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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.

INTRODUCTION

Alkanes have been detected in several rivers around the world[1,2] 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 Sea[7] 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.[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.[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,

$$dc\ /\ dt = \text{Input}\ (p,\ q) - \text{Output}(p,\ q). \qquad (1)$$

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.

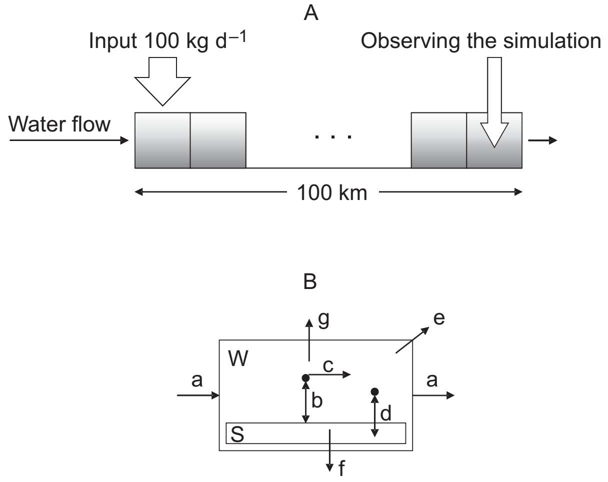


Figure 1. A) Partition of a river into several segments (boxes) in EXWAT, and B) the processes considered within each box (see text).

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[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.

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.

River parameters	H	L
River length / km	100	100
Box length[(a)] / km	2	2
Volume flow / m^3 s^{-1}	500	1000
Water body depth / m	2.5	3.5
Sediment depth / m	0.05	0.05
Width / m	150	300
Wind / m s^{-1}	5	5
Suspended matter content / g m^{-3}	100	100
w(Organic carbon in suspended matter)[(b)]	0.02	0.04
w(Organic carbon in sediment matrix)[(b)]	0.02	0.04
Sinking velocity of suspended matter / m d^{-1}	10	15

(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.[13] 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 posetic 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: Total concentration of chemicals in the fluid phase, γ_w / µg L^{-1};

D_2: Total concentration of chemicals in sediment, γ_s / µg L^{-1};

D_3: Deposition flux: Concentration of sorbed chemicals on suspended sediment, γ_{ws}, times deposition velocity, Depos. $D_3 = (\gamma_{ws} * \text{Depos.})$ / (µg · m) (L · d)$^{-1}$.

Note that the values of γ_w and γ_s refer to different compartments; for example, in the hilly scenario γ_w refers to the water body with a volume of 7.5×10^5 m^3 whereas γ_s refers to the sediment compartment with a volume of 1.5×10^4 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,[11,14] 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 $x \le y$ if $D_i\,(x) \le D_i\,(y)$ for all i. This specific order relation is called a product- (or component-wise-) order and obeys the following axioms of order:

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

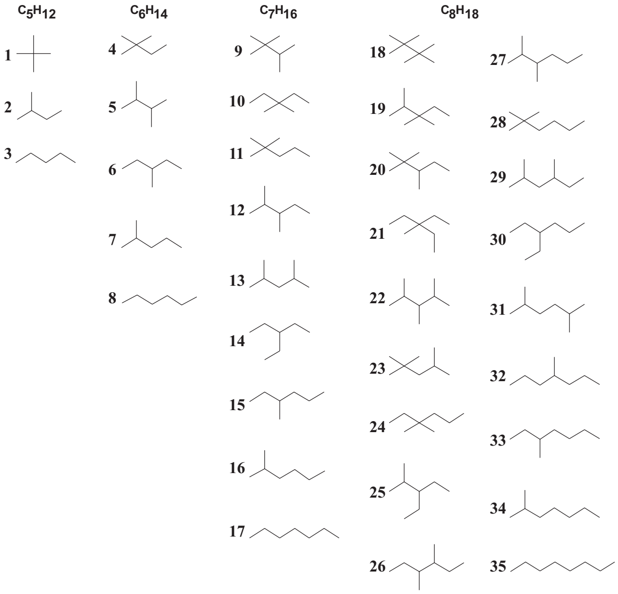
ii) antisymmetry: $\forall\ x, y \in G,\ x \le y$ and $y \le x \Rightarrow x = y$ (if x is better than y, then y is worse than x);

iii) transitivity: $\forall\ x, y, z \in G,\ x \le y$ and $y \le z \Rightarrow x \le z$ (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 $(G, \le)$ is used for a partially ordered set.[15] 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.[16] The reason for writing D instead of $\le$ 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 $D_i\,(x) \le D_i\,(y)$ for some indices i and $D_i\,(y) \le D_i\,(x)$ 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,[17] where the order relation $\le$ 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[18] 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.

TABLE II. Molecular graphs and labels for the 35 alkanes considered in the fate analysis.



RESULTS

The set G of chemicals in this study is made from the complete set of 35 acyclic alkanes ranging from C_5H_{12} to C_8H_{18}: three C_5H_{12}, five C_6H_{14}, nine C_7H_{16} and eighteen C_8H_{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[19] and the Handbook of Physical Properties of Organic Chemicals;[20] 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[21] (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(H) and D_1(L) 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_5H_{12}, C_6H_{14}, C_7H_{16} and C_8H_{18} isomers, respectively. We found that D_1 values for both scenarios fulfil this order relationship: $C_8H_{18} > C_7H_{16} > C_6H_{14} > C_5H_{12}$. 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_7H_{16} reached the value of D_1 corresponding to the C_8H_{18} isomers (Figure 2). This result

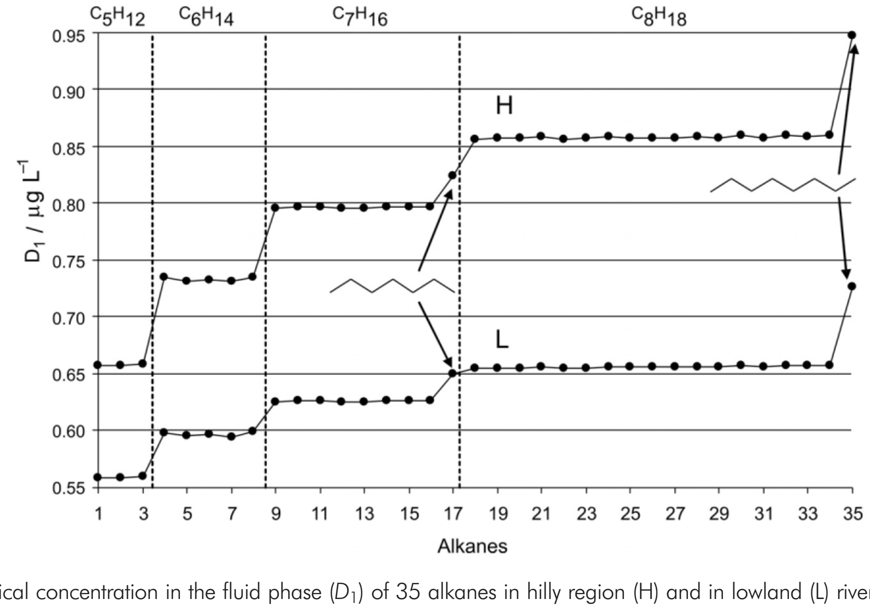


Figure 2. Total chemical concentration in the fluid phase (D_1) of 35 alkanes in hilly region (H) and in lowland (L) rivers. Some structures are drawn (see text).

TABLE III. Values of the fate descriptors for the alkanes studied. D_i(H) and D_i(L) stand for the D_i values in the hilly region (H) and lowland river (L) scenarios, respectively

Alkanes	D_1(H)	D_2(H)	D_3(H)	D_1(L)	D_2(L)	D_3(L)
	μg L^{-1}	μg L^{-1}	(μg · m) (L · d)$^{-1}$	μg L^{-1}	μg L^{-1}	(μg · m) (L · d)$^{-1}$
1	0.658	0.078	0.010	0.559	0.065	0.018
2	0.657	0.088	0.002	0.559	0.045	0.003
3	0.658	0.092	0.020	0.560	0.093	0.034
4	0.735	0.169	0.060	0.598	0.209	0.096
5	0.732	0.105	0.024	0.596	0.104	0.038
6	0.733	0.127	0.036	0.596	0.140	0.058
7	0.731	0.091	0.015	0.595	0.077	0.024
8	0.736	0.191	0.072	0.599	0.245	0.116
9	0.796	0.136	0.038	0.626	0.144	0.060
10	0.796	0.150	0.046	0.626	0.166	0.072
11	0.796	0.150	0.046	0.626	0.166	0.072
12	0.796	0.143	0.042	0.626	0.154	0.065
13	0.796	0.143	0.042	0.626	0.154	0.065
14	0.797	0.158	0.050	0.626	0.178	0.079
15	0.797	0.158	0.050	0.626	0.178	0.079
16	0.797	0.158	0.050	0.626	0.178	0.079
17	0.824	0.882	0.448	0.651	1.279	0.682
18	0.856	0.284	0.117	0.655	0.361	0.178
19	0.857	0.305	0.129	0.656	0.392	0.195
20	0.857	0.305	0.129	0.655	0.392	0.195
21	0.859	0.346	0.151	0.657	0.453	0.229
22	0.856	0.284	0.117	0.655	0.361	0.178
23	0.857	0.305	0.129	0.655	0.392	0.195
24	0.859	0.346	0.151	0.657	0.453	0.229
25	0.858	0.322	0.138	0.656	0.417	0.209
26	0.858	0.322	0.138	0.656	0.417	0.209
27	0.858	0.322	0.138	0.656	0.417	0.209
28	0.858	0.346	0.151	0.657	0.453	0.229
29	0.858	0.322	0.138	0.656	0.417	0.209
30	0.860	0.372	0.166	0.658	0.493	0.251
31	0.858	0.322	0.138	0.656	0.417	0.209
32	0.860	0.372	0.166	0.658	0.493	0.251
33	0.859	0.372	0.166	0.658	0.493	0.251
34	0.860	0.372	0.166	0.658	0.493	0.251
35	0.947	2.938	1.572	0.727	4.001	2.172

may suggest that when considering isomers of the set C_9H_{20} (not studied here), perhaps the linear isomer of C_8H_{18} could reach the values of D_1 for C_9H_{20} isomers, which is supported by the high D_1 value of the linear C_8H_{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).[22] After these calculations, we found a high Pearson correlation ($R > 0.9$) between D_1 and several molecular branching indices (W, $^1\chi$, 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.

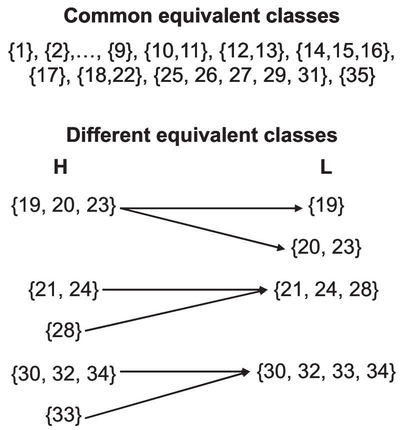
Regarding D_2 and D_3, we found a high correlation between these fate descriptors ($R > 0.9$). However, in contrast to D_1, we found no clear distinction between groups according to molecular weight (Figure 3). When looking for correlations between D_2 and D_3 through our pool of molecular descriptors, 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 γ_{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 (C_5H_{12}, C_6H_{14}, C_7H_{16} and C_8H_{18}) in each Hasse diagram (Figure 4) and we will discuss some of their features in the following text.



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

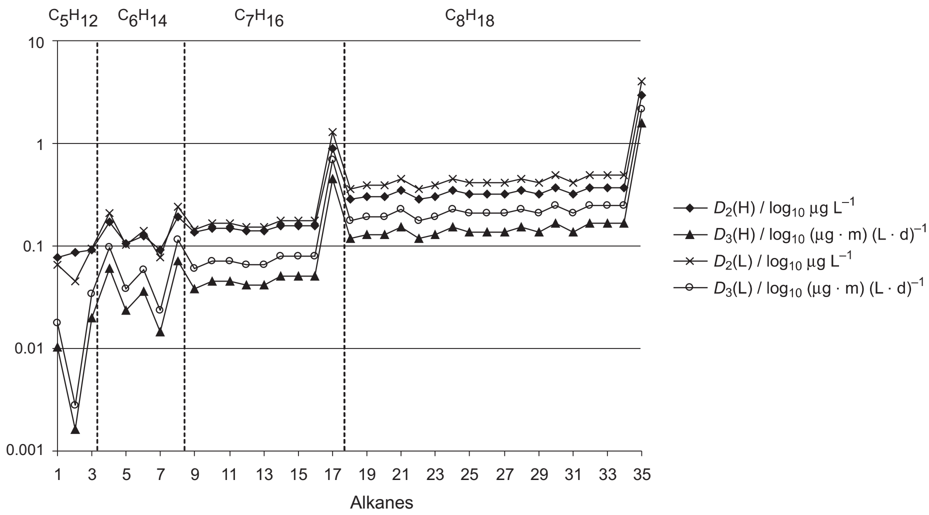


Figure 3. Total chemical concentration in sediment (D_2) and deposition flux (D_3) of 35 alkanes in hilly region (H) and in lowland rivers (L). D_i(H) and D_i(L) stand for the values of the $\log_{10}$ of D_i in the H and L scenarios, respectively.

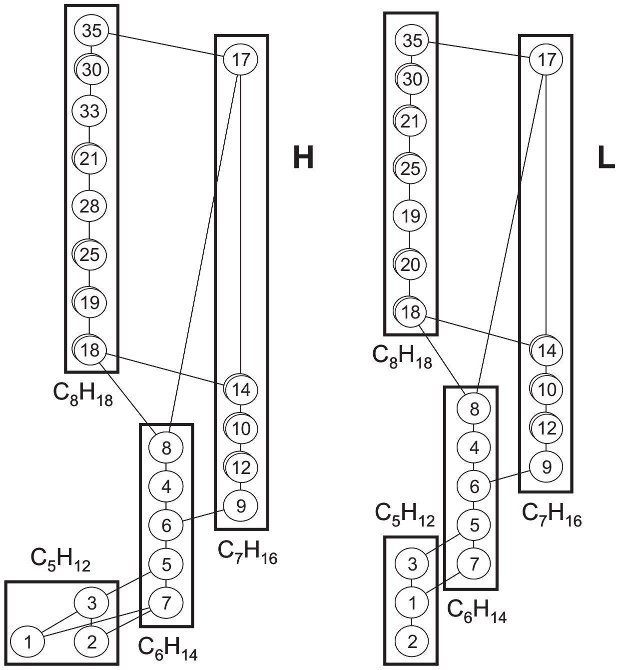


Figure 4. Hasse diagrams of 35 alkanes in the river scenarios H (hilly regions) and L (lowland). Double circles indicate equivalence classes with more than one alkane.

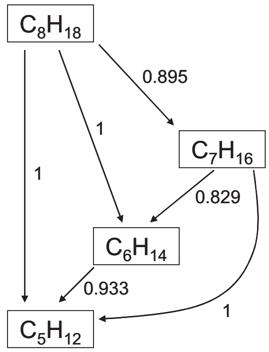


Figure 5. Dominance diagram: The scheme corresponds to the location of subsets in Figure 4 (see text).

General Observations

Brüggemann and co-workers have demonstrated the versatility of using Hasse diagrams in ranking[17,23] 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_8H_{18} isomers. Then, going down in the diagram, we found C_7H_{16} isomers, then C_6H_{14}, and finally C_5H_{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 $G' \cap G'' = \varnothing$; if $\forall x \in G'$, $\forall y \in G''$, $x > y$ then G' dominates G'' and we write $G' \blacktriangleright G''$. 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 realized) $= |\{(x, y), x \in G', y \in G''$ and $x > y\}|$ and $N_T = |G'| \cdot |G''|$. 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 $G' \blacktriangleright G''$. We show schematically in Figure 5 the Dom (G', G'') results for each pair of isomer groups. For example, the calculation of Dom (C_6H_{14}, C_5H_{12}), in both scenarios, is performed by determining $N_R = |\{(4, 1), (4, 2), (4, 3), (5, 1), (5, 2), (5, 3), (6, 1), (6, 2), (6, 3), (7, 1), (7, 2), (8, 1), (8, 2), (8, 3)\}| = 14$ and $N_T = |C_6H_{14}| \cdot |C_5H_{12}| = 15$. Then, Dom ($C_6H_{14}$, C_5H_{12}) = 14 / 15 = 0.933.

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

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

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 $C_8H_{18} \blacktriangleright C_7H_{16} \blacktriangleright C_6H_{14} \blacktriangleright C_5H_{12}$, 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_8H_{18}, 17 for C_7H_{16}, 8 for C_6H_{14} and 3 for C_5H_{12} (compare Table II). Now, from a general analysis of the Hasse diagrams we can say that the maximal[15] element is 35, which is also the greatest[15] element. There are two minimal[15] 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_8H_{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.

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_5H_{12}, C_6H_{14}, C_7H_{16} and C_8H_{18}) appears as a chain or as belonging to a chain,[15] except for the C_5H_{12} subset where there is no linear order[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_5H_{12} subset becomes a linear order, a chain.

ii) There are some internal rearrangements within C_7H_{16} and C_8H_{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 || 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_5H_{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_5H_{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, then 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_8H_{18} ► C_7H_{16} ► C_6H_{14} ► C_5H_{12}, where G' ► 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_8H_{18} isomers dominate the C_7H_{16} ones, more than 50 % of the C_7H_{16} isomers dominate the C_6H_{14} 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 posetic results such as the ones shown in this manuscript are the relations in the graph, rather than the geometrical ones. This enables, when assessing chemicals, 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 ppb < 2 ppb < 3 ppb. In fact, $x < y < z$ might mean 1.001 ppb < 1.002 ppb < 1.003 ppb, and if the uncertainty of the measure is ± 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[14,26] have pointed out that posetic structures are present in different fields of chemistry and particularly Brüggemann[14] 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[27] and Daza and Bernal,[28] among others.

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SAŽETAK

Parcijalno uređeni skupovi u analizi sudbine alkana u rijekama

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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 analizi sudbine 35 acikličkih alkana (od C_5H_{12} do C_8H_{18}) prema riječnim scenarijima za brdska i nizinska područja. Svakom kemijskom spoju pridružena su tri deskriptora sudbine, određena pomoću modula EXWAT iz programskog paketa E4CHEM. Utvrđeno je da C_nH_{2n+2} dominira nad C_mH_{2m+2} kad je $n > m$, što znači da deskriptori za C_nH_{2n+2} imaju uglavnom veće vrijednosti od onih za C_mH_{2m+2}. Određeni rezultati dobiveni su za linearne izomere iz svakog podskupa.