Partially Ordered Sets in the Analysis of Alkanes Fate in Rivers*

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Dominance degree is introduced as a mathematical procedure to quantify the order relations between a pair of subsets contained in a partially ordered set obtained from the features of its elements. Dominance degree summarizes the partial order relations of the members of two subsets. If a member of one subset follows an order relation to a member of another subset, then the dominance degree informs how far this relation can be transferred to all elements of the two subsets. Dominance degree was applied to the study of 35 acyclic alkanes (from $C_5H_{12}$ to $C_8H_{18}$) in two river-scenarios: hilly regions and lowland rivers. Each chemical was defined by three fate descriptors estimated by applying the module EXWAT from the E4CHEM package. It was found that $C_nH_{2n+2}$ dominates $C_mH_{2m+2}$ if $n > m$, which means that when considering the fate descriptors simultaneously, those of $C_nH_{2n+2}$ are higher than those of $C_mH_{2m+2}$. Finally, some particular results were found for the linear isomer of each subset.

Keywords
partially ordered sets
alkanes
environmental scenarios
Hasse diagrams
WHASSE software
E4CHEM software

INTRODUCTION

Alkanes have been detected in several rivers around the world1,2 and their presence is derived from natural biogenic, geologic and industrial sources.3–6 In fact, it was estimated in 1991 that approximately 750,000 tons of hydrocarbons are annually transported by rivers to the Mediterranean Sea7 and a large proportion of them are alkanes. Furthermore, in natural aquatic systems, for instance rivers, the freely dissolved fractions of hydrophobic organic contaminants, like alkanes, generally have the greatest impact on aquatic organisms representing the most ecotoxicologically relevant environmental residues.8

Hence, studies of the distribution and fate of these chemicals in rivers are of the utmost environmental importance.

In this work, we use the module EXWAT from the software package E4CHEM in order to assess the risk of 35 acyclic alkanes in rivers. E4CHEM (available from the second author) consists of a system of modules describing the behaviour of chemicals in different environmental targets and depending on different stages of data availability. E4CHEM makes it possible to study the fate of chemicals in different targets (troposphere, stratosphere, plants, soil and rivers)9 by the application of single

* Dedicated to Professor Haruo Hosoya in happy celebration of his 70th birthday.
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simulation models for each target. Especially for rivers, E4CHEM includes the model EXWAT, which in an appropriate way combines environmental parameters of the river where the chemical is present with the substance properties. It is important to note that the use of EXWAT is supported by the agreement obtained between EXWAT predictions and experimental results for some other cases of chemicals in rivers.\textsuperscript{10}

We consider two different river scenarios, each defined by its special features: a river in a hilly region and a lowland river. In this way, we can obtain descriptors for the fate of chemicals in each scenario that allow a comparison of the behaviour of the substances involved. This procedure may be considered as a ranking process of the chemicals and it can be studied by applying the concept of partially ordered sets (posets), as Brüggemann has shown in several studies.\textsuperscript{11} The use of partial orders as a data exploring concept is called the Hasse diagram technique (abbreviated HDT) and here it is applied to an environmental chemistry case. By the application of the HDT, a Hasse diagram of a set under study is found. In chemical applications this type of diagram show which chemical/s is/are the most pollutant or the environment friendliest substance/s as well as which chemicals are in-between these substances. We show in this paper how some subsets of the chemicals under study can be analyzed by characterization of their order relationships, which are represented in the structure of the Hasse diagram.

**Exposure Model EXWAT**

A study of the fate of a substance in an environmental target cannot be based only on substance data but must also include environmental parameters of the media where the chemical is present. Thus the substance properties and environmental parameters are coupled by a deterministic mathematical exposure model (stationary). Such a model must be based on the differential mass balance,

\[
dc / dt = \text{Input}(p, q) - \text{Output}(p, q). \tag{1}
\]

where \(p\) is the tuple of environmental parameters and \(q\) is the tuple of chemical properties. The Input\((p, q)\) term includes the input due to the upstream concentration as well as the input by human activity into the first box modelling the river stretch.

However, real cases, such as a river for a particular case of EXWAT, have different targets. For instance, a river has two targets, sediment and water body of surface water. In these cases, a differential equation is needed for each target, which indeed is considered by EXWAT (mathematical details on the particular mass balance equations for these two targets are given in reference 10). Once the stationary concentration in the outflow of one river segment is determined, the inputs of the downstream section can be calculated. As we are interested in studying the fate of alkanes, we modelled each river scenario just by one segment, consisting of a water (W) and sediment (S) body (Figure 1) where all relevant processes are adequately described. Representation of a river segment, according to EXWAT, is depicted in Figure 1B.

There is water inflow (a) with an upstream concentration of the substance and water outflow (a) with the resulting concentration due to different processes within the compartment. In W, suspended material that can be deposited or resuspended (b) is transported (c) (black circles). It is assumed that the dissolved substance is in equilibrium with its sorbed form on the suspended material. By dispersive forces, the dissolved chemical enters the interstitial water (d), which is assumed to be approximately in the order of amount of the molecular diffusion coefficient. Processes of degradation (e) can be included in the model; however, we considered the chemicals as conservative, i.e., without degradation. Sediment burial (f) and volatilization (g) are considered as sinks; metabolites are not considered.

Once the missing physicochemical properties of the substance have been estimated by DTEST\textsuperscript{12} (an E4CHEM module giving a high degree of automatic estimation of required chemical properties), the model EXWAT couples them with environmental data and physical parameters of the river. Some of the physicochemical properties estimated by DTEST are water solubility, vaporization entropy, vapour pressure and the partitioning coefficients \(K_{OW}, K_{OC},\) and \(K_{AW}\). Some of the river parameters of EXWAT are the ones listed in Table I and the concentration of suspended solids, temperature, pH, porosities, water discharge, and some others. Having this information and ignoring the temporal behaviour of the environmental system, EXWAT yields chemical concentrations in: the fluid phase (water and suspended matter), sediment, water (not including suspended matter), sediment matrix, pore water, suspended sediments and biomass.

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*Figure 1. A) Partition of a river into several segments [boxes] in EXWAT, and B) the processes considered within each box (see text).*

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TABLE I. Parameters input to EXWAT describing two scenarios of a river. H and L stand for the river in a hilly region and the lowland river, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>H</th>
<th>L</th>
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<tr>
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<td>100</td>
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<tr>
<td>Box length (a) / km</td>
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<td>2</td>
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<tr>
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<td>1000</td>
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<tr>
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<td>0.05</td>
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</tr>
<tr>
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<tr>
<td>Suspended matter content / g m⁻³</td>
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</tr>
<tr>
<td>w (Organic carbon in suspended matter)</td>
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<td>0.04</td>
</tr>
<tr>
<td>w (Organic carbon in sediment matrix)</td>
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<td>0.04</td>
</tr>
<tr>
<td>Sinking velocity of suspended matter / m d⁻¹</td>
<td>10</td>
<td>15</td>
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</table>

(a) See Figure 1A.
(b) w = mass fraction.

These concentrations can be regarded as fate descriptors or can be combined with flux parameters in order to yield additional descriptors. Further, EXWAT, as a simple stationary model, provides a set of linear equations in its state variables; these equations may be mathematically related to each other and allows additionally the derivation of descriptor-descriptor relations. However, our interest in this paper is not to go into the details of those relationships but to show how the chemical fate is related to a poset structure.

METHODS

A Chemical in Two River Scenarios

The river we studied was divided into two different scenarios: 1) river in a hilly region (H) and 2) lowland river (L). Parameters defining each scenario are given in Table I.

We selected three fate descriptors from the EXWAT results: 

\[ D_1: \text{Total concentration of chemicals in the fluid phase, } \gamma_f / \mu g \text{ L}^{-1}, \]

\[ D_2: \text{Total concentration of chemicals in sediment, } \gamma_s / \mu g \text{ L}^{-1}, \]

\[ D_3: \text{Deposition flux: Concentration of sorbed chemicals on suspended sediment, } \gamma_{ws}, \text{ times deposition velocity, } \text{Depos. } D_3 = (\gamma_{ws} \times \text{Depos.}) / (\mu g \text{ m}) (\text{L} \cdot \text{d})^{-1}. \]

Note that the values of \( \gamma_f \) and \( \gamma_s \) refer to different compartments; for example, in the hilly scenario \( \gamma_f \) refers to the water body with a volume of \( 7.5 \times 10^5 \text{ m}^3 \) whereas \( \gamma_s \) refers to the sediment compartment with a volume of \( 1.5 \times 10^4 \text{ m}^3 \).

Each descriptor was calculated by considering as the input rate of alkanes into the river a constant value of 100 kg d⁻¹ in order to differentiate the descriptor values of alkanes in the river (Figure 1A). The three concentrations estimated by EXWAT were performed in the box shown in Figure 1A. Note that our interest concerns the fate of chemicals and its methodological evaluation rather than the modelling of real amounts of alkanes in rivers. Our modelled river must be considered as a fictitious system.

General Remarks on the Hasse Diagram Technique

We introduce some definitions in order to illustrate some basic functionalities of the Hasse diagram technique, implemented in the WHASSE software, available from the second author. WHASSE makes it possible to draw Hasse diagrams and to explore the influence of different parameters on them.

Definition 1. – We call \( x \) a chemical and \( G \) the ground set that is the set of chemicals.

Definition 2. – \( D_i(x) \) is the numerical value of the \( i \)-th fate descriptor of the chemical \( x \).

According to EXWAT, we have \( D_i(x) = f[p, q(x)] \), where \( p \) is a tuple of environmental and physical parameters of the river and \( q(x) \) is a tuple of properties of the chemical \( x \). Then, \( D_i(x) \) values characterize the fate of the chemical \( x \) in the river considered. In order to rank the chemicals according to their \( D_i(x) \), the procedure followed by the Hasse diagram technique is to compare the fate descriptors of all chemicals.

Definition 3. – Let \( x, y \in G \), then \( x \leq y \) if \( D_i(x) \leq D_i(y) \) for all \( i \). This specific order relation is called a product-(or component-wise-) order and obeys the following axioms of order:

i) reflexivity: \( \forall x \in G, x \leq x \) (a chemical can be compared with itself);

ii) antisymmetry: \( \forall x, y \in G, x \leq y \land y \leq x \Rightarrow x = y \) (if \( x \) is better than \( y \), then \( y \) is worse than \( x \));

iii) transitivity: \( \forall x, y, z \in G, x \leq y \land y \leq z \Rightarrow x \leq z \) (if \( x \) is better than \( y \) and \( y \) is better than \( z \), then \( x \) is better than \( z \)).

Note that in most mathematical textbooks the symbol \( (\leq) \) is used for a partially ordered set. However, Brüggemann and co-workers have introduced the notation \( (G, D) \), where \( D \) is called the "information base" and is the set of \( D_i \) descriptors. The reason for writing \( D \) instead of \( \leq \) is to emphasize that the order relation between the chemicals depends on the descriptors selected. Thus, the fact of having certain order relations between the chemicals in one scenario does not imply that those chemicals will have the same order relations in another. The cause of this behaviour is that \( D_i(x) \) depends, besides chemical properties, on the river parameters, as mentioned above.

If \( D_i(x) \leq D_i(y) \) for some indices \( i \) and \( D_i(y) \leq D_i(x) \) for one or some other indices, then \( x \) and \( y \) are "incomparable", denoted as \( x \parallel y \). A graph \( P \) representing the order relations found in \( G \) can be drawn, where the order relation \( \leq \) is represented by an arrow going, for instance, from the better chemical to the worse. But \( P \) contains unnecessarily many edges, which can be avoided by a transitive reduction eliminating all edges that arise solely from the transitivity axiom. After such "transitivity reduction", a more parsimonious graph \( H \), called the Hasse diagram, can be drawn.
RESULTS

The set $G$ of chemicals in this study is made from the complete set of 35 acyclic alkanes ranging from C$_5$H$_{12}$ to C$_8$H$_{18}$: three C$_5$H$_{12}$, five C$_6$H$_{14}$, nine C$_7$H$_{16}$ and eighteen C$_8$H$_{18}$ isomers (Table II). The physicochemical properties of each alkane (water solubility, vapour pressure, melting point, boiling point and octanol/water partition coefficient) were taken from the Chemical Properties Handbook\(^1\) and the Handbook of Physical Properties of Organic Chemicals;\(^2\) the missing values were estimated using the module DTEST of E4CHEM. Having the complete pool of physicochemical properties coming from the literature and from estimations by DTEST, we use the EXWAT model of E4CHEM in order to generate the three fate descriptors $D_1$, $D_2$ and $D_3$ for each scenario.

General Dependences of the Descriptors

The alkane labels were assigned following the increasing values of the Wiener index\(^2\) (as a measure of branching index) of each molecule (Table II). The values of the three fate descriptors for each alkane appear in Table III. Note that concentrations $D_1$ and $D_3$ relate to the volume of the water body while those of $D_2$ (H) and $D_2$ (L) relate to the volume of the sediment. A simple equilibrium calculation shows that, due to the small volume of the sediment, the variation of $D_1$ can be quite low whereas that of $D_2$ can be rather high.

Before discussing the results obtained using the Hasse diagram technique, we analyze separately the behaviour of each fate descriptor for the 35 alkanes in both, H and L, scenarios.

We found that the trends present in H are also present in L (Figure 2). We observed that $D_1$ (chemical concentration in the fluid phase) is mainly determined by the molecular weight of the molecules. Thus, we classified $D_1$ into four subsets of values corresponding to C$_5$H$_{12}$, C$_6$H$_{14}$, C$_7$H$_{16}$ and C$_8$H$_{18}$ isomers, respectively. We found that $D_1$ values for both scenarios fulfill this order relationship: C$_8$H$_{18}$ > C$_7$H$_{16}$ > C$_6$H$_{14}$ > C$_5$H$_{12}$. In all the cases, the $D_1$ values of isomers are nearly the same; however, with the increase of the molecular weight, the linear isomer of each subset increases its $D_1$ value (Table III, Figure 2). We observed, for the case of alkanes in L, that the linear isomer of C$_7$H$_{16}$ reached the value of $D_1$ corresponding to the C$_8$H$_{18}$ isomers (Figure 2). This result

![Figure 2. Total chemical concentration in the fluid phase ($D_1$) of 35 alkanes in hilly region (H) and in lowland (L) rivers. Some structures are drawn (see text).](image-url)
may suggest that when considering isomers of the set C_{9}H_{20} (not studied here), perhaps the linear isomer of C_{8}H_{18} could reach the values of D_{1} for C_{9}H_{20} isomers, which is supported by the high D_{1} value of the linear C_{8}H_{18} isomer.

In order to relate D_{1} with some molecular structural parameter, we calculated the complete pool of 708 molecular descriptors available in the MOLGEN-QSPR software (arithmetical, topological, electrotopological, and geometrical descriptors). After these calculations, we found a high Pearson correlation (R > 0.9) between D_{1} and several molecular branching indices (W, 1_c, MTI, and MTI'), which are in turn highly correlated to molecular weight. Thus, the fate of alkanes in the fluid phase is determined mainly by the molecular weight of the substances.

Regarding D_{2} and D_{3}, we found a high correlation between these fate descriptors (R > 0.9). However, in

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<td>µg L⁻¹</td>
<td>(µg · m) (L · d)⁻¹</td>
<td>µg L⁻¹</td>
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</tbody>
</table>
contrast to $D_1$, we found no clear distinction between groups according to molecular weight (Figure 3). When looking for correlations between $D_2$ and $D_3$ through our pool of molecular descriptors, we did not find any relevant ($R > 0.8$) relationship. This result suggests that $D_2$ and $D_3$, contrary to $D_1$, are not related to the molecular parameters of alkanes. The high correlation between $D_2$ and $D_3$ suggests a similar trend in the alkane concentrations in sediments and also in suspended sediments. Note that $D_3$ contains the term $\gamma_{ws}$, the concentration of chemicals on suspended sediment. Despite the lack of correlation between the degree of branching and $D_2$ and $D_3$, it is important to note the high $D_2$ and $D_3$ values of alkanes 17 and 35, which correspond to the linear structures of $C_7H_{16}$ and $C_8H_{18}$, respectively (Figure 3). This trend is not observed for the linear structures of the light alkanes $C_5H_{12}$ and $C_6H_{14}$. A similar behaviour was observed for the same linear alkanes when considering $D_1$.

Having described each fate descriptor separately, we can discuss the effect on each descriptor of changing the river parameters from H to L. We observe that $D_1$ decreases when we change from H to L (Figure 2). This means that the concentration of alkanes in fluid phase is lower in lowland rivers than in rivers in hilly regions. The reason is the high dilution due to higher discharge in the lowland river. Now, considering $D_2$, we observe a small increment in L compared to H. On the other hand, $D_3$ increases in L compared to H, because the deposition of alkanes on suspended sediments is faster in L than in H. In general, the change of scenario, from H to L, makes $D_1$ decrease in contrast to increasing $D_2$ and $D_3$. All in all, even if we consider structurally simple alkanes, it is difficult to oversee their fate in different environmental scenarios. Here, the concept of partially ordered sets is helpful and is applied in the next section.

**Hasse Diagram of Alkanes in Hilly Region and Lowland Rivers**

It was mentioned in the above section that some alkanes share some fate descriptor values; it means that two alkanes $x, y \in G$ may have $D_i(x) = D_i(y)$ for $i = 1, 2, 3$. We say that then $x$ and $y$ belong to an equivalence class $K$, and we select one representative of such a class. These selected chemicals together with the chemicals for which $D_i(x) \neq D_i(y)$ for $i$’s, are gathered in the set $T$ of representatives. Thus, we draw the Hasse diagram over the set $T$ of representatives. The equivalence classes for both scenarios are shown in Scheme 1.

The set of representatives for scenario H is \{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 17, 18, 19, 21, 25, 28, 30, 33, 35\} and the one for L is \{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 17, 18, 19, 20, 21, 25, 30, 35\}. We note four subsets of isomers (C5H12, C6H14, C7H16 and C8H18) in each Hasse diagram (Figure 4) and we will discuss some of their features in the following text.

**Common equivalent classes**

\{1, 2\}, \{3\}, \{4, 5, 6, 7\}, \{8, 9\}, \{10, 11\}, \{12, 13\}, \{14, 15, 16\}, \{17\}, \{18, 22\}, \{25, 26, 27, 29, 31\}, \{33\}

**Different equivalent classes**

**H**

\{19, 20, 23\}

**L**

\{19\}

\{21, 24\}

\{28\}

\{30, 32, 34\}

\{33\}

Scheme 1. Equivalence classes in H and L and their relationships.

**Figure 3.** Total chemical concentration in sediment ($D_2$) and deposition flux ($D_3$) of 35 alkanes in hilly region (H) and in lowland rivers (L). $D_1(H)$ and $D_1(L)$ stand for the values of the log$_{10}$ of $D_1$ in the H and L scenarios, respectively.
Therefore we are introducing the dominance degree *empirical posets* the condition "for all" is too hard.

In our particular case, the rank is built from fate descriptors (Dom). Let us assume that *G* is a complete ranked subset of alkanes. Then, going down in sediments (chemical time bomb effect). In contrast, if *G* dominates *G'*, we show schematically in Figure 5 the Dom (*G', G*) results for each pair of isomer groups. For example, the calculation of Dom (C\(_6\)H\(_{14}\), C\(_5\)H\(_{12}\)), in both scenarios, is performed by determining \(N_R = \mid (4, 1), (4, 2), (4, 3), (5, 1), (5, 2), (5, 3), (6, 1), (6, 2), (6, 3), (7, 1), (7, 2), (8, 1), (8, 2) (8, 3) \mid = 14\) and \(N_T = \mid C_8H_{18} \mid \cdot \mid C_6H_{14} \mid = 15\). Then, Dom (C\(_6\)H\(_{14}\), C\(_5\)H\(_{12}\)) = 14 / 15 = 0.933.

An arrow \(\rightarrow\) is drawn for each dominance relation; each of these relations is characterized by its dominance degree and, in this case:

\[
\text{Dom} (C_nH_{2m+2}, C_mH_{2m+2}) = \begin{cases} 
> 0.5 & \text{for all } n > m \\
0 & \text{for all } n < m 
\end{cases}
\]

Note that the case \(n = m\) is not considered because the subsets compared ought to be disjoint (by definition). It is important to note that the same dominance diagram holds for both scenarios. In summary, we find C\(_8\)H\(_{18}\) \(\rightarrow\) C\(_7\)H\(_{16}\) \(\rightarrow\) C\(_6\)H\(_{14}\) \(\rightarrow\) C\(_5\)H\(_{12}\), which generalizes our finding with only one descriptor (\(D_1\)), as discussed above. Further discussion on the mathematical properties of the dominance degree is given in reference 24; another application of this concept to environmental studies can be found in reference 25.

### Particular Object Related Observations

For each isomer subset, the linear alkane is the chemical presenting simultaneously high values of its fate descriptors. They are 35 for C\(_8\)H\(_{18}\), 17 for C\(_7\)H\(_{16}\), 8 for C\(_6\)H\(_{14}\) and 3 for C\(_5\)H\(_{12}\) (compare Table II). Now, from a general analysis of the Hasse diagrams we can say that the maximal element is 35, which is also the greatest element. There are two minimal elements, 1 and 2, for the H diagram and only one, 2, for the L diagram, which becomes the smallest element of this diagram. This means that the linear C\(_8\)H\(_{18}\) alkane is the substance from the complete set of 35 alkanes whose fate descriptors make it the most potentially problematic compound in environmental terms.

**Figure 5.** Dominance diagram: The scheme corresponds to the location of subsets in Figure 4 (see text).

\(x \in G', y \in G'' \text{ and } x > y\) and \(N_T = \mid G' \cdot G''\). Note that the counting is based on the complete object set (35 objects) rather than that on \(T\), because different equivalence classes appear in \(H\) and \(L\). If Dom (*G', G") > 0.5, then we write *G' \rightarrow G"*. In the practice of interpreting as a rank of alkanes in the given scenario. If we consider the H diagram, we can see that the most pollutant alkanes are the C\(_8\)H\(_{18}\) isomers. Then, going down in the diagram, we found C\(_7\)H\(_{16}\) isomers, then C\(_6\)H\(_{14}\), and finally C\(_5\)H\(_{12}\). In summary, having classified the alkanes into four isomer subsets, it seems possible to establish one ranking according to their fate descriptors. In order to do that, we introduce the concept of dominance degree (Dom). Let us assume that \(G' \subset G\) and \(G'' \subset G\) with \(G' \cap G'' = \emptyset\); if \(\forall x \in G', \forall y \in G'', x > y\) then \(G'\) dominates \(G''\) and we write \(G' \rightarrow G''\). In the practice of empirical posets the condition "for all" is too hard. Therefore we are introducing the dominance degree Dom (*G', G") = \(N_R / N_T\), where \(N_R (N \text{ realized}) = \mid \{ (x, y),

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**General Observations**

Bruggemann and co-workers have demonstrated the versatility of using Hasse diagrams in ranking the chemicals in a given environmental space defined by descriptors.

In our particular case, the rank is built from fate descriptors (\(D_1, D_2\) and \(D_3\)) and in all the cases their high values (upper part of the diagram) may imply a hazard: either by being transported downstream with adverse effects on aquatic organisms or because of accumulation in sediments (chemical time bomb effect). In contrast, if \(D_1, D_2\) and \(D_3\) have low values for an alkane, then this substance is "better" or "less unfriendly" regarding the environment and is located in the lower part of the diagram. Hence, the diagrams shown in Figure 4 can be interpreted as a rank of alkanes in the given scenario. If we consider the H diagram, we can see that the most pollutant alkanes are the C\(_8\)H\(_{18}\) isomers. Then, going down in the diagram, we found C\(_7\)H\(_{16}\) isomers, then C\(_6\)H\(_{14}\), and finally C\(_5\)H\(_{12}\). In summary, having classified the alkanes into four isomer subsets, it seems possible to establish one ranking according to their fate descriptors. In order to do that, we introduce the concept of dominance degree (Dom). Let us assume that \(G' \subset G\) and \(G'' \subset G\) with \(G' \cap G'' = \emptyset\); if \(\forall x \in G', \forall y \in G'', x > y\) then \(G'\) dominates \(G''\) and we write \(G' \rightarrow G''\). In the practice of empirical posets the condition "for all" is too hard. Therefore we are introducing the dominance degree Dom (*G', G") = \(N_R / N_T\), where \(N_R (N \text{ realized}) = \mid \{ (x, y),

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Similarly, the fact of having two minimal elements in H means that there is no alkane with simultaneous fate descriptors lower than 1 and 2. When considering the L diagram, 2 becomes the least alkane.

**Comparing H and L Hasse Diagrams**

In the H diagram, each subset of isomers (C\textsubscript{5}H\textsubscript{12}, C\textsubscript{6}H\textsubscript{14}, C\textsubscript{7}H\textsubscript{16} and C\textsubscript{8}H\textsubscript{18}) appears as a chain or as belonging to a chain,\textsuperscript{15} except for the C\textsubscript{5}H\textsubscript{12} subset where there is no linear order\textsuperscript{15} between its members. When we analyze the effect of changing the river parameters from hilly regions to a lowland river, we found two general changes:

i) C\textsubscript{5}H\textsubscript{12} subset becomes a linear order, a chain.

ii) There are some internal rearrangements within C\textsubscript{7}H\textsubscript{16} and C\textsubscript{8}H\textsubscript{18} subsets.

The reason for i) can be explained first by mentioning the reason why 1 and 2 in H are incomparable and then why it changes in L. Chemical 1 is incomparable with chemical 2 (1 \parallel 2) in H because \(D_1(1) > D_1(2), D_2(1) < D_2(2)\) and \(D_3(1) > D_3(2)\) (Table III); hence \(D_2\) is the cause of incomparability. The reasons are difficult to explain because there are many competitive processes, which, on the one side, depend on the chemical properties and, on the other side, on the environmental ones. For example, high accumulation in the sediment need not necessarily be implied by a high deposition velocity of suspended matter. When we analyze the order relations for these two alkanes in the L diagram, we find that \(D_1(1) > D_1(2), D_2(1) > D_2(2)\) and \(D_3(1) > D_3(2)\), hence 1 > 2. In summary, the linear order of the C\textsubscript{5}H\textsubscript{12} subset in the L diagram is due to the change in the \(D_2\) order relation for 1 and 2. In other words, the change in the concentration of alkanes 1 and 2 in sediments is the cause of the linear order in the C\textsubscript{5}H\textsubscript{12} subset.

The second change in Hasse diagrams, when comparing H and L, is caused by the redistribution of some equivalence classes (Scheme 1), which do not alter the order relations among the chemicals. This is due to small numerical variations of the descriptors defining each chemical in each scenario. These variations normally occur just in one descriptor while the remaining two keep their order relations. Moreover, these variations are within the limits of discriminatory power of the descriptors since they occur in the last decimal position. For instance, the relation \(\{28\} < \{21, 24\}\) is found in H and these chemicals are rearranged to \(\{21, 24, 28\}\) in L. The cause of \(\{28\} < \{21, 24\}\) in H is that \(D_1(28) = 0.858\) is lower than \(D_1(21) = D_1(24) = 0.859\) since \(D_2(28) = D_2(21) = D_2(24)\) and \(D_3(28) = D_3(21) = D_3(24)\). When varying the river conditions from H to L, the small numerical difference between \(D_1(28)\) and \(D_1(21) = D_1(24)\) becomes an equality and 28 joins 21 and 24 in an equivalence class. In general, all the rearrangements within isomer subsets obey these kinds of small numerical differences.

**CONCLUSIONS**

The combination of basic chemical fate properties with partial ordering concepts is an interesting tool for drawing general conclusions on simultaneous analysis of fate descriptors. The dominance degree was introduced in this paper as a mathematical tool able to quantify the simultaneous effect of different descriptors on the general ranking of subsets of chemicals. The dominance degree is a measure of the number of real comparabilities between the members of two different subsets and the theoretical number of comparabilities holding if all the members in one subset are "greater" or "lower" than the members of the other subset. By applying this measure to the hilly and lowland Hasse diagrams of alkanes we found that the isomers with highest molecular weight dominate, or are more problematic than the rest of the isomer subsets following this relationship: C\textsubscript{8}H\textsubscript{18} \(\succ\) C\textsubscript{7}H\textsubscript{16} \(\succ\) C\textsubscript{6}H\textsubscript{14} \(\succ\) C\textsubscript{5}H\textsubscript{12}, where \(G' \succ G''\) means that the subset \(G'\) dominates the subset \(G''\). According to our definition of Dom \((G', G'') > 0.5\), the above result means that more than 50 % of the C\textsubscript{8}H\textsubscript{18} isomers dominate the C\textsubscript{7}H\textsubscript{16} ones, more than 50 % of the C\textsubscript{6}H\textsubscript{14} isomers dominate the C\textsubscript{5}H\textsubscript{12} ones, etc.

The order relationships found in the dominance of heavy alkanes over the light ones suggest the possibility of interdependence between the dominance degree and the molecular weight of the alkanes. To test this hypothesis, it would be interesting to consider more acyclic alkanes as objects of study.

It was found that, within each isomer subset, the linear alkane is the most environmentally problematic substance because of its relatively high concentrations in the water and the sediment bodies of the river scenarios considered.

Analysis of fate descriptors allows the conclusions that 1) the concentration of alkanes in the fluid phase of each scenario was determined mainly by the molecular weight, 2) the chemical concentration in sediments and the deposition flux were not related to the molecular weight, nor to any molecular parameter of the alkanes, and 3) the change of the river parameters from a river in hilly regions to a lowland scenario caused the chemical concentration in the fluid phase to decrease while the concentration in sediments and the deposition flux increased.

A general feature of the Hasse diagram technique is that it is based on the qualitative comparison of the descriptors characterizing the objects. Hence, the fact of having two chemicals \(x\) and \(y\) with \(x < y\) does not necessarily exclude that their actual concentrations might be so close that an experimental determination might yield identical values for both \(x\) and \(y\). Then, the practical importance of the poset results such as the ones shown in this manuscript are the relations in the graph, rather than the geometrical ones. This enables, when assessing che-
micals, to determine pollutant substances, or potentially problematic ones. However, these results must not be interpreted from a geometrical point of view where, for instance, $x < y < z$ means $1 \text{ ppb} < 2 \text{ ppb} < 3 \text{ ppb}$. In fact, $x < y < z$ might mean $1.001 \text{ ppb} < 1.002 \text{ ppb} < 1.003 \text{ ppb}$, and if the uncertainty of the measure is $\pm 0.002$, then $x$, $y$ and $z$ become an equivalence class. A similar case as the one described here are the concentrations shown in Table III, where the aqueous concentrations are close to each other for the majority of the alkanes belonging to a particular isomer subset. This situation causes minor variations within the subsets for the other two descriptors to be responsible of the comparabilities found between isomers but it does not mean that the "higher" chemical represents a markedly different chemical concentration when compared to a "lower" chemical in the ranking.

In this research, we considered just two river scenarios with the aim of checking how the order relations between chemicals change from scenario to scenario. However, this methodology can be applied to new river scenarios, perhaps defined by local parameters pertaining to particular rivers, particular sets of pollutants and particular input patterns. It may also be applied to chemicals characterized by some other risk-relevant factors such as toxicities or some other combinations of chemical attributes.

Several authors have pointed out that posetic structures are present in different fields of chemistry and particularly Brüggemann has shown the advantages of their study in environmental chemistry. The procedure developed here to deal with the order relations between subsets of objects may be applied to any poset and it is interesting to go into more details of its application when considering chemical posets like those developed by Randić and Daza and Bernal, among others.

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SAŽETAK

Parcialno uređeni skupovi u analizi sudbine alkana u rijekama

Guillermo Restrepo, Rainer Brüggemann i Kristina Voigt

Kao matematičku mjeru uređaja za podskupove parcijalno uređenog skupa uveli smo stupanj dominacije koji se izvodi iz svojstava njihovih elemenata. U stupnju dominacije sažima se parcijalni uređaj parova elemenata iz dvaju podskupova. Stupanj dominacije pokazuje koliko je uređaj između neka dva elementa iz različitih podskupova, svojstven svim parovima njihovih elemenata. Stupanj dominacije primijenjen je u komparativnoj analizii sudbine 35 acikličkih alkana (od C₃H₁₂ do C₈H₁₈) prema riječnim scenarijima za brdskoa i nizinsko područja. Svakom kemijskom spoju pridružena su tri deskriptora sudbine, određena pomoću modula EXWAT iz programskog paketa E4CHEM. Utvrđeno je da CₙH₂ₙ₊₂ dominira nad CₘH₂ₘ₊₂ kad je n > m, što znači da deskriptori za CₙH₂ₙ₊₂ imaju uglavnom veće vrijednosti od onih za CₘH₂ₘ₊₂. Određeni rezultati dobiveni su za linearne izomere iz svakog podskupa.