (iv) the biodegradation (BD) the number of changes is 22. These numbers indicate the respective importance of the descriptors used in our ranking exercise. Details about sensitivity and structure analysis can be found in refs 13 and 21.

For the MCA methods the uncertainty associated with the input data has a significant influence on the results, whereas it has been demonstrated that HDT is relatively robust to uncertainties on the input data.[34] This is because HDT is not concerned with the metric value but the relative difference between the descriptors. HDT demonstrates to be more reliable, even though or actually because it is a less specific method. The transparency of HDT is estimated to be higher than for the MCAs. This is due to the fact that a minimum of external input is needed.

The Issue of Subjectivity in Ranking Methods. When comparing priority setting methodologies it is important to identify additional external information. For all the methods considered a choice is made by choosing the descriptors. The choice of descriptors is however often based on key parameters from risk assessment schemes or environmental fate models, which makes it less subjective. In this paper exposure (given by production volume), aquatic toxicity, bioaccumulation and persistence were chosen as descriptive parameters. For HDT the selection of the descriptors is the main contribution of subjectivity. Additionally, some indirect weighting can be added if the data are separated into classes.

For the MCAs another level of subjectivity is added when the descriptors are weighted. Then the more important descriptors have to be identified. This often raises more debate than the actual choice of the descriptors. It is easy to imagine discussions concerning the relative importance for the ranking of, for example, persistence and bioaccumulation or even between exposure and effect. The choice of the weights might thus be considered more subjective than the choice of descriptors.

In HDT the descriptors are not weighted. A priori we argue that this makes the method more scientifically based than the MCAs.

Compared with the Utility Function approach, PROMETHEE and the Concordance Analysis contain an additional level of subjectivity. On top of the choice of the weights for the descriptors PROMETHEE needs information on delta zero value. In the Concordance Analysis a reference element is needed. Table 5a,b demonstrates the influence on the ranking result.

Even though not analyzed in the present paper, MCA methods, like the Analytical Hierarchy Process (AHP),[35,36] are available, which rely solely on the weighting of the descriptors. In AHP the descriptors do not need to fulfill the consistency constraint i.e., if descriptor q_1 is twice as important as descriptor q_2, and descriptor q_2 is 3-fold as important as descriptor q_3, then q_1 does not need to be 6-fold as important as descriptor q_3. In AHP the importance of the descriptors and the preferences can be found freely. Only after finishing this first part of decision making, a correction mode is added to resolve logical discrepancies.

Considering the issue of subjectivity in the choice of weights the use of the Monte Carlo simulations, as demonstrated in this paper, is an important measure if one wishes to make the MCAs more objective. Using the Monte Carlo simulation on the Utility Function it is actually possible to make it independent of the weights and present the results as ordinal ranking probabilities rather than specific ranks. The use of the Monte Carlo version of the MCA can maybe be seen as a "sister" methodology lying next to the original methodology on a "subjectivity scale".

The various ranking methods are built on sets of assumptions. In the Utility Function it is assumed that there is a numerical (often linear) relation among the individual descriptors. When ranking is made based on PROMETHEE it is assumed that all preferences are linearly comparable. Finally, in the Concordance Analysis it is assumed that not only are the weights linearly additive but also that it is possible to establish a reference compound. The HDT do not assume anything about linearity among the descriptors. It only assumes one can find a common orientation of the descriptors.

The essence of the discussion on subjectivity contra objectivity or the scientific method versus public participation is captured in Figure 6. With respect to a "fine-tuning" of public participation the briefly mentioned methods ELECTRE, ORESTE and NAIADE are valuable tools and worth enough to be included in Figure 6, albeit their discussion would be far above the scope of this paper.

Order Preserving Maps. Having to take into account more than one descriptor it is rather natural that different ranking methods come up to different partial orderings according to their different aggregation schemes. Consequently, the methods of priority setting, namely HDT, the Utility Function approach, PROMETHEE and Concordance Analysis, may all be seen as different partial orders (the total

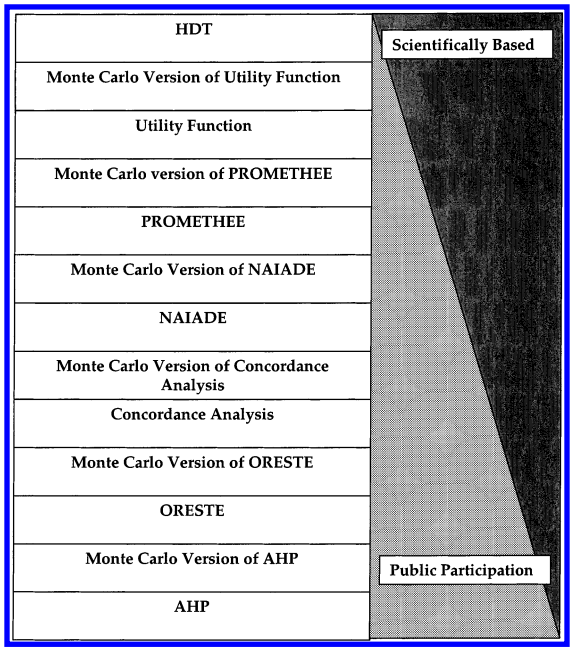

Figure 6. The degree of subjectivity or public participation for HDT and MCAs.

one is here just seen as a limiting case) based on the same groundset, i.e., here the 12 HPVC substances. Hence, if it is possible it is convenient to discuss all partial orders as vertices in a general directed graph. Whereas each decision tool is a vertex, the relations among pairs of vertices are analyzed in terms of order preserving or embedding maps or even as order theoretical isomorphisms. The commutativity diagram which summaries the findings for HDT, the Utility Function and PROMETHEE (Figure 5a) is thus a first step in developing and characterizing such a general framework.

The role of MCA in relation to HDT can be rather generally explained as follows: Each MCA enriches the order relation found by HDT by use of additional information. If we assume an order preserving map, φ_i

$$HDT \xrightarrow{\varphi_i} MCA_i$$

the map, φ_I, has two effects: i) The number of linear extensions decreases. ii) Consequently the range of variability of ranks must be lower. The higher probabilities and the sharper distribution function can thus be explained, as was already done in detail in the presentation of the MCAs.

In some cases the order preserving mapping approach may appear to be restricted. It might thus be more fruitful to use methodologies such as the generalized Tanimoto index, which expresses the degree of order similarity between two sets.[37]

VII. CONCLUSION

In addition to providing the most general rank, HDT further provides additional information on levels, groups and the importance of the descriptors. It is rather insensitive to data uncertainty and seems methodologically transparent. This makes HDT suitable not only as an individual ranking tool but also as an additional tool for MCAs. Nevertheless, if scientifically well-founded information or agreement can be obtained on weights, the delta zero (Δq^o) and/or a reference substance and the assumptions on the relation among the descriptors are fulfilled, the MCAs do give a more specific rank than the HDT.

The difference between the HDT and the MCA also illustrates the concept of scientifically based ranking versus public participation. The study reveals that if a ranking of high scientific degree is desired, HDT is to be preferred, whereas if some room for public participation or negotiation among parties is desired one of the MCA methods might be a better choice.

The work further demonstrates the first step in finding a general framework for ranking methods. Beyond the specific result obtained from comparing four methods, we come up with a more general point, namely to see all ranking methods under the unifying scheme of mathematical maps among partial orders and to discuss the edges of the graphs in terms of order preserving potencies.

Based on the conclusion the following tired approach for obtaining the most scientific rank is suggested. A priori a HDT analysis should be performed. The results can be thus considered as the scientific base result. On top of this analysis, if needed, MCAs can be undertaken allowing the use of additional external information on the ranking that are not sufficiently clarified by HDT.

ACKNOWLEDGMENT

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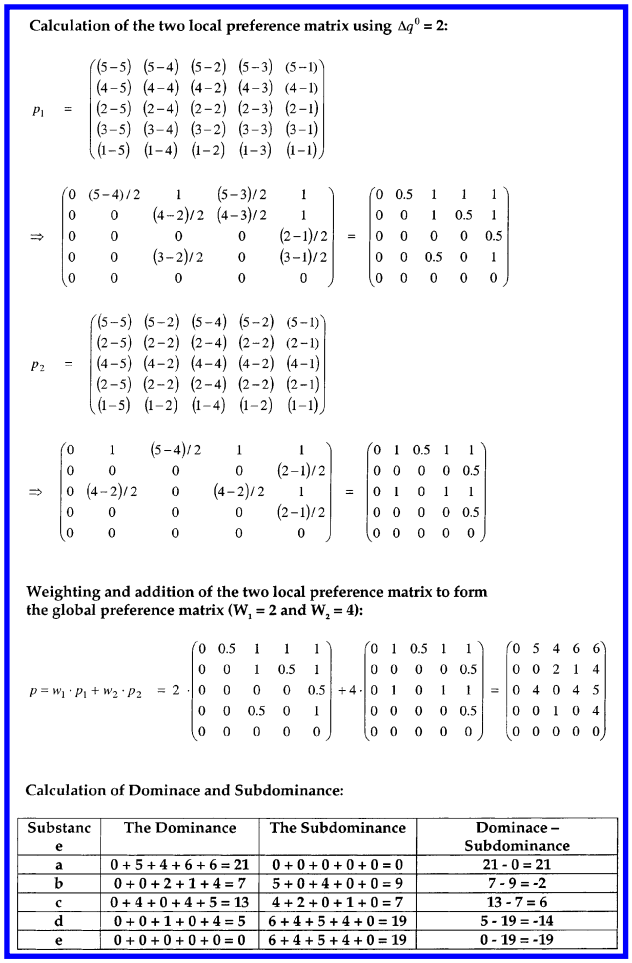
APPENDIX I

Utility Function Approach. The ranking vector or the "Utility", Γ, is calculated by summing the normalized descriptors multiplied with the belonging weights. Here the simplest concept of the Utility Function is applied. For the rather sophisticated background, ref 15 should be consulted. In mathematical terms the Utility Function approach can be described as

$$\Gamma_i = \sum g_j * v_j(q_{ij}) \qquad \text{(A1)}$$

where Γ_i is the Utility for the substance i, from which ranks of the substances, i.e., a total order can be derived. The entry q_{ij} is the numerical value for the substance i and the descriptor j, and g_j is the weighting factor for the descriptor j. $v_j(q_{ij})$ is called the individual Utility Function. It allows for quantification on a detailed basis as to how q_{ij} contributes to the ranking vector, Γ. Here we selected the normalization function: $v_j(q_{ij}) = (q_{ij} - \min(q_j))/(\max(q_j) - \min(q_j))$. Note that when normalizing the descriptors in this manner, it is required that the maximum and minimum values are not outliers. Another normalization procedure with respect to priority setting of chemicals is described by Halfon and Brüggemann.[38]



Substance	The Dominance	The Subdominance	Dominace – Subdominance
a	0 + 5 + 4 + 6 + 6 = 21	0 + 0 + 0 + 0 + 0 = 0	21 - 0 = 21
b	0 + 0 + 2 + 1 + 4 = 7	5 + 0 + 4 + 0 + 0 = 9	7 - 9 = -2
c	0 + 4 + 0 + 4 + 5 = 13	4 + 2 + 0 + 1 + 0 = 7	13 - 7 = 6
d	0 + 0 + 1 + 0 + 4 = 5	6 + 4 + 5 + 4 + 0 = 19	5 - 19 = -14
e	0 + 0 + 0 + 0 + 0 = 0	6 + 4 + 5 + 4 + 0 = 19	0 - 19 = -19

Figure 7. The principle of PROMETHEE using the same decision matrix as in Figure 2.

APPENDIX II

PROMETHEE. In PROMETHEE, for each descriptor, q_j, a "local preference matrix", $\mathbf{p_j}$, is calculated. $\mathbf{p_j}$ is derived as the differences between the descriptors for each pair of substances: $\mathbf{p_j} = f_j(\Delta q)$.

$$\mathbf{p_j} = f_j(\Delta q) = \begin{pmatrix} f_j(q(1)-q(1)) & f_j(q(1)-q(2)) & f_j(q(1)-q(3)) & \dots & f_j(q(1)-q(i)) \\ f_j(q(2)-q(1)) & f_j(q(2)-q(2)) & f_j(q(2)-q(3)) & \dots & . \\ . & . & . & \dots & . \\ . & . & . & \dots & . \\ f_j(q(i)-q(1)) & . & . & \dots & f_j(q(i)-q(i)) \end{pmatrix} \quad \text{(A2)}$$

It is convenient to normalize f to be in the range [0, 1) or [0, 1] depending on the type of function, f. Often f is selected as a monotonically increasing function of Δq_j.[28] In the following a simple realization has been chosen. This is one of six possibilities presented by Brans and Mareschal:[17]

$$\Delta q(i,k) \le 0,\ f_j(\Delta q(i,k)) = 0$$

$$0 < \Delta q(i,k) \le \Delta q^o\ f_j(\Delta q(i,k)) = \Delta q(i,k)/\Delta q^o \quad \text{(A3)}$$

$$\Delta q^o < \Delta q(i,k)\ f_j(\Delta q(i,k)) = 1$$

The indices i and k in eq A3 refer to two different substances i and k. The index j in the terms Δq (eq A3) has been suppressed, but keep in mind that the preference function will be selected individually for each attribute, q_j. Successively, all the local preference matrices $\mathbf{p_j}$ are weighted and summed up to form a "global preference matrix", $\mathbf{p}$

$$\mathbf{p} = \sum g_j * \mathbf{p_j} \quad \text{(A4)}$$

where $\mathbf{p}$ is the global and $\mathbf{p_j}$ the local preference matrix entry, and g_j is the weights. The term "local" refers to the fact that $\mathbf{p_j}$ is the preference function of only the jth descriptor, specifically. From the global preference matrix the "dominance" and the "sub-dominance" are calculated. The sum of each row, $d\pi_i$, of the global preference matrix, $\mathbf{p}$, describes how i is preferred relative to all other substances. Therefore the sum $d\pi_i$ is denoted as the dominance of the substance, i, over all other substances. On the other hand each column of the preference matrix describes how the other substances are preferred relative to i. Thus the sum of each column, $sd\pi_i$, is a measure of the subdominance of i. The total order is simply the balance between $d\pi_i$ and $sd\pi_i$:

$$\Gamma_i := d\pi_i - sd\pi_i \quad \text{(A5)}$$

Γ_i thus depends on the differences between the descriptors of all substance pairs, the weights and the way f_j, i.e., the significance of numerical differences is formulated. The principle of PROMETHEE has been illustrated in Figure 7 using the data matrix from Figure 2.

APPENDIX III

Concordance Analysis. In the Concordance Analysis for each descriptor the normalized values are compared with the normalized value of a reference substance. A Concordance set "$l(x)$" related to each substance, x, is an index set formed by those descriptors of x whose numerical values are higher than that of the reference substance "ref":

$$l(x) := \{j \mid v_j(q_j(x)) > v_j(q_j(ref))\} \quad \text{(A6)}$$

where $q_j(ref)$ is the numerical value for the reference substance and for the descriptor j and $q_j(x)$ is the numerical value for the substance x and the descriptor j (For the sake of clarity of the formulas we change the notation slightly.). The function v_j is a normalization function as used for the Utility Function approach. Similarly a discordance set for each substance is defined containing those descriptor indices where the substance has numerical values lower or equal than that of the reference element, i.e., the discordance set refers to those criteria where substance x is not preferred to the reference substance.

$$\not{l}(x) := \{j \mid v_j(q_j(x)) \le v_j(q_j(ref))\} \quad \text{(A7)}$$

For each substance, x, a Concordance index, C(x), is calculated as the sum of the weights belonging to the descriptors of the Concordance set, $l(x)$. g_j is the weight for the descriptor j.

$$C(x) = \sum g_j\ j \in l(x) \quad \text{(A8)}$$

Using the descriptors in the discordance set, $\not{l}(x)$, a discordance index, D(x), is found as the weighted maximum

Substance	q_1	q_2	Concordance set (ℓ):	Discordance sets ($\wp$):	Concordance index, C	Discordance index, D	Γ = C - D
a	5	5	$\{q_1, q_2\}$	{ }	2+4 = 6	-	6
b	4	2	$\{q_1\}$,	$\{q_2\}$	2+0 = 2	4 * (3-2) = 4	-2
c	2	4	$\{q_2\}$	$\{q_1\}$,	0+4 =4	2 * (3-2) = 2	2
d	3	2	{ }	$\{q_1, q_2\}$	-	4 * (3-2) = 4	-4
e	1	1	{ }	$\{q_1, q_2\}$	-	4 * (3-1) = 8	-8
Weights	2	4					
Reference Substance	3	3					

Figure 8. The principle of the Concordance Analysis using the same decision matrix as in Figure 2.

difference between the descriptors of the discordance set and those of the reference substance.

$$D(x) = \max \{g_j [v_j(q_j(x)) - v_j(q_j(\mathrm{ref}))]\}\ j \in \wp(x) \quad \text{(A9)}$$

The maximum is to taken over all descriptors of the discordance set.

The rank for the substances is then successively found as

$$\Gamma_i = C_i - D_i \quad \text{(A10)}$$

This antisymmetry between advantageous and disadvantageous descriptors may be seen as a methodological drawback, albeit Opperhuizen and Hutzinger[18] gave some arguments for this. The principle of the Concordance Analysis based on the data matrix of Figure 2 is illustrated in Figure 8.

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