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ENVIRONMENTAL HAZARD RANKING OF CHEMICALS SPILLED IN THE RHINE RIVER IN NOVEMBER 1986

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ABSTRACT

In 1986 a chemical spill took place from the Sandoz plant in Basel, Switzerland, into the Rhine River. Several chemicals entered the River and were transported downstream. In this paper we rank the environmental hazard of eight chemicals, Disulfoton, Dinitroorthocresol, Propetamphos, Thiometon, Parathion, Etrimphos, Metoxuron and Fenitrothion found in the German section of the Rhine River. Five attributes related to the toxicity, physico-chemical characteristics and fate are used to rank the chemicals. The fate attributes were derived using the fate model E4CHEM. Two ranking methods were used and results compared. One method is based on the standardization of the data into attributes and aggregation into an index. The second method allows one to visually compare chemicals based on a large number of test results which might otherwise be very confusing when displayed in a Table form: The Hasse diagram is an effective graphical display of data difficult to understand otherwise. Results by both ranking methods show that these chemicals can be divided into two groups, the most hazardous include Dinitroorthocresol, Propetamphos and Parathion, and the least hazardous include Disulfoton, Thiometon, Etrimphos, Metoxuron and Fenitrothion.

RÉSUMÉ

En 1986, des produits chimiques provenant de l'usine Sandoz de Bâle en Suisse ont été déversés accidentellement dans le Rhin. Plusieurs produits chimiques ont atteint le fleuve et ont été transportés en aval. Le présent document donne un classement du danger que représentent pour l'environnement huit produits chimiques, soit le disulfoton, le dinitro-orthocrésol, le propétamphos, le thiométon, le parathion, l'étrimfos, le métoxuron et le fénitrothion. Ces produits ont été retrouvés dans la partie allemande du Rhin. Le classement utilise cinq caractéristiques liées à la toxicité, aux propriétés physico-chimiques et au devenir de ces produits chimiques. Les caractéristiques liées au devenir ont été tirées du modèle de devenir E4CHEM. On a utilisé deux méthodes de classement dont on a comparé les résultats. La première consiste à normaliser les données pour obtenir des caractéristiques et à les réunir pour former un indice. La deuxième méthode consiste à comparer visuellement les produits chimiques en se basant sur un grand nombre de résultats d'essais, résultats qui autrement pourraient être source de confusion s'ils étaient disposés sous forme de tableau : Le diagramme de Hasse est un moyen efficace d'exposer graphiquement des données qui sont difficiles à saisir quand elles sont présentées autrement. D'après les résultats des deux méthodes de classement, les produits chimiques peuvent être divisés en deux groupes : les plus dangereux qui comprennent le dinitro-orthocrésol, le propétamphos et le parathion, et les moins dangereux dont font partie le disulfoton, le thiométon, l'étrimfos, le métoxuron et le fénitrothion.

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MANAGEMENT PERSPECTIVE

Ranking chemicals in terms of their environmental hazard by prespecified criteria, has been the subject of much research. In this paper we compare two ranking procedure to analyze the environmental hazard posed to the Rhine River by eight chemicals spilled by Sandoz in the river in 1986. One ranking method combines fate and toxicity data into a standardized index. The second ranking method is a vectorial approach, developed in Canada, which recognizes that the higher the number of criteria used, the higher the probability that contradictions exist between the criteria. This method not only ranks chemicals but also identifies contradictions in the criteria used to rank the chemicals. Analysis of the data used in the ranking scheme is an important part of the ranking scheme itself. Results are displayed on paper or on a TV monitor driven by a desk top personal computer. Five attributes related to the toxicity, physico-chemical characteristics and fate are used to rank the chemicals.

PERSPECTIVES - GESTION

Le classement des produits chimiques en termes de leur danger pour l'environnement selon des critères préétablis a fait l'objet de bon nombre de recherches. Le présent document compare deux méthodes de classement visant à analyser le danger pour l'environnement créé par le déversement accidentel dans le Rhin en 1986 de huit produits chimiques de l'usine Sandoz. La première méthode combine les données sur le devenir et la toxicité pour obtenir un indice normalisé. L'autre méthode est une approche vectorielle élaborée au Canada, selon laquelle plus le nombre de critères utilisés est grand, plus la probabilité qu'il existe des contradictions entre les critères est élevée. Cette méthode permet non seulement de classer les produits chimiques mais elle identifie aussi les contradictions entre les critères sur lesquels est basé le classement. L'analyse des données employées dans le plan de classement constitue une partie importante de ce plan. Les résultats sont affichés sur papier ou sur un écran cathodique par un micro-ordinateur. Le classement est basé sur cinq caractéristiques liées à la toxicité, aux propriétés physico-chimiques et au devenir des produits chimiques.

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INTRODUCTION

In 1986 a chemical spill took place from the Sandoz plant in Basel, Switzerland, into the Rhine River (Bundesminister fur Umwelt, 1987). Several chemicals entered the River and were transported downstream into Germany and the Netherlands. In this paper we rank the environmental hazard of eight chemicals, Disulfoton, Dinitroorthocresol, Propetamphos, Thiometon, Parathion, Etrimphos, Metoxuron and Fenitrothion found in the German section of the Rhine River. Five attributes (Nachrichten aus Chemie, 1986; Bruggemann, 1987) related to the toxicity, physico-chemical characteristics and fate are used to rank the chemicals.

Ranking chemicals in terms of their environmental hazard by prespecified criteria, has been the subject of much research (Freitag et al., 1984; Kaiser et al., 1984, Klein et al., 1984; Halfon and Reggiani, 1986). In this paper we compare two ranking procedure to analyze the environmental hazard posed to the Rhine River by these chemicals. The first ranking method (PUC, 1986; Rohleder et al., 1986) combines fate and toxicity data into a standardized index with range 0-1. The second ranking method (Halfon and Reggiani, 1986) is a formal procedure, based on set theory and systems analysis. In this method no subjective index is used but ranking is obtained by comparing test results for one chemicals with results obtained from the same tests on other chemicals; this approach is called partial ordering. Partial ordering is a vectorial approach which recognizes that not all chemicals can be directly compared with all other chemicals in terms of environmental hazard when several criteria (test results or attributes) are used. In fact, the higher the number of criteria used, the higher the probability that contradictions exist between the criteria so that different ranking results might originate if each criteria was used alone. With the approach presented here

contradictions are solved in a holistic way using decision theory. Results are displayed on paper or on a TV monitor driven by a desk top personal computer using Hasse diagrams (Harary, 1969; Preparate, 1973; Reggiani and Marchetti, 1975), a useful graphic tool commonly used in algebra to display lattices (a genealogical tree is a special case of a Hasse diagram). This method not only ranks chemicals but also identifies contradictions in the criteria used to rank the chemicals. Analysis of the data used in the ranking scheme is an important part of the ranking scheme itself.

The basic assumption of both ranking schemes (Halfon and Reggiani, 1986; PUC, 1986; Rohleder et al., 1986) is that a low numerical value on a test indicates less environmental hazard. Therefore, if for some tests the opposite assumption is valid, i.e., a high numerical value means less environmental hazard, then the ranking must be inverted by multiplying all values by -1. For example, a high volatilization rate indicates less environmental hazard for surface water bodies and therefore the reciprocal or the negative of this rate is used given the assumption that the lower the value of an element, the lower the environmental hazard. In fact high values of bioaccumulation indicate possible environmental hazard whereas high volatilization rates indicate less environmental hazard.

For each chemical, a given number of tests, called attributes, is performed. Once several attributes are chosen the next step is to assign them weighting factors. This step can be left to the expert (Keeley and Raiffa, 1976) and can be included or bypassed; we also have to check the set of attributes for completeness; i.e. if the set is adequate and contains enough information, nonredundant (to avoid double counting), to rank the chemicals for environmental hazard.

The number of attributes should be minimal to reduce the number of

experiments required for each chemical; this condition implies that the properties of the attributes should be independent of one another. The attributes and their values can be expressed in a simple mathematical form: Each chemical is linked to a set of numbers, each number corresponding to the result of a single test; as explained before, the ranking is defined in such a way to decrease as the environmental hazard decreases.

THE FIRST RANKING PROCEDURE (Bruggemann)

This ranking procedure (PUC, 1986; Rohleder et al., 1986) uses the same data set (Table 2) as the procedure described below. This data set might include exposure and fate attributes as well as effect attributes such as toxicity data. In this procedure three steps are performed:

1) The raw data are transformed so that the range of the standardized data is the same for all data, namely zero to one. As before, the higher the value the higher the environmental hazard. This standardization is performed as follows. Given attribute i for chemical j, $x_{i,j}$, the mean value x_i, of attribute i for all chemicals in the list, and s_x, the standard deviation of attribute i for all chemicals, then the standardized attribute $x'_{i,j}$ is

$$x'_{i,j} = a * [\log (x_{i,j}) - \log (x_i)] / s_x \qquad (1)$$

This transformation leads to a statistical distribution with zero mean of the $x'_{i,j}$ set. The constant a has a value of 1 if the higher the value of x_i the higher the hazard, or a value of -1 if the higher the value of x_i the lower the hazard (for example in the case of toxic concentrations in water). A second transformation is used to obtain values within the range of zero to one. This transformation is

$$y_i = \begin{cases} 1 & \text{if } \dfrac{x'_{ij} + 3}{6} > 1.0 \\ \dfrac{x_{ij} + 3}{6} & \text{if } 0 \leq \dfrac{x'_{ij} + 3}{6} \leq 1.0 \\ 0 & \text{if } \dfrac{x'_{ij} + 3}{6} < 1.0 \end{cases} \qquad (2)$$

Note that the probability of $(x-\mu)$ being outside of the interval $-3 \leq (x-\mu) \leq 3$ is only about 11%, where μ is the expectation value of the distribution. This transformation has the effect of initially giving the same weight to all attributes. If this equal weight is not desirable, the y_i can be multiplied by an appropriate factor or weight.

2) The standardized data are aggregated into an index using the following formula:

$$d_i = \text{sqrt}\ \{(1/n) \sum_{i=1}^{N} y_i\} \qquad (3)$$

3) The ranking of the chemicals is performed by sorting the index d_i.

THE SECOND RANKING PROCEDURE (Halfon and Reggiani)

The method (Reggiani and Marchetti, 1975; Halfon and Reggiani, 1986) is based on the hypothesis that a set of numbers (attributes) is generally necessary to create a ranking file; these numbers can be considered the elements of a vector, the "vector performance". This "vector approach method" is different from the "scalar approach method", where a single number (a

scalar performance index) is said to be sufficient to interpret fate and toxicity data and to compare chemicals and rank them according to their environmental hazard.

The formal logical development of the method can be found in Preparate (1973). A BASIC program to display results with a desk top personal computer is available from the author. The hazard levels are determined by comparing the test data for each chemical with all the others according to prespecified logical rules. These rules are the definition of binary relations between pairs of set elements and are based on principles of lattice and graph theory developed during the 1970's (Harary, 1969; Preparate, 1973; Reggiani and Marchetti, 1975); the methodology is therefore well established and the procedure is described here with an example. A computer program has been developed for easy usage of the method, but the method is simple enough that calculations can be done also by hand even if they are lengthy.

In a Hasse diagram (Halfon and Reggiani, 1986) the chemicals closer to the bottom of the figure are the least hazardous. The numbers in each circle are labelled (Table 1) and the lines between the circles mean that the given chemicals can be directly compared with each other following any path. By definition the chemicals on the same level are "incomparable" (see example in Fig. 1b and explanation in the theory section for definition of incomparability).

A set of data is partially ordered if contradictions exist in the test data that prevent us from ranking the contaminants in a chain (Fig. 1a). If contradictions exist for the ranking of two chemicals, then the two chemicals may be assigned to the same hazard level (Fig. 1b) depending also on their relative ranking with the other chemicals in the list.

Two examples

a) Let C1 and C2 be two chemicals and V_{c1} and V_{c2} their respective vector performances. If every component of V_{c1} is lower than the corresponding one of V_{c2}, C1 is obviously the safer of the two. Should any two successive chemicals C2, C3; C3, C4; ... of the considered set (C1, C2, ...) behave in the same fashion we could draw the diagram (Fig. 1a) known in set theory as the Hasse diagram. Here C1 is better than C2; C2 better than C3, and so on. The chemicals can be ranked in a chain. Unfortunately, such a situation, so simple to be understood and sketched, is seldom verified in reality. Consider, for example, the chemical C7 having as components for the vector distance the numbers [4,4] and the chemicals C5 and C6 characterized by the components [2,3] and [3,2]. Both C5 and C6 are better than C7 because they have smaller components than C1. Nevertheless, they are "incomparable" to each other (C5 is better than C6 as far as the first component is concerned, but the opposite is true for the second component (see Fig. 1b). Under these circumstances, it is not immediately apparent which of the two chemicals C5 and C6 is environmentally safer. With a larger number of chemicals and a larger number of attributes the ranking becomes even more complicated.

b) In the general case, the formal ranking procedure can be explained by analyzing a small set of data (Table 1): the chemicals are identified as #1; #6; #23; #24; #28; and #34. The Hasse diagram for these six chemicals can be derived as follows: Assume that the six chemicals are positioned at the vertices of a regular polygon, in this case an hexagon (see Fig 2). Now, compare one chemical, e.g. #1 with all others (#6, #23, #24, #28, #34) one at the time. In practice this comparison of chemicals implies the comparison of each individual test (each vector element) performed on one chemical with the respective tests on all the other chemicals, one chemical at the time. In

principle, there are four possible relationships to describe the outcome:

#1 = #6	case A
#1 >/ #6	case B
#1 \< #6	case C
#1 and #6 are incomparable	case D

The notation >/ (greater or equal) of case B) means that each element of chemical #1 is greater or equal than each element of #6, i.e $\#1_1$ >/ $\#6_1$; $\#1_2$ >/ $\#6_2$; ... with the constraint that the sign = can not be valid for all elements, since this is case A or the two chemicals occupy the same place in the ranking scheme. If the symbol >/ is interpreted as a parental relation (father-son; father-grandson; grandfather-grandson, etc.) within a family, the Hasse diagram becomes a genealogical tree. The lines represent the direct relation father-son and each two successive levels represent the passage of a generation. For example if we compare each element of #1 with each element of #6 (that is each element on line one in Table 1 with each element in line two) we find that

$\#1_1$ (380) > $\#6_1$ (6);

$\#1_2$ (94) > $\#6_2$ (5.1);

$\#1_3$ (0.1) = $\#6_3$ (0.1);

$\#1_4$ (19) > $\#6_4$ (13);

$\#1_5$ (.30) > $\#6_5$ (.10);

$\#1_6$ (119) > $\#6_6$ (98).

Since each element of #1 is greater than or equal to each respective element of #6, we can draw an oriented line in Fig. 2b from #1 to #6. This example reflects case B. Case C is the the inverse of Case B. If in the present example case C had been true then #6 and #1 would have been connected with an

oriented line from #6 to #1, the opposite of case B. If by chance the results of all tests were the same for #6 and #1 then we could say that #1 and #6 rank exactly the same or #1 = #6 (case A) and graphically the hexagon would then become a pentagon since #1 and #6 would occupy the same space.

Case D is most interesting from the point of view of data analysis. In the Hasse diagram two elements (for example #1 and #23 in Fig 2b) are not connected because contradictions exist among the different tests; these elements are called "incomparable". This contradiction exists also between chemicals #24 and #28. From analysis of Table 1 we see that

$\#24_1$ (2690) < $\#28_1$ (11500);

$\#24_2$ (2420) > $\#28_2$ (2320);

$\#24_3$ (0.1) < $\#28_3$ (39.8);

$\#24_4$ (63) < $\#28_4$ (278);

$\#24_5$ (10) > $\#28_5$ (3.33);

$\#24_6$ (286) > $\#28_6$ (192).

Out of six experiments #24 less hazardous than #28 (lower numerical value) in three experiments and more hazardous in the other three. Therefore the results are inconclusive and overall we cannot say whether #24 is better than #28 or viceversa. The Hasse diagram (Fig. 2b) identifies #24 and #28 as incomparable by not connecting the two circles; lack of connection identifies contradiction in data. By definition all chemicals located in the same ranking level in a Hasse diagram are incomparable. Similar contradictions exist between #23 and #24 and between #1 and #23. The results of this analysis show that this method is useful not only for ranking but also, and perhaps even more importantly, for data analysis to identify contradictions in the test results.

Continuing the analysis of the example, we compare the pairs #1-#23, #1-#24, #1-#28 and #1-#34 and oriented lines are drawn accordingly following the same rules explained in the previous paragraph. The next step is to compare the pairs #6-#23, #6-#24, #6-#28 and #6-#34; and so on until #24-#28; #24-#34 and finally #28-#34. When this analysis is completed, then we have Fig. 2b, or the relation diagram.

The next step is to eliminate all redundant oriented lines. For example the line #34-#23 in Fig. 2b is redundant since the lines #34-#28 and #28-#23 already exist. That is, we know that #23 is less hazardous than #34 since all tests in #23 have numerical values lower than in #34 and all test values of #23 are lower than those of #28 which in turn are lower than those of #34. Therefore, the line between #34 and #23 becomes superfluous since this information already is displayed in the Hasse diagram with the two lines #34-#28 and #28-#23. Likewise, we can eliminate #28-#6 (the information is contained in #28-#23 and #23-#6); #24-#6; #34-#6 and #34-#1. Figure 2c shows the simplified diagram after all eliminations have been done. The next step is to reorganize the diagram so that the oriented lines are directed towards the bottom of the page (Fig. 2d) so that the arrows become unnecessary. Chemicals of greater environmental hazard are located above those of less hazard. In the final drawing the number of horizontal levels which contain the incomparable elements must be minimized and therefore the chemicals #28 and #24 and the chemicals #23 and #1 are presented in the same level.

We can also introduce the concept of tolerance or weighting factors for each attribute. This option may be necessary when results from laboratory tests have some uncertainty or measurement errors associated with them. For example in test example analyzed above (Table 1) we noted that element $\#24_2$ with a value of 2420 was larger that element $\#28_2$ with a value of 2320. These

experimental results are quite similar and if we are not absolutely sure that the difference is real our interpretation of the results might be flawed. In this example, if we decide that 2320 and 2420 are practically the same, compared for example with other test results of 280 (element $\#23_2$) or 94 (element $\#1_2$), then the solution is to categorize the experimental results into classes. The total range of an attribute is divided, or quantized, into equal or nonequal parts (or categories). In this case, the second vector element of Table 1 can be divided into three arbitrary classes (0-100; 100-1000; 1000-10000). Using this classification scheme elements $\#24_2$ and $\#28_2$ are now equal. From a practical point of view we have added weights to the data. The more confidence we have in the individual test values, the larger the number of classes and vice versa. Thus, an attribute which is divided into few classes (limit case is 2) is given less importance while an attribute which is divided into an infinite number of classes (i.e. we use the raw data), is considered very important.

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The solution is to categorize the experimental results into classes. The total range of an attribute is divided, or quantized, into equal or nonequal parts (or categories). From a practical point of view we have added weights to the data. The more confidence we have in the individual test values, the larger the number of classes and vice versa. Thus, an attribute which is divided into few classes (limit case is 2) is given less importance while an attribute which is divided into an infinite number of classes (i.e. we use the raw data), is considered very important.

DATA

The Chemical Act in Germany (Bundesminister fur Jugend, 1980) identifies some chemical characteristics that can be used to define the environmental hazard of contaminants in the environment. The characteristics are the octanol-water partition coefficient k_{ow} (usually expressed in $\log_{10}$ form; attribute D1 in Table 2), the Henry Law's constant (attribute D5) and the toxicity of the chemical to the carp fish (attribute D2). These three attributes are used here to rank eight chemicals (Table 2) found in the spill from the Sandoz company in November 1986. Furthermore, a mathematical model, EXWAT, which is part of the EDV-code E4CHEM (Rohleder et al., 1986), and which calculates the fate of chemicals in surface water bodies like QWASI (Mackay et al., 1983), was used to compute two attributes, D3 and D4, which integrate the physico-chemical information with environmental fate to understand the main processes governing the distribution of the contaminants in the aquatic environment. The information obtained from running the model E4CHEM was integrated into the two attributes D3 (% accumulation in bottom sediments of a river) and D4 (average residence time [days] in water). This information is also shown in Table 2. This ranking exercise therefore uses five attributes to identify the environmental hazard of the eight contaminants. The attributes are physico-chemical characteristics, one is toxicity and two are identified by the mathematical model as an index of fate. The Henry Law's constant of these eight chemicals range from a high of 1.5×10^{-4} [dimensionless] for Fenitrothion to a low of 6×10^{-7} [dimensionless] for Metoxuron. Since these volatilization constants are quite low, we decided to classify the chemicals into two classes according to their volatilization potential. Class one includes contaminants with a Henry Law's constant of 10^{-4} or higher and class two includes contaminants with a Henry Law's constant

less than 10^{-4}. As explained in the Theory section this division in classes implies that volatilization is given a relatively low weight in relation to the other four attributes.

RESULTS (Standardized ranking)

Table 3 shows the same data presented in Table 2 after the transformation to the new variables y_i using the procedure described in Eqs. 1-3. The purpose of this transformation is to give the five attributes an equal weight, independently of the values of the individual tests. Table 4 shows the ranking of the eight chemicals either using either the two fate attributes D3 and D4 (case 1), or the three attributes D1, D2 and D5 (case 2) associated with the physico-chemical characteristics and toxicity, or all five attributes (case 3). In case 1, the most hazardous chemical is Propetamphos, because of its high accumulation and long residence time in the river, followed by Parathion, Dinitroorthocresol and Fenitrothion. In case 2, the ranking is Parathion, because of its relatively high octanol water partition coefficient and high toxicity, followed by Dinitroorthocresol, Etrimphos (previously ranked fifth) and Propetamphos; Fenitrothion is ranked fifth. Therefore the same chemicals are ranked hazardous using either of these two sets of criteria. In case 3, the most hazardous contaminant is Parathion, followed by Propetamphos, Dinitroorthocresol, Etrimphos and Fenitrothion. Thiometon is the least hazardous chemical.

RESULTS (Hasse diagrams)

The ranking of the eight chemicals according to their expected fate using attributes D3 and D4 (case 1) is shown in Fig. 3. The two chemicals Propetamphos and Parathion are ranked at the highest level because of their

high accumulation and long residence time in the river. Note that the Hasse diagram adds an item of information not immediately evident from the analysis of numerical values in Table 1. These two contaminants are ranked at the same level, i.e. they are "incomparable" and contradictions exist in the test results between the two chemicals; an analysis of Table 1 shows that Propetamphos has a lower accumulation potential than Parathion but it has a longer residence time in the river. Therefore, these two chemicals are equally hazardous since we can not say whether accumulation is a less desirable property than a short residence time. Both these chemicals however have a higher accumulation and residence time than all the other six. On the second level we find Dinitroorthocresol and Fenitrothion. Thiometon is the least dangerous according to its expected fate.

The ranking of the eight chemicals according to three criteria (case 2) related to its physico-chemical characteristics (k_{ow} and volatility potential) and toxicity (LC_{carp}) is given in Fig. 4. According to this analysis Parathion ranks highest followed at the next level by Dinitroorthocresol, Etrimphos and Fenitrothion together. Etrimphos is located in the third level according to is expected fate. The reason for this higher ranking is its toxicity to carp, similar to the toxicity of Fenitrothion. Again the ranking using this method is similar to using an index function with the additional information of contradictions in test results among Dinitroorthocresol, Etrimphos and Fenitrothion. The Hasse diagram therefore suggests that it is incorrect to rank there three chemicals in a chain since each of these three chemicals might be less hazardous than the other two according to some attribute. Each of the three should rank more or less the same.

The ranking of the eight chemicals according to all five attributes (case 3), which include fate, toxicity and physico-chemical properties, is shown in

Fig. 5. Here the levels have been reduced to two because of the relative contradictions among the five attributes. Dinitroorthocresol, Propetamphos and Parathion are ranked the most hazardous while the other five chemicals are ranked together. The Hasse diagram points out that when using all five attributes to obtain a ranking the differences among chemicals are not very large and therefore only two groups can be distinguished. From Fig. 5 we can also notice that while Parathion is definitely more hazardous than all the other five remaining contaminants on level two, Dinitroorthocresol and Propetamphos are incomparable with Etrimphos and Fenitrothion. An analysis of Table 1 shows that Dinitroorthocresol is incomparable with Etrimphos because :

(D1,D2,D3,D5) Etrimphos > (D1,D2,D3,D5) Dinitroorthocresol

but

D4 Etrimphos < D4 Dinitroorthocresol

Similar arguments are valid when Propetamphos is compared with Etrimphos and Fenitrothion.

DISCUSSION

The Rhine River crosses three countries, Switzerland, Germany and The Netherlands before entering the Atlantic Ocean at Rotterdam. The river is heavily polluted from the large number of cities and industries located along its shores. The spill that occurred in Basel in 1986 is interesting for the magnitude of the spill which perturbed the river ecosystem for more than 200 kilometres downstream (Bundesminister fur Umwelt, 1987). The eight chemicals analyzed in this study are water soluble with a relatively low octanol water partition coefficient, between 0.51 for Thiometon to 3.4 for Fenitrothion.

These coefficients are quite low compared for example with Hexachlorobenzene (log k_{ow}=5.1) and Mirex and PCB's (log k_{ow}=7). Nevertheless, these contaminants have perturbed the Rhine ecosystem.

Both ranking schemes have identified Parathion, Propetamphos and Dinitroorthocresol and the most environmentally hazardous to the Rhine River. The ranking scheme using Hasse diagrams has also identified contradictions in the the test results, attributes, contradictions not immediately evident when an index function is used. The visual identification of these contradictions is as useful as the ranking itself; in fact Hasse diagrams with their connecting lines between comparable chemicals identify a structure in the ranking; where conflicting results are present (Table 2), the Hasse diagram shows the chemicals not connected by a line. From the analysis of these graphs it is therefore possible to reconstruct the decision making process in ranking the chemicals.

Hasse diagrams allow one to visually compare chemicals based on a large number of test results which might otherwise be very confusing when displayed in a Table form: The Hasse diagram is an effective graphical display of data difficulty understandable otherwise. The truth is the reality that we wish to represent is difficult to classify and comprehend by the human mind. When reality is simple (elements in a chain) there are no problems of visual display, when, however, much information has to be understood, a graphic method is useful. Another interesting result is that the Hasse diagram identifies the eight chemicals into only two groups. This result is significant because it shows that these eight contaminants are not very different in fate or chemical properties. In fact, if we compare these eight chemicals with more hydrophobic or persistent ones, such as PCB's, chlorobenzenes and Mirex, they can be considered as belonging to the same

class of soluble and less hazardous chemicals.

The ranking procedure using a vectorial approach is applicable to variety of problems in environmental toxicology. Once data have been collected, a computer can process them in a few seconds. A graphical display program has been developed for desk top computers and is available on request. The number of different classification levels is directly proportional to the number of chemicals and inversely proportional to the number of criteria; in fact, the more criteria are considered at the same time, the higher is the probability of contradictions in the data and therefore higher the probability of having fewer discrimination levels.

Hasse diagrams show which chemicals are the most environmentally hazardous. When a new chemical is developed and its properties known, it can be easily ranked and compared with other known chemicals or any arbitrary standards. The availability of the program in microcomputer form make routine application easy.

A final comment: The development of a suitable index for environmental risk has been widely discussed in the literature (Koch, 1984; Freitag et al., 1984; Kaiser et al., 1984; Klein et al., 1984; Halfon and Reggiani, 1986; PUC, 1986; Rohleder et al., 1986). In this paper we have also suggested a novel index (PUC, 1986; Rohleder et al., 1986). An index is a suitable scalar function of the vector distance components with the best chemicals having the lowest index. Since an index is a scalar quantity, problems concerned with the incomparability of chemicals cannot arise since the chemicals can always be ranked and represented as a chain in a Hasse diagram. Unfortunately, ranking chemicals using an index function does not allow the identification of contradictions in the data as esemplified in this paper. We should be careful when using some procedures that are apparently simpler (scalar indices)

because we may run the risk that we gain simplicity by misunderstanding the reality.

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FIGURE LEGENDS

Figure 1. a) Hasse diagram of ranked chemicals C1-C4. C1 is less hazardous than C2, C2 less than C3, etc. b) Hasse diagram of partially ordered chemicals. Both C5 and C6 are better than C7 but they are incomparable with each other. Thus, it is not immediately clear which chemical should be chosen as the safest.

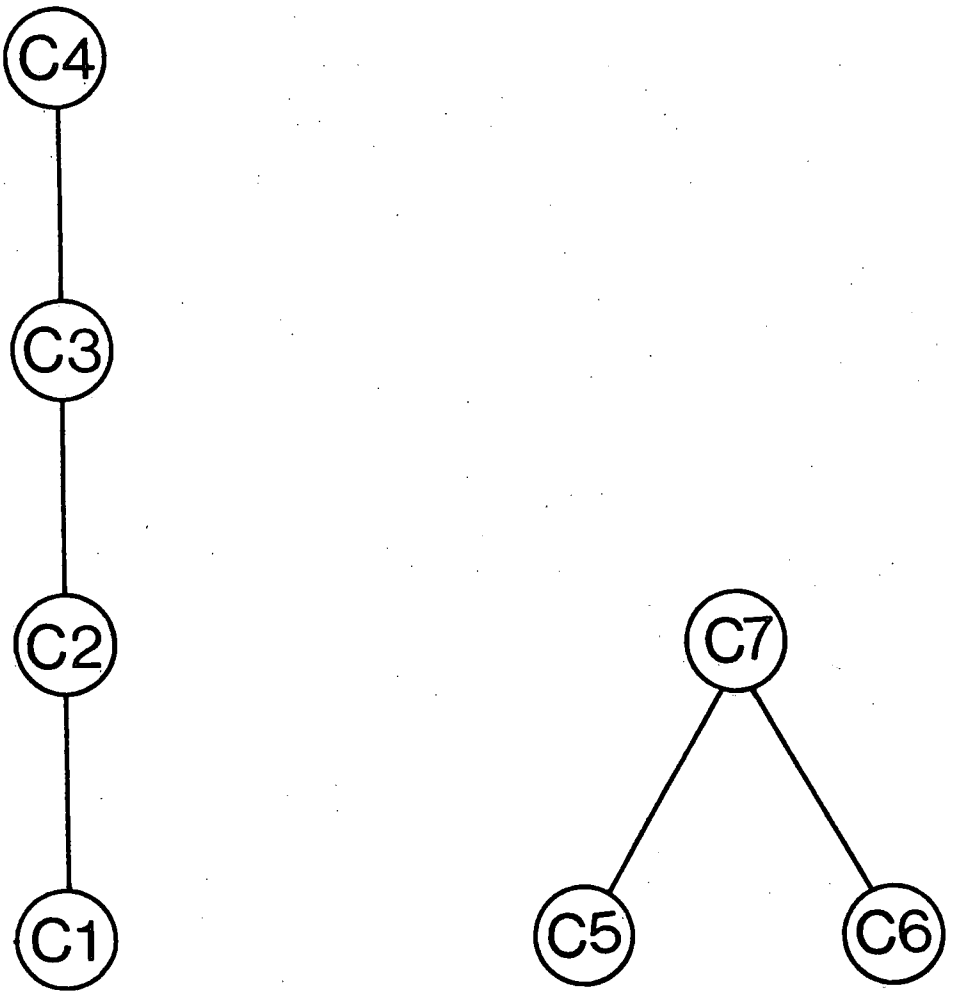
Figure 2. The formal procedure to rank chemicals according to environmental hazard is explained using six chemicals from Table 1. See text for additional explanations. a) set chemicals at vertices of regular polygon. b) rank chemical with one another. c) remove redundant lines d) rotate diagram and eliminate arrows, i.e. Hasse diagram.

Figure 3. Ranking of the eight chemicals found in the Rhine River after the Sandoz spill according to the two fate attributes D3 and D4 (see Table 2). The numbers inside the circles identify the chemicals as follows: (1) Disulfoton, (2) Dinitroorthocresol, (3) Propetamphos, (4) Thiometon, (6) Parathion, (7) Etrimphos, (8) Metoxuron and (9) Fenitrothion.

Figure 4. Ranking of the eight chemicals found in the Rhine River after the Sandoz spill according to the attributes D1, D2 and D5. The numbers inside the circles identify the chemicals as follows: (1) Disulfoton, (2) Dinitroorthocresol, (3) Propetamphos, (4) Thiometon, (6) Parathion, (7) Etrimphos, (8) Metoxuron and (9) Fenitrothion

Figure 5. Ranking of the eight chemicals found in the Rhine River after the Sandoz spill according to the all fate attributes D1 to D5. The numbers inside the circles identify the chemicals as follows: (1) Disulfoton, (2) Dinitroorthocresol, (3) Propetamphos, (4) Thiometon, (6) Parathion, (7) Etrimphos, (8) Metoxuron and (9) Fenitrothion

MORE HAZARD



(a) (b)

LESS HAZARD

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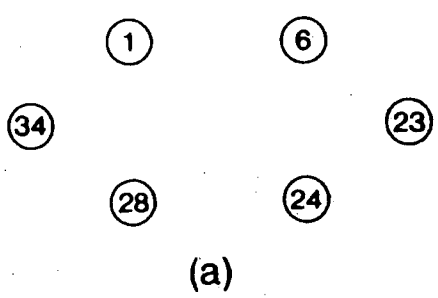

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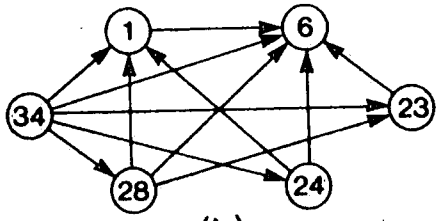

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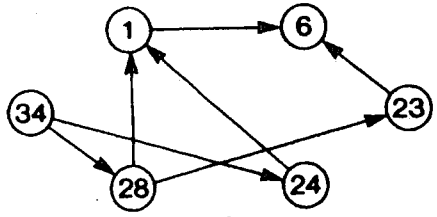

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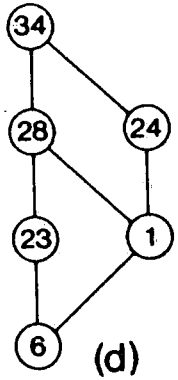

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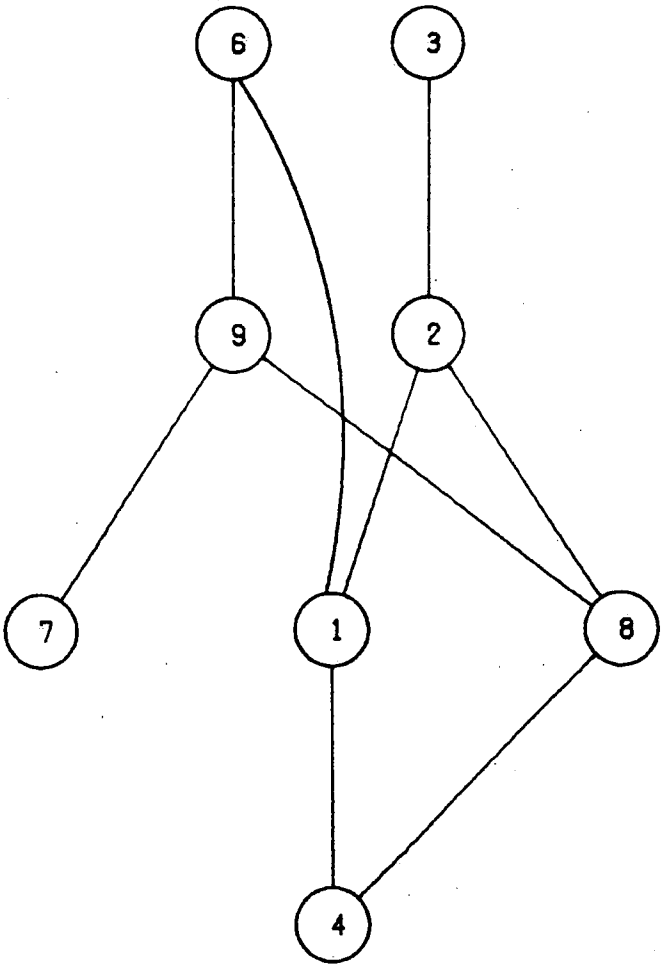
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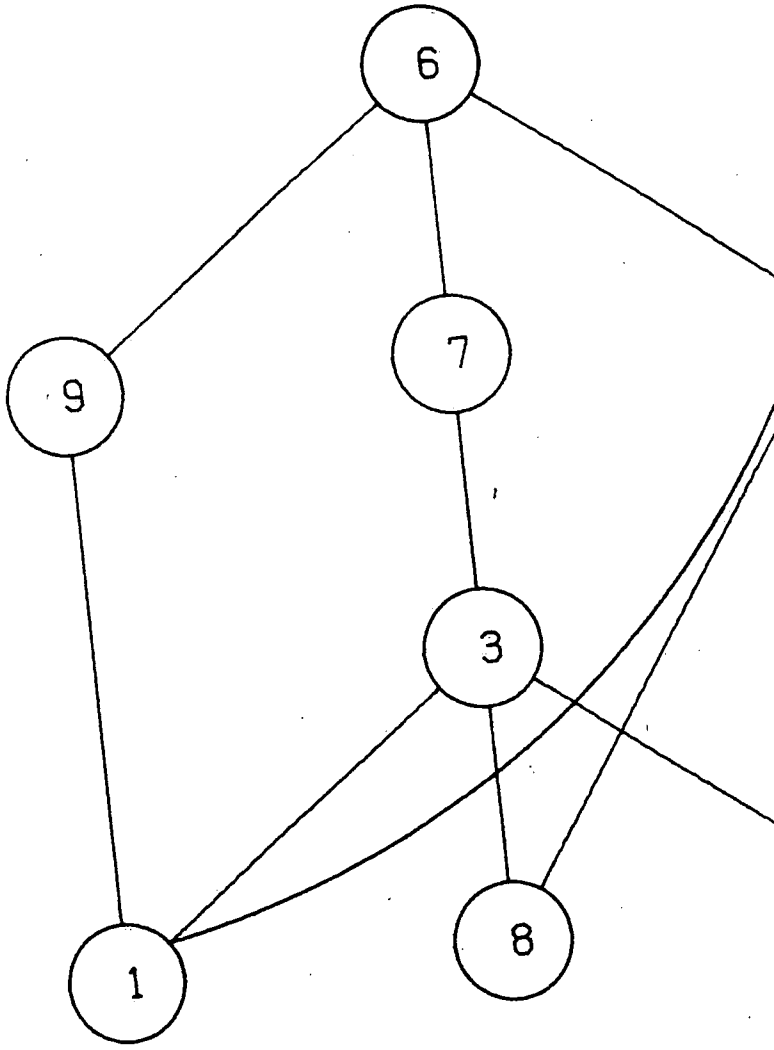
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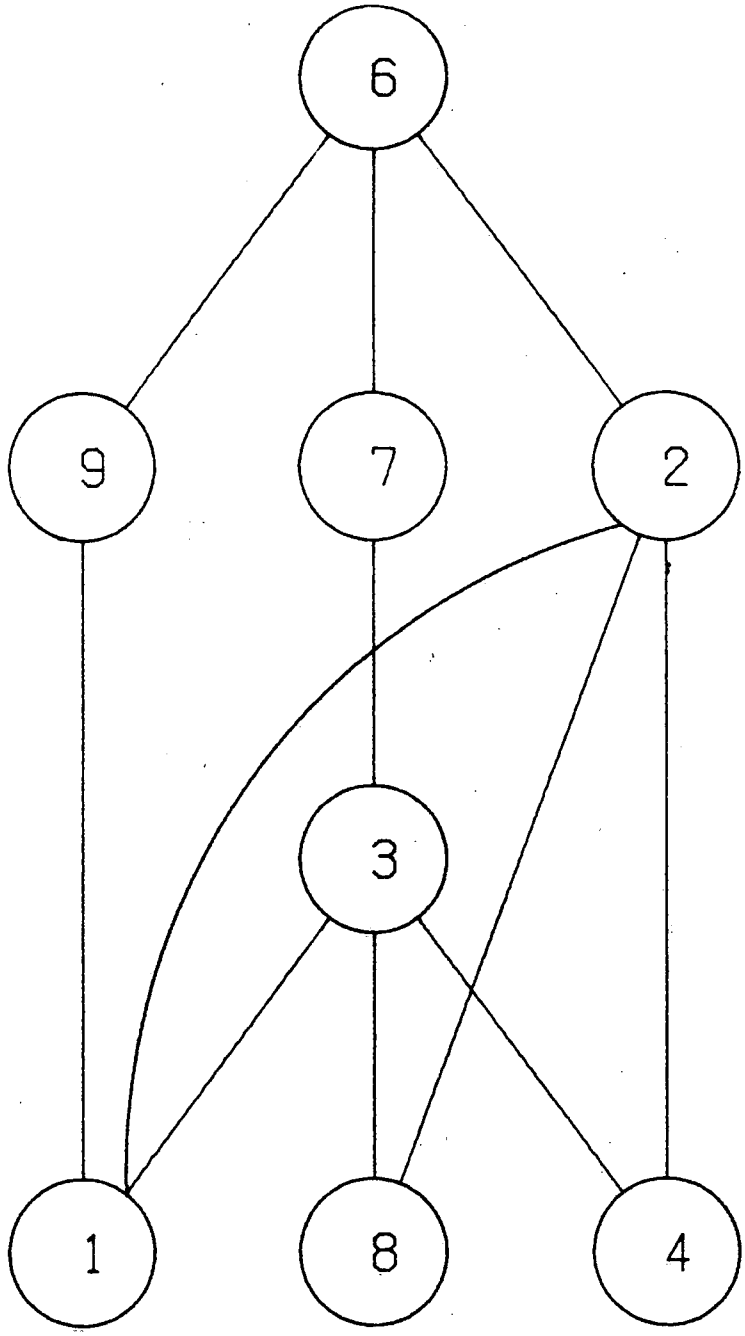
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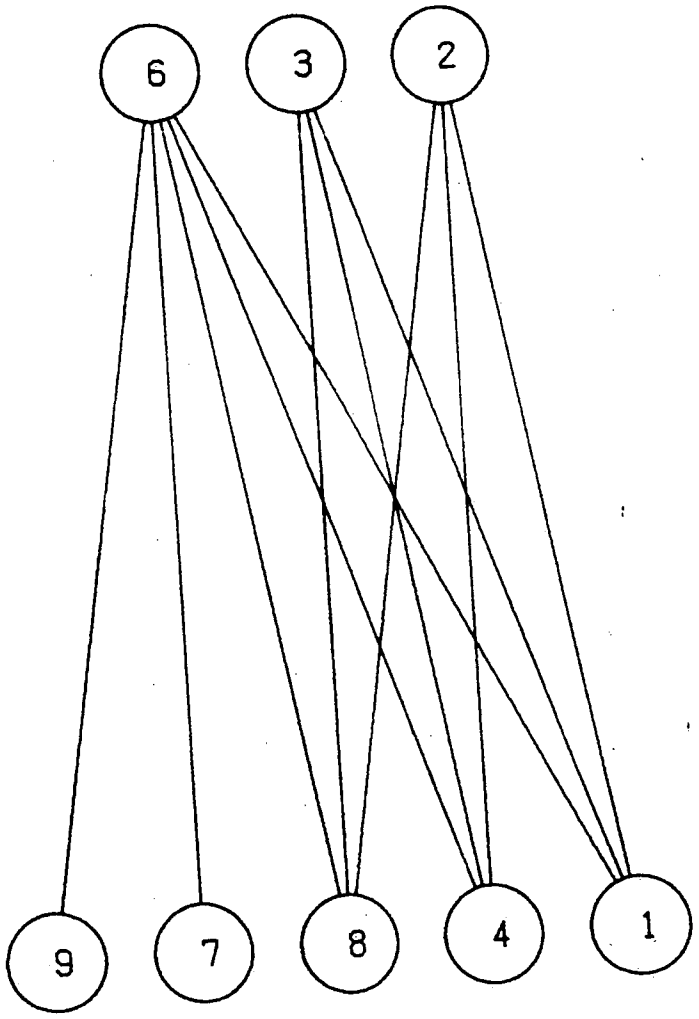
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Table 1: Vector distance components*: data from Freitag et al.

identification number	name of chemical	algae BF_1 (1)	fish BF_2 (2)	rat % retention (3)	act. sludge BF_S (4)	act. sludge % CO_2 (5)	% CO_2 (6)
1	toluene	380	94	0.1	19	0.3	119
6	benzoic acid	6	5.1	0.1	13	0.1	98
23	biphenyl	540	280	0.4	26	0.6	105
24	2,2'-dichlorobiphenyl	12690	2420	0.1	63	10.	286
28	2,4,6,2',4'-pentachlorobiphenyl	11500	2320	39.8	278	3.3	192
34	hexachlorobenzene	24800	2600	55.7	350	10.	667

*The first four columns are the relative bioaccumulation rates. The last two columns are the scaled inverse of the degradation rates. Inverse because higher values of degradation are preferable while high bioaccumulation is not. The ranking direction must be the same in absolute terms.

Table 2: Physico-chemical, toxicity and fate data of the chemicals spilled in the Rhine River by Sandoz.

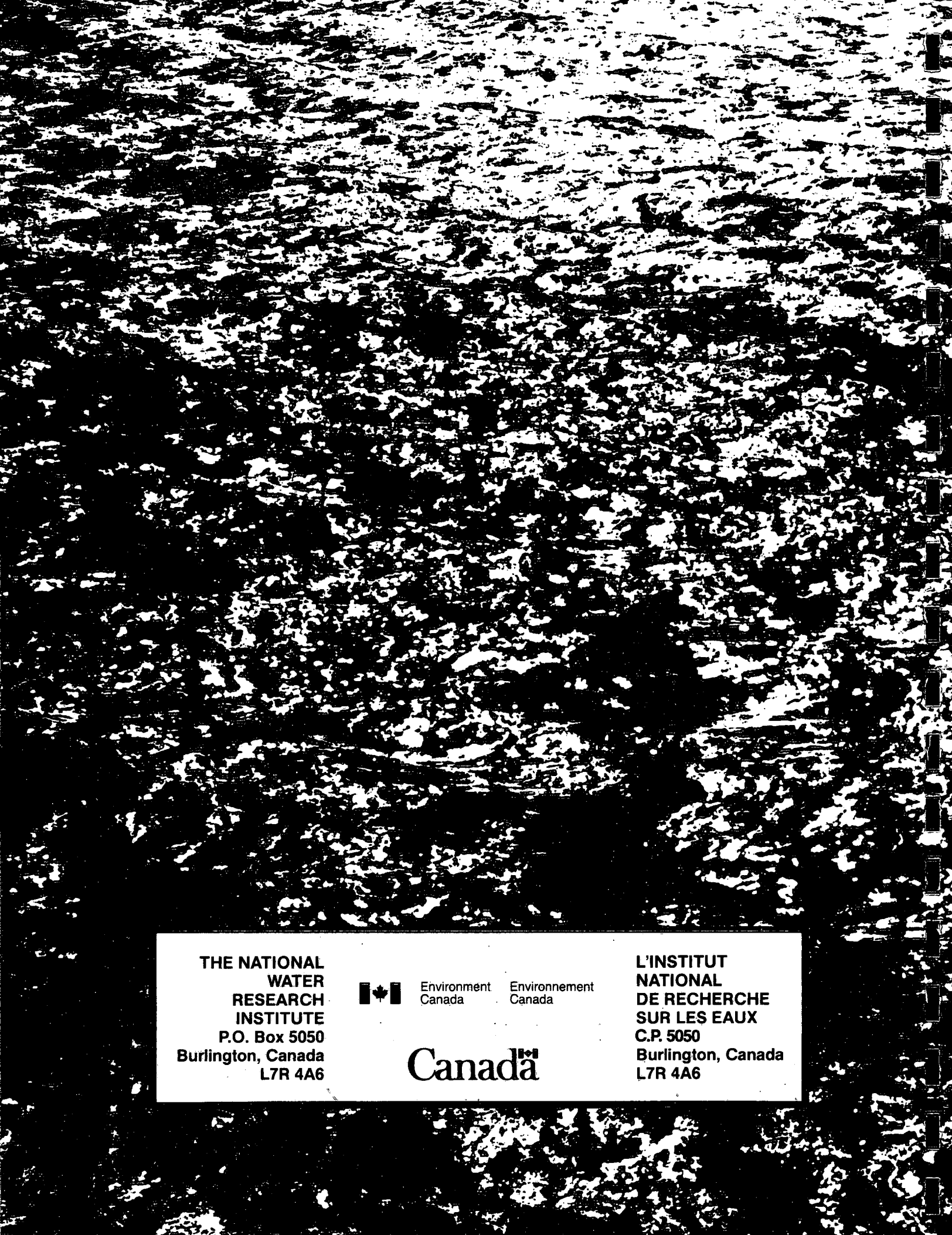
	Chemical	$\log_{10} k_{ow}$	LC_{carp} mg/l	%-accumulation	residence time (days)	volatilization (in classes)
		D1	D2	D3	D4	D5
1	Disulfoton	1.93	11.3	1.19	80.	1
2	Dinitro-orthocresol	2.86	3.5	9.26	774.	2
3	Propetamphos	2.90	6.4	10.30	2411.	2
4	Thiometon	.51	13.2	.05	32.	2
6	Parathion	3.81	3.0	47.32	411.	2
7	Etrimphos	3.20	5.5	16.50	23.	2
8	Metoxuron	2.50	81.0	4.10	34.	2
9	Fenitrothion	3.40	4.1	25.84	77.	1

Table 3: Standardized (within the range 0-1) physico-chemical, toxicity and fate data of the chemicals spilled in the Rhine River by Sandoz.

Chemical	$\log_{10}K_{ow}$	LC_{carp}	bioaccumulation	residence time	volatilization (in classes)
	D1	D2	D3	D4	D5
1 Disulfoton	.4523	.4479	.3887	.4479	.23
2 Dinitro-orthocresol	.5537	.6305	.5453	.6700	.59
3 Propetamphos	.5573	.5365	.5534	.7813	.59
4 Thiometon	.1091	.4237	.1468	.3582	.59
6 Parathion	.6277	.6545	.6698	.6083	.59
7 Etrimphos	.5827	.5601	.5894	.3259	.59
8 Metoxuron	.5190	.1410	.4831	.3642	.59
9 Fenitrothion	.5983	.6058	.6236	.4442	.23

Table 4: Ranking of the eight chemicals according to the standardized index (Eq. 3) using table shown in Table 2.

Chemical	index value given attributes					
	D3+D4	(rank)	D1+D2+D5	(rank)	all	(rank)
1 Disulfoton	.2652	(7)	.3027	(8)	.4024	(7)
2 Dinitro-orthocresol	.3863	(3)	.4587	(2)	.5998	(3)
3 Propetamphos	.4282	(1)	.4351	(4)	.6104	(2)
4 Thiometon	.1731	(8)	.3285	(7)	.3713	(8)
6 Parathion	.4046	(2)	.4838	(1)	.6307	(1)
7 Etrimphos	.3012	(5)	.4475	(3)	.5394	(4)
8 Metoxuron	.2706	(6)	.3570	(6)	.4480	(6)
9 Fenitrothion	.3424	(4)	.3944	(5)	.5223	(5)



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