THESE

présentée à l'université de Metz
pour l'obtention du Diplôme de Doctorat
Spécialité Toxicologie de l'Environnement

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OPTIMISATION ET VALIDATION DE CHEMFRANCE: UN MODELE REGIONAL DE FUGACITE NIVEAU III APPLIQUE A LA FRANCE

Soutenue le 31 Octobre 1996 devant la Commission d'Examen:

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-1996-

A Sandra

A mes parents

A mes frères et soeurs

Aux mineurs

Je remercie Monsieur J. Devillers de m'avoir accueilli dans son équipe et de m'avoir fourni un sujet de recherche aussi porteur et intéressant que celui-ci. Qu'il trouve ici l'expression de toute ma reconnaissance pour la compétence scientifique et le soutien quotidien qu'il a su m'apporter.

Je remercie Monsieur J.M. Jouany et Monsieur W. Karcher pour m'avoir fait l'honneur de juger cette thèse et de participer au jury. Je voudrais également exprimer ma reconnaissance à Monsieur W. Karcher pour avoir permis le financement par la Communauté Européenne de la plupart des études présentées dans cette thèse.

Je remercie Mademoiselle P. Vasseur de m'avoir permis d'intégrer cette formation doctorale et pour l'honneur qu'elle m'a fait de bien vouloir juger mon travail.

Enfin, je voudrais exprimer ma reconnaissance à toutes les personnes qui m'ont aidé à divers titres. Mes remerciement vont plus particulièrement:
- à mes collègues de laboratoire pour leur disponibilité et notamment à D. Domine pour son accueil chaleureux, son aide et ses produits régionaux,
- à tous les exilés du Nord et du Grand Nord pour leur amitié,
- aux "Bachelardiens" pour tous les moments de bonheur qu'ils m'ont procurés.

SOMMAIRE

Cette thèse est constituée des articles suivants:

1. INTRODUCTION

Le comportement d'une substance chimique dans l'environnement est complexe. Il met en jeu de nombreux phénomènes liés à ses propriétés physico-chimiques et aux caractéristiques des écosystèmes. Pour les produits que l'on souhaite introduire sur le marché ou ceux déjà présents, l'estimation de leur devenir dans l'environnement est primordiale. Le nombre considérable de composés chimiques employés dans nos activités rendant inconcevable la réalisation exclusive d'études *in situ*, on fait de plus en plus appel aux techniques de modélisation. La souplesse de ces approches permet de concevoir des modèles globaux (e.g., Mackay *et al.*, 1992) ou restreints à un phénomène particulier (e.g., PRZM (Carsel *et al.*, 1985)). Ces outils mathématiques sont utilisés pour comparer le comportement de plusieurs molécules, rechercher des informations avant la réalisation d'essais en laboratoire ou sur le terrain, ou encore identifier des compartiments ou des secteurs à risques. Cependant, l'emploi de modèles dans les analyses de risques exige une grande sûreté dans les résultats obtenus et une connaissance parfaite de leurs limites d'utilisation. Dans ces conditions, l'objet de notre travail a été d'optimiser et de valider CHEMFRANCE, un modèle régional de fugacité niveau III appliqué à la France (Chancrogne, 1991). Nous devions élaborer de nouvelles relations structure-bioconcentration et structure-adsorption possédant un large domaine d'application, mais également confirmer les fondements théoriques et empiriques de CHEMFRANCE en mettant en parallèle les observations faites en laboratoire ou sur le terrain et les résultats des simulations effectuées sur ordinateur.

2. ESTIMATION DE LA BIOCONCENTRATION ET DE L'ADSORPTION (Articles I et II)

Les modèles de distribution sont pour la plupart fondés sur la notion de répartition compartimentale nécessitant l'utilisation de coefficients de partage. Chacun d'eux, défini pour deux phases, gouverne la distribution à l'équilibre du composé et donc de sa concentration finale dans les différents compartiments de l'environnement. Ainsi, pour estimer le potentiel d'accumulation des molécules dans les sols, les sédiments et les matières en suspension, on utilise le coefficient d'adsorption (i.e., Kp). De même, le facteur de bioconcentration (i.e., BCF) permet d'évaluer l'accumulation des substances chimiques chez les êtres vivants par des voies non-alimentaires. La plupart des études sur la bioconcentration sont réalisées sur le poisson, compte tenu de son importance économique et de la disponibilité de tests standardisés. De ce fait, cet organisme est fréquemment utilisé pour représenter le compartiment biotique dans les modèles de distribution. Le Kp et le BCF peuvent être déterminés expérimentalement ou par des relations de type structure-activité (i.e., QSAR). Depuis le début des années 80, l'importance considérable de ces deux paramètres a engendré la publication d'une multitude d'équations (Lyman *et al.*, 1990; ECETOC, 1995; Güsten et Sabljic, 1995). En dépit de ce fait, des problèmes de modélisation restaient en suspens. La première partie de notre travail a donc consisté à établir de nouvelles équations possédant un domaine d'application plus étendu. Pour estimer la bioconcentration, les modèles régressifs linéaires entre les transformations logarithmiques des BCF et des coefficients de partage *n*-octanol/eau (i.e., log

P) sont couramment utilisés. Cependant, pour les substances très hydrophobes (log P > 6), ils ne sont plus applicables (Banerjee et Baughman, 1991). Cette cassure dans la relation linéaire entre une activité biologique et le caractère hydrophobe des molécules a été soulignée dans diverses études (Devillers et Lipnick, 1990; Hansch et Leo, 1995). En pharmacologie et en toxicologie, ce problème de linéarité a été résolu grâce à l'utilisation de modèles paraboliques et bilinéaires (Kubinyi, 1993; Hansch et Leo, 1995). **L'article I** présente l'aptitude de ces techniques non-linéaires à modéliser la bioconcentration chez le poisson. Dans un premier temps, une analyse bibliographique a été réalisée pour obtenir de nombreuses valeurs de BCF et de log P. Une banque de données contenant 154 molécules dont les valeurs de BCF suivaient des critères de sélection précis a été constituée. A partir de cet échantillon, trois équations (i.e., linéaire, parabolique, bilinéaire) reliant le BCF au log P ont été développées. L'analyse des paramètres statistiques et des résidus correspondant à ces relations a mis en évidence, le faible pouvoir prédictif du modèle linéaire dans notre étendue de log P (i.e., 1,12 à 8,60) et la supériorité du modèle bilinéaire face à l'équation parabolique. Un échantillon test constitué de 29 molécules a permis de confirmer ces conclusions et d'étendre la validité de la relation bilinéaire aux substances possédant une valeur de log P comprise entre 0,39 et 9,50.

Les problèmes de modélisation du coefficient d'adsorption sont différents. En effet, la trop grande spécificité et l'absence de paramètres prenant en compte le degré d'ionisation des acides et des bases correspondent aux principaux défauts des équations existantes. La finalité de l'étude décrite dans **l'article II** était donc de pallier ces problèmes en élaborant un modèle général

intégrant le caractère hydrophobe et le potentiel d'ionisation des substances (i.e., log P et pKa, respectivement) ainsi que le pH et le pourcentage de carbone organique (i.e., %OC) pour décrire le substrat. Ce modèle a été construit à partir de 229 valeurs de Kp correspondant à 53 composés et a été testé sur 500 Kp mesurés pour 87 molécules. Ces données ont été extraites d'articles originaux et non de compilations. Trois étapes ont été nécessaires pour obtenir une équation applicable aux composés ionisés et non-ionisés. Dans un premier temps, une relation intégrant le log P et le %OC a confirmé la nécessité d'introduire des facteurs correctifs intégrant le degré de dissociation des molécules. En effet, il est admis que pour les substances capables de former des ions (i.e., acides, bases) des phénomènes de répulsion ou d'affinité avec les colloïdes du substrat chargés négativement induisent, respectivement, une baisse du coefficient d'adsorption pour les substances présentant une charge négative et une augmentation pour celles chargées positivement (Bailey *et al.*, 1968; Jafvert, 1990). Pour prendre en compte ces phénomènes, le pKa des molécules et le pH de la solution des sols ou des sédiments ont été incorporés dans une seconde équation. Leur intégration a provoqué un net accroissement de la qualité des résidus pour les composés ionisés, tout en conservant un haut pouvoir prédictif pour les autres substances. Cependant, une analyse précise des résidus a mis en évidence une sous-estimation générale des valeurs de Kp pour les bases. Cette tendance s'explique par le fait que l'adsorption de ces molécules dépend de l'acidité de surface inférieure de deux unités de pH à celle de la solution. L'intégration de cette observation empirique dans notre équation a permis d'obtenir une distribution aléatoire des résidus pour les bases. La supériorité de cette

dernière équation a été confirmée par les simulations réalisées sur notre échantillon test, qui ont également permis d'étendre son domaine d'application à de nouvelles classes de substances chimiques et à des conditions pédologiques très variées.

3. CHEMFRANCE (Article III)

Les modèles de distribution peuvent être ponctuels ou globaux. Les premiers permettent d'obtenir, en fonction de leur degré de complexité, des résultats précis et une bonne compréhension des phénomènes étudiés. Cependant, la masse d'information nécessaire à leur emploi limite leur domaine d'application. A l'inverse, la finalité des modèles globaux est d'estimer le comportement des molécules dans un environnement représenté par plusieurs compartiments. Pour cela, un compromis entre la réduction des informations nécessaires à leur fonctionnement et la pertinence des résultats fournis doit être trouvé. Ces outils de simulation sont fondés, en quasi-totalité, sur le concept de fugacité (Mackay, 1991; Cowan *et al.*, 1995). Parmi eux, on distingue les modèles régionaux et les modèles d'évaluation employant un "monde unité" représentant un environnement hypothétique. Les premiers tentent de s'approcher le plus possible d'une situation réelle afin d'obtenir des informations comparables aux données expérimentales. Les seconds permettent uniquement de comparer les molécules entre elles ou d'identifier les principaux processus mis en jeu. **L'article III** présente CHEMFRANCE, un modèle régional de fugacité niveau III appliqué à la France. Le niveau III

signifie que le système est à l'état stable (i.e., flux d'entrée = flux de sortie) mais que des transferts entre les compartiments sont possibles (e.g., volatilisation, ruissellement, lessivage). CHEMFRANCE comprend six compartiments globaux (i.e., air, eaux de surface, sol, sédiments, eaux côtières, eaux souterraines). Les quatre premiers sont constitués de sous-compartiments (e.g., poissons, matières en suspension). CHEMFRANCE permet de simuler, pour les quatre saisons, le comportement des molécules en France et dans 12 régions françaises définies en fonction de leurs caractéristiques pédologiques, climatiques et hydrologiques. Les paramètres environnementaux (e.g., pH du sol, volume des eaux de surface) indispensables au fonctionnement de CHEMFRANCE ont été déterminés pour chacune de ces régions. Ainsi, l'utilisateur doit fournir simplement les propriétés physico-chimiques et les quantités d'émissions de la molécule à analyser pour obtenir la concentration, la quantité absolue, les cinétiques d'élimination et d'échange pour chaque compartiment...

4. "VALIDATION" DE CHEMFRANCE (Articles IV à VI)

Afin d'obtenir un outil de simulation efficace et fiable, tout logiciel doit être vérifié et testé (Devillers *et al.*, 1992, 1995; Fredenslund *et al.*, 1995; Vincent *et al.*, 1996). Pour les modèles de distribution, la validation des informations produites présente le niveau de difficulté le plus élevé. La complexité de cette procédure est due à la rareté mais surtout à la variabilité spatiale et temporelle des données expérimentales utilisées comme éléments de

comparaison. Dans ces conditions, la validité d'un modèle ne pourra jamais être pleinement affirmée. On pourra simplement confirmer la pertinence des résultats obtenus en démontrant les concordances entre observations et prédictions. Dans ce contexte, le pouvoir de simulation de CHEMFRANCE a été évalué sur le lindane (**Article IV**) et l'atrazine (**Articles V et VI**). Du fait de l'utilisation massive de ces pesticides, de multiples études ont été entreprises afin de connaître avec précision tous les aspects de leur comportement dans l'environnement. Une synthèse de ces informations nous a permis d'établir un profil environnemental assez précis de ces molécules. Une fois cette base de travail établie, les données indispensables au fonctionnement du programme (i.e., propriétés physico-chimiques, tonnages émis) ont été déterminées le plus précisément possible pour faciliter la comparaison entre les valeurs expérimentales et celles calculées par CHEMFRANCE. Quatre scénarios intégrant les méthodes d'application de ces substances actives et leurs déversements dans les eaux de surface ont été simulés. Cette approche possède deux intérêts. D'une part, elle permet d'identifier les risques de contamination et les principaux processus mis en jeu en fonction des compartiments d'émission et d'autre part, d'obtenir une variabilité dans les résultats. De fortes similitudes entre les résultats extraits de ces simulations et ceux obtenus en laboratoire ou sur le terrain ont été observées. Ainsi, le lindane est présent principalement dans les sols, les sédiments et les éléments biotiques du fait de ses capacités d'adsorption et de bioconcentration. A l'inverse, l'atrazine se retrouve principalement dans les milieux aquatiques bien que la contamination atmosphérique ne puisse pas être écartée. Cette molécule est faiblement adsorbée par les sols induisant par conséquent un fort

potentiel de ruissellement et de lessivage. Enfin, elle est très peu bioaccumulée. Une analyse sensitive portant sur le temps de demi-vie de l'atrazine dans les sols est présentée dans **l'article VI**. Cette étude montre que la concentration dans les sols et les eaux souterraines et les processus de volatilisation au niveau du sol, de ruissellement et de lessivage sont les paramètres les plus sensibles aux variations de la vitesse de dégradation de l'atrazine dans les sols.

5. ETUDE COMPARATIVE DES EQUATIONS ESTIMANT LA BIOCONCENTRATION (Article VII)

Les modèles de type QSAR peuvent s'avérer des outils précieux pour évaluer les risques écotoxicologiques s'ils sont performants et surtout utilisés à bon escient. Il est donc indispensable de connaître précisément leurs limites d'utilisation. Dans ce contexte, nous avons entrepris de comparer différents modèles permettant d'estimer la bioconcentration des molécules organiques. Tous les modèles testés utilisaient le log P comme descripteur moléculaire.
La sélection des équations a été motivée par une étude d'occurrences effectuée à partir de rapports élaborés pour des organisations officielles (e.g., OCDE, EPA, UE). L'intégration de ces équations dans les modèles de distribution a également influencé notre choix. La réalisation de nos études comparatives soulevait un certain nombre de problèmes méthodologiques. En effet, les données expérimentales sur la bioconcentration des molécules sont relativement peu nombreuses et ont donc largement été utilisées pour élaborer

les équations à comparer. Or, lorsque l'on veut estimer le pouvoir prédictif d'un modèle de type QSAR, il est indispensable d'utiliser un échantillon test constitué de molécules n'appartenant pas à l'échantillon d'apprentissage. La solution optimale aurait été de mesurer des valeurs de BCF pour de nouvelles substances. Dans le cadre de notre travail, pour des raisons de temps et de coût, une telle alternative ne pouvait être envisagée. Nous n'avons donc pas cherché à sélectionner une seule valeur par composé mais plutôt, dans la mesure du possible, à retenir un ensemble de résultats expérimentaux cohérents permettant de fournir un profil de bioconcentration pour une molécule donnée. Une étude bibliographique visant à récolter un grand nombre de valeurs expérimentales a été réalisée à partir de publications originales et non de compilations afin d'obtenir des informations sur les conditions expérimentales. **L'article VII** présente une étude comparative réalisée sur sept équations linéaires ou non-linéaires permettant d'estimer le BCF à partir du log P (Veith *et al.*, 1979, 1980; Mackay, 1982; Connell et Hawker, 1988; Isnard et Lambert, 1988; Nendza, 1991; Bintein *et al.*, 1993). Cette analyse a été effectuée à partir d'une banque de données constituée de 342 valeurs de BCF provenant d'essais dynamiques et 94 déterminées par essais statiques ou semi-statiques. Pour des valeurs de log P inférieures à 6, les différents modèles testés donnent des résultats équivalents. Par contre, pour les substances très hydrophobes (i.e., log P > 6), les relations linéaires ne sont plus applicables et sont nettement devancées par les équations non-linéaires. Parmi celles-ci, notre équation possède le meilleur pouvoir prédictif et le plus large domaine d'application.

6. CONCLUSION

En élaborant de nouvelles relations structure-bioconcentration et structure-adsorption nous avons accru le domaine d'application et le pouvoir de simulation de CHEMFRANCE. Les études réalisées sur le lindane et l'atrazine ont démontré le haut potentiel de simulation de CHEMFRANCE et ont permis d'effectuer une synthèse du comportement dans l'environnement de ces pesticides. Cependant, nous envisageons de poursuivre ce processus de validation avec d'autres molécules aux propriétés physico-chimiques variées pour définir d'une façon plus précise les limites d'utilisation de ce logiciel. Nous prévoyons également d'intégrer dans CHEMFRANCE la méthode SIRIS (Vaillant *et al.*, 1995) ainsi que des informations écotoxicologiques afin de mieux appréhender les risques (éco)toxicologiques et de créer un outil d'aide à la décision plus facile à utiliser.

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ARTICLE I

SAR and QSAR in Environmental Research, Vol. 1, pp. 29–39
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NONLINEAR DEPENDENCE OF FISH BIOCONCENTRATION ON *n*-OCTANOL/WATER PARTITION COEFFICIENT

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(accepted July 28, 1992)

The log-log relationship between the bioconcentration tendency of organic chemicals in fish and the *n* -octanol/water partition coefficients breaks down for very hydrophobic compounds. The use of parabolic and bilinear models allows this problem to be overcome. The QSAR equation log BCF = 0.910 log P − 1.975 log (6.8 10^{-7} P + 1) − 0.786 (n = 154; r = 0.950; s = 0.347; F = 463.51) was found to be a good predictor of bioconcentration in fish.

KEY WORDS: Bioconcentration; BCF; fish; bilinear model; linear model; parabolic model.

INTRODUCTION

Bioconcentration is the process of accumulation of chemicals by organisms through nondietary routes.[1] In aquatic ecosystems, the bioconcentration factor (BCF) of an organic chemical is defined as the ratio of its concentration in a target organism to that in water at steady state.[2] Typically, fish are the target organisms of BCF assessments due to their importance as a human food source and the availability of standardized testing protocols.[1] The most common method for estimating chemicals' BCFs consists of establishing correlations between BCFs and hydrophobicity of the chemicals. The majority of these are obtained from linear regression models between the log transformations of the BCF values and the *n*-octanol/water partition coefficients (log P) of the chemicals.[3–6] The regression equations have the following general form:

$$\log \text{BCF} = a \log P + b \tag{1}$$

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where a and b are constants. In most published BCF equations, the slope (a) is <1 and the intercept (b) is negative.[6] Equation 1 breaks down for strongly hydrophobic chemicals (log $P > 6$).[7] The break in the linear relationship between a biological activity (BA) and the hydrophobic character of the organic molecules has been stressed by different authors in numerous QSAR studies.[8] Hansch initiated the use of a simple parabolic model[8] in log P (Eq. 2) to overcome this problem.

$$\log \mathrm{BA} = a \log P + b (\log P)^2 + c \tag{2}$$

Kubinyi[9–12] subsequently proposed a better model (Eq. 3) that adequately accounted for the fact that the biological activity and partition coefficient initially vary in a linear fashion on a log–log scale, reaching an optimum value, followed by a second decreasing linear portion.

$$\log \mathrm{BA} = a \log P - b \log (\beta P + 1) + c \tag{3}$$

This bilinear model (Eq. 3) has been successfully used in many drug design and environmental QSAR studies.[13–18]

The aim of this paper is to compare the performance of the parabolic and bilinear models to overcome the "cut-off" problem encountered in the estimation of BCF values from the n-octanol/water partition coefficient (log P).

MATERIALS AND METHODS

Data selection

BCF values for 154 chemicals (Figure 1) were obtained from an extensive compilation.[19] Data were selected according to the following criteria:

1) Only experimental data, measured in whole fish (wet weight), and obtained under flow-through conditions, were used.

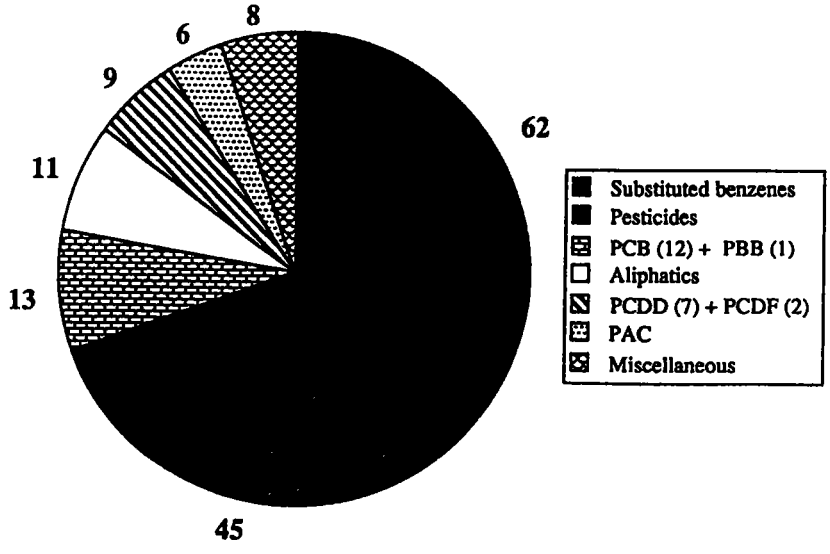

Figure 1 Data set constitution. (PCB = polychlorobiphenyls; PBB = polybromobiphenyls; PCDD = polychlorodibenzo-*p*-dioxins; PCDF = polychlorodibenzofurans; PAC = polyaromatic compounds).

2) Data were included only if a steady state was reached or when BCF values were obtained from the kinetic method.

3) BCF data were rejected if contamination by food and/or presence of adsorbents (e.g., suspended sediments) was suspected.

4) Only studies using freshwater fish were considered. Five families were represented in the selected data:

— Salmonidae: rainbow trout, whitefish,

— Cyprinidae: fathead minnow, goldfish, carps (from different geographical origins), zebrafish, bleak, and topmouth gudgeon

— Centrarchidae: bluegill sunfish,

— Poeciliidae: guppy,

— Cyprinodontidae: American flagfish and killifish.

Fish species distribution in the study is summarized in Figure 2. The log P values were retrieved from an extensive bibliographical review aimed at preferentially selecting data obtained by direct methods (e.g., shake-flask, generator column).

Model development

Description and calculation procedures for the bilinear model can be found in numerous comprehensive papers.[9–12] Briefly, the bilinear model is derived from the McFarland multicompartmental model which allows the estimation of the probability p of a molecule crossing aqueous-lipid interfaces and reaching its receptor site. Thus, if we consider a hypothetical biological system made up of alternating aqueous phases A and lipid (membrane) phases L (Figure 3), the probability of a

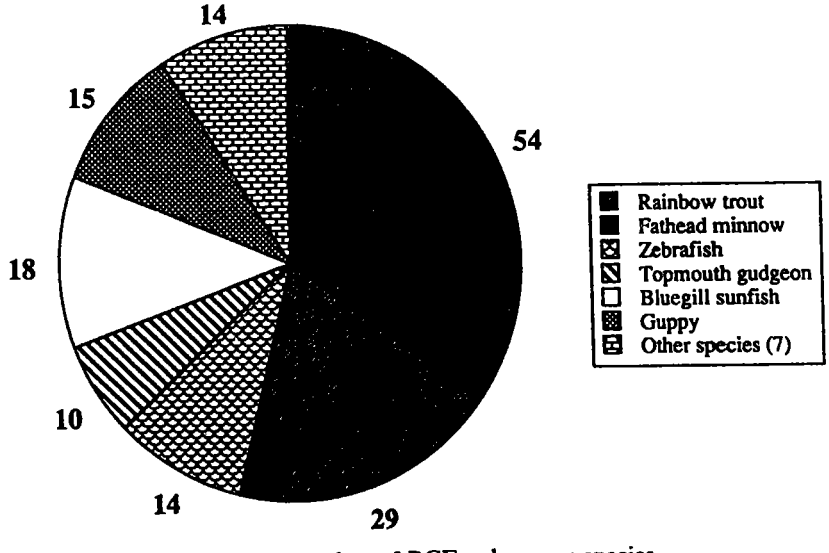

Figure 2 Number of BCF values per species.

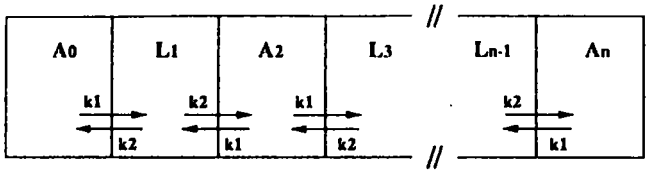

Figure 3 The McFarland hypothetical biological system (k_1 and k_2 are the rate constants of the distribution process).

molecule leaving A_0 and entering into L_1 is:

$$p_{0,1} = \frac{k_1}{k_1 + k_2} \tag{4}$$

In the same way, the probability that a molecule goes from L_1 to A_2 is:

$$p_{1,2} = \frac{k_2}{k_1 + k_2} \tag{5}$$

If both parts of the fractions in Eqs. 4 and 5 are divided by k_2 and if k_1/k_2 is replaced by P (the partition coefficient), we obtain:

$$p_{0,1} = \frac{P}{P + 1} \tag{6}$$

$$p_{1,2} = \frac{1}{P + 1} \tag{7}$$

Therefore, the probability that a molecule goes from A_0 to A_2 and more generally from A_0 to A_n is given by Eqs. 8 and 9 respectively.

$$p_{0,2} = p_{0,1} \times p_{1,2} = \frac{P}{(P + 1)^2} \tag{8}$$

$$p_{0,n} = p_{0,1} \times p_{1,2} \times \cdots \times p_{n-1,n} = \frac{P^{n/2}}{(P + 1)^n} \tag{9}$$

If we consider first that the biological activity (BA) of a molecule is a function of its intrinsic activity and of its probability of reaching the receptor site, and second that the intrinsic activities of homologous series of chemicals are identical, we can write:

$$\mathrm{BA} = \frac{\text{constant} \times P^n}{(P + 1)^{2n}} \tag{10}$$

The logarithmic transformation of Eq. 10 leads to Eq. 11.

$$\log \mathrm{BA} = n \log P - 2n \log (P + 1) + c \tag{11}$$

Symmetrical curves with linear ascending and descending sides and a parabolic part within the range of optimum lipophilicity result from Eq. 11.

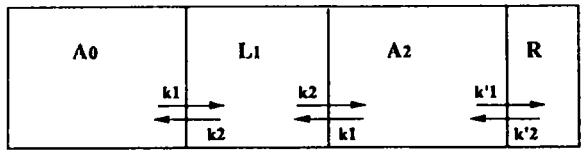

Figure 4 Hypothetical biological system for the bilinear model (k_1 and k_2 are the rate constants of the distribution process).

The bilinear model is derived from the McFarland model (Eq. 11) by taking into account the different volumes of the aqueous and organic phases in a biological system comprising four phases (Figure 4). The general equation of the bilinear model (Eq. 3) applied to BCF and log P is:

$$\log \text{BCF} = a \log P - b \log (\beta P + 1) + c \tag{12}$$

where β is the ratio volume between the lipid and the aqueous phases. For small P values, $(\beta P + 1)$ is approximately equal to one, therefore $\log (\beta P + 1)$ equals zero. For large P values $(\beta P + 1)$ is nearly equal to βP, therefore $\log (\beta P + 1)$ is proportional to log P.

The parameters a, b and c are linear terms, which can be calculated by linear multiple regression analysis, β is a nonlinear parameter, which is generally estimated by a Taylor series iteration method.[20]

Calculations were performed as described by Kubinyi and Kehrhahn,[10] from software written in Turbo basic and running on an IBM PC compatible.

RESULTS AND DISCUSSION

Figure 5 depicts the ability of the linear (Eq. 13), parabolic (Eq. 14) and bilinear (Eq. 15) models to describe the set of 154 BCF values from log P.

$$\log \text{BCF} = 0.516 \log P + 0.576 \tag{13}$$

$$n = 154; \quad r = 0.772; \quad s = 0.702; \quad F = 224.32$$

$$\log \text{BCF} = -0.164 (\log P)^2 + 2.059 \log P - 2.592 \tag{14}$$

$$n = 154; \quad r = 0.914; \quad s = 0.450; \quad F = 382.09$$

$$\log \text{BCF} = 0.910 \log P - 1.975 \log (6.8\ 10^{-7} P + 1) - 0.786 \tag{15}$$

$$n = 154; \quad r = 0.950; \quad s = 0.347; \quad F = 463.51$$

From the above and from Figure 5, it is obvious that Eq. 15 is the best regression model and that the linear solution given by Eq. 13 is not valid in our range of log P values (i.e. 1.12–8.60). This is confirmed by inspection of the statistical parameters of Eq. 13 and the graphical analysis of the residuals in Figures 6 and 7. Furthermore, we can note the unsatisfactory behaviour of the residuals in Figure 6 which are displayed according to a "parabolic band". This confirms the possibility of using a

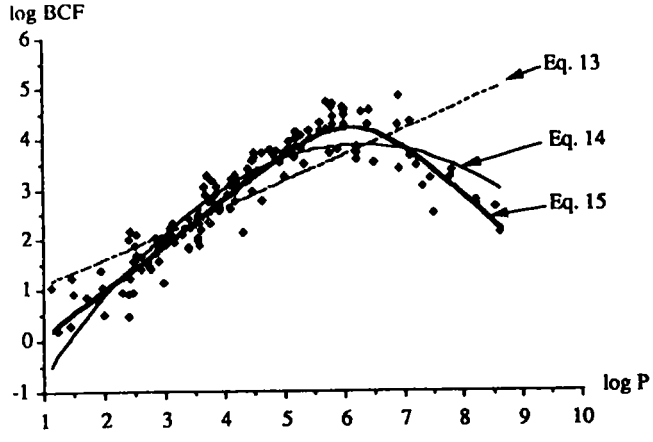

Figure 5 Relationships between log BCF and log *P*.

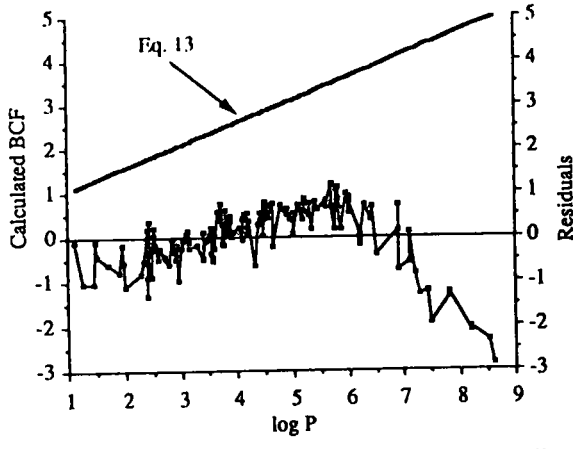

Figure 6 Distribution of the residual values obtained with the linear model (Eq. 13).

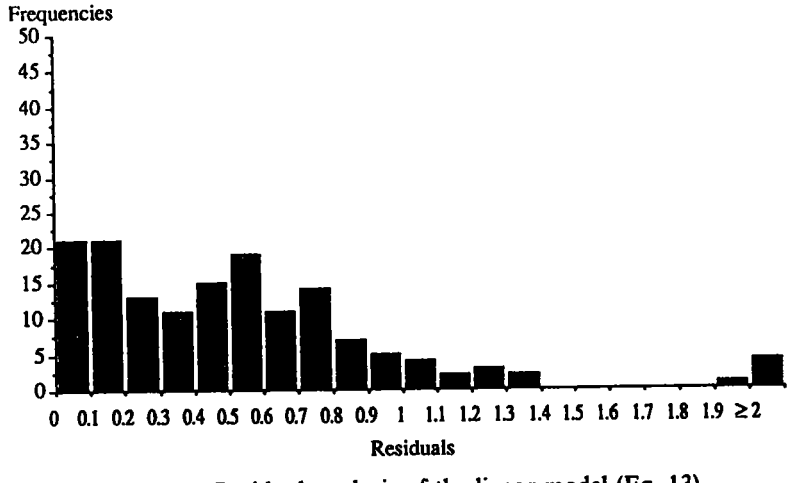

Figure 7 Residual analysis of the linear model (Eq. 13).

quadratic term in the BCF model in order to increase its statistical qualities and predictive power.[20] Thus, introduction of $(\log P)^2$ in the model (Eq. 14) leads to a better distribution of the residuals (Figures 8 and 9). In the same way, the high quality of the bilinear model (Eq. 15) is confirmed by analysis of the residuals (Figures 10 and 11) which reveals that no chemicals can be considered as outliers. To estimate the predictive power of the bilinear model (Eq. 15) a testing set of 29 chemicals has been constituted (Table I). In Table I, experimental BCF values were obtained under flow-through or static conditions and generally did not satisfy all the other constraints defined for the selection of the training set. Comparison of the expected BCF values obtained from the different models (i.e., Eq. 13 to 15) shows that the bilinear model (Eq. 15) is the most suitable to describe the BCF behaviour of the chemicals listed in Table I.

While it is recognised that the bioconcentration of organic chemicals in fish is a complex phenomenon involving numerous biotic and abiotic factors, our results underline the ability of the bilinear model of Kubinyi[9–12] to simulate this process in

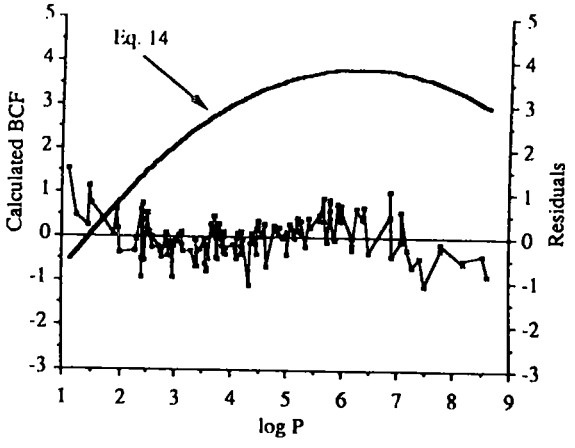

Figure 8 Distribution of the residual values obtained with the parabolic model (Eq. 14).

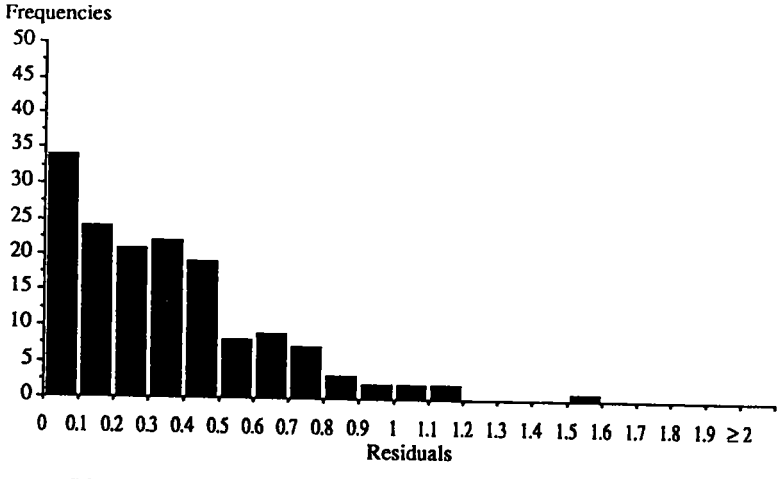

Figure 9 Residual analysis of the parabolic model (Eq. 14).

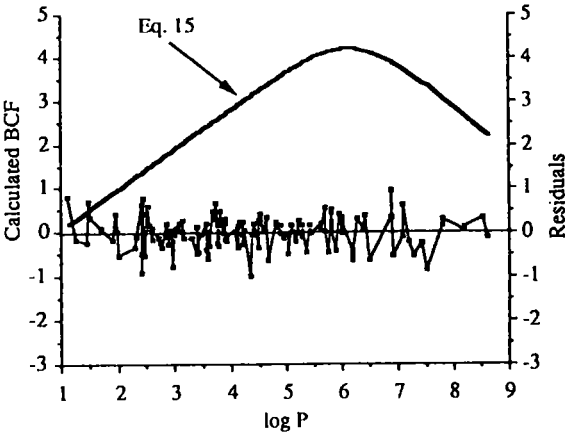

Figure 10 Distribution of the residual values obtained with the bilinear model (Eq. 15).

a rather simplistic way. If only a few data points are available or if the log P values are not too high, the linear models[3–6] are the most suitable to describe the bioconcentration in fish due to their simplicity. However, if enough data points are present and if the log P values vary over a wide range, the parabolic model and preferentially the bilinear model are more relevant. Thus, it is interesting to note that if we consider the range of log P values in our training and testing sets, the bilinear model (Eq. 15) allows the prediction of the bioconcentration factor of organic chemicals having log P values between 0.39 and 9.50.

Chemicals which are released to the environment as the result of a variety of human-related activities migrate through the ecosystems according to their physicochemical properties (e.g., vapour pressure, hydrosolubility). Numerous models varying in complexity are available to evaluate such behaviour.[32] Among them, the fugacity models of Mackay[33] provide a convenient and accurate simulation tool for exposure and risk analysis. In the classical fugacity models,[33] the bioconcentration

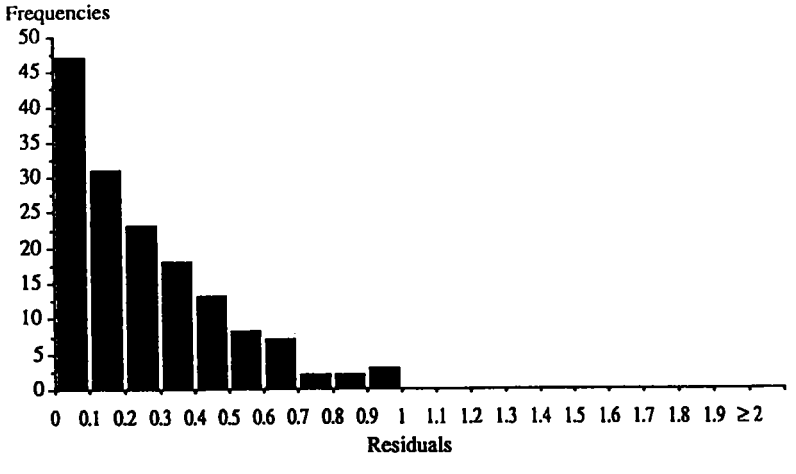

Figure 11 Residual analysis of the bilinear model (Eq. 15).

Table I Comparison between experimental and calculated BCF values for 29 chemicals.

No.	*Chemical*	*log P*	*log BCF_{exp} (ref)*	*Calculated log BCF*		
				Eq. 13	*Eq. 14*	*Eq. 15*
1	2-(*t*-Butoxy) ethanol	0.39[a]	−0.22 (21)	0.78	−1.81	−0.43
2	*t*-Butyl isopropyl ether	2.14[a]	0.76 (21)	1.68	1.06	1.16
3	Octachloronaphthalene	8.40[b]	2.52 (22)	4.91	3.13	2.44
4	Pigment, monoazo[c]	9.50	0.70 (23)	5.48	2.17	1.28
5	Pigment, monoazo[c]	9.30	0.50 (23)	5.37	2.37	1.49
6	Aniline	0.90	0.41 (24)	1.04	−0.87	0.03
7	*t*-Butylphenyldiphenyl phosphate	5.12	3.04 (25)	3.22	3.65	3.80
8	2-Chloroaniline	1.90	1.18 (24)	1.56	0.73	0.94
9	3-Chloroaniline	1.88	1.06 (24)	1.55	0.70	0.92
10	4-Chloroaniline	1.83	0.91 (24)	1.52	0.63	0.88
11	2-Chloronaphthalene	4.19	3.63 (26)	2.74	3.16	3.02
12	2,4-Dichloroaniline	2.79	1.98 (24)	2.02	1.88	1.75
13	3,4-Dichloroaniline	2.79	1.48 (24)	2.02	1.88	1.75
14	1,4-Dichloronaphthalene	4.88	3.36 (26)	3.09	3.55	3.61
15	1,8-Dichloronaphthalene	4.41	3.79 (26)	2.85	3.30	3.21
16	2,3-Dichloronaphthalene	4.71	4.04 (26)	3.01	3.47	3.47
17	2,7-Dichloronaphthalene	4.81	4.04 (26)	3.06	3.52	3.55
18	2-Nitroaniline	1.78	0.91 (24)	1.49	0.55	0.83
19	3-Nitroaniline	1.31	0.92 (24)	1.25	−0.18	0.41
20	4-Nitroaniline	1.31	0.64 (24)	1.25	−0.18	0.41
21	2,3,7,8-TCDD	6.42[d]	3.90 (27)	3.89	3.87	4.18
22	3,3',4,4'-Tetrachlorobiphenyl	5.82	4.59 (28)	3.58	3.84	4.19
23	3,3',4,4'-Tetrachlorodiphenyl ether	5.78	4.51 (28)	3.56	3.83	4.18
24	2,4,5-Trichlorobiphenyl	5.51	4.26 (28)	3.42	3.77	4.06
25	2,4,5-Trichlorodiphenyl ether	5.44	4.18 (28)	3.38	3.76	4.02
26	3,4,5-Trichloroveratrole	4.60	3.50 (29)	2.95	3.41	3.38
27	Tetrachloroveratrole	5.80	4.40 (29)	3.57	3.83	4.19
28	1,3,7-Trichloronaphthalene	5.59	4.43 (26)	3.46	3.79	4.10
29	Triphenyl phosphate	3.90[e]	2.76 (25)	2.59	2.94	2.76

[a] mean of two values.
[b] Ref. 26.
[c] Chemicals no. 45 and 46 in Anliker *et al.*,[23] (Table I [part B] p. 267).
[d] Ref. 30.
[e] Ref. 31.

in the biota (i.e., fish) is estimated from a simple linear regression equation (Eq. 1). This induces erroneous estimations for highly lipophilic chemicals. To overcome this problem, we propose to introduce in the fugacity models our bilinear model (Eq. 15) in order to stretch their domain of application.

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ARTICLE II

Pergamon

Chemosphere, Vol. 28, No. 6, pp. 1171-1188, 1994

0045-6535/94 $6.00+0.00

0045-6535(94)E0050-4

QSAR FOR ORGANIC CHEMICAL SORPTION IN SOILS AND SEDIMENTS

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(Received in Germany 30 November 1993; accepted 18 January 1994)

ABSTRACT

Sorption phenomena exert important influences on the environmental fate of anthropogenic organic substances. Under these conditions, the aim of this study was to propose a general QSAR model using the physicochemical properties of the molecules (i.e. log K_{ow} and pKa) and some relevant properties of soils or sediments (i.e. pH and %OC) to estimate the sorption behavior of both ionized and non-ionized chemicals. The proposed model was elaborated from 229 K_p values recorded for 53 chemicals. The model was then tested on 500 other K_p values obtained for 87 chemicals.

INTRODUCTION

The fate of the organic chemicals introduced into the environment depends on a variety of physicochemical and biological processes.[1-2] Mathematical models which attempt to integrate these phenomena are widely used to predict the environmental transport and distribution of the organic pollutants between the different compartments of the biosphere.[3-7] Use of these models requires a variety of abiotic and biotic parameters as inputs. Among them, the soil or sediment sorption coefficient of chemicals (K_p) is one of the key input parameters in models used to estimate the environmental mobility and fate of the pollutants.[8] Because its experimental determination is time-consuming and expensive, estimated values based on QSAR (Quantitative Structure-Activity Relationship) equations are now widely used.
The distribution of organic chemicals between soils or sediments and water can be quantified

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through the use of the Freundlich isotherm:

$$S = K_p * C^N \qquad (1)$$

where S is the sorbed concentration, C is the solution concentration, and K_p and N (traditionally expressed as 1/n) are empirical constants. The values of N commonly range between 0.7 and 1.2.[9]

The influence of the organic matter from soils and sediments on the sorption behavior of the organic chemicals has been discussed in many studies.[10-12] Consequently, the sorption partition coefficient K_p is generally related to the fraction of organic carbon (f_{oc}) associated with the sorbent to yield an organic-carbon-partition coefficient, K_{oc},

$$K_{oc} = (K_p * 100)/\%OC \qquad (2)$$

Sometimes, sorption coefficients are normalized to the organic matter content instead of the organic carbon content. This yields an organic-matter-partition coefficient, K_{om},

$$K_{om} = (K_p * 100)/\%OM \qquad (3)$$

Several regression equations, developed with physicochemical properties such as the *n*-octanol/water partition coefficient (K_{ow}) or aqueous solubility have been used to estimate K_{oc} or K_{om}.[13-18] Topological descriptors (e.g. molecular connectivity indices) have also been used to predict K_{oc} or K_{om}.[1, 19-23] However, many of these correlations were developed for specific classes of compounds (e.g. PAH[13]) and are not applicable to particular chemicals such as acids and bases. Furthermore, some of these models fail by using in the same data set K_{om} and K_{oc} values without correction factors. Indeed, the relationship $K_{oc} = 1.724 * K_{om}$ must be used to convert K_{om} to K_{oc}.[1, 15, 23] Last, in ecotoxicology modeling, it is obvious that K_p is more interesting to model than K_{om} or K_{oc}. Under these conditions, the aim of this study was to present a K_p equation easily incorporable in the main environmental fate models and allowing the prediction of the sorption behavior of structurally diverse chemicals in various sediments and soils.

MODEL DEVELOPMENT

K_p values for 53 organic chemicals including aliphatics, aromatics, pesticides, PCB, PAH, and related compounds (Table 1) were retrieved from the literature.[9, 13, 16, 24-34] They were selected according to the following criteria:

- only experimental results obtained from Freundlich isotherms with $N = 1$ were selected in order to standardize the units,[35]
- K_p data recorded in soils or sediments having a $\%OC < 0.1$ were rejected since for organic-poor sorbents, the interactions of the chemicals with the inorganic matrix of sorbent may become important,[8, 28, 36, 37]
- values corresponding to suspended sediments were rejected.

When necessary, the relationship $\%OC = \%OM/1.724$ was used to convert %OM to %OC. The log K_{ow} and pKa values (Table 1) were obtained from the literature.[13, 16, 24, 26-30, 32, 38-49] Experimental values or data obtained from critical compilations were preferentially selected.

Table 1: Training set.

Chemical	n#	log K_{ow}	pKa	%OC	pH
Acetophenone	12(24*)	1.59(24)		0.15-2.38**	
Acridine	12(25)	3.40(38)	5.68(39)	0.48-2.38	4.54-7.83**
Acrylonitrile	2(26)	0.12(26)		0.66-1.49	
2-Aminoanthracene	13(27)	4.13(27)	4.10(38)	0.15-2.38	4.54-8.32
6-Aminochrysene	13(27)	4.98(27)	3.70(38)	0.15-2.38	4.54-8.32
Anisole	1(16)	2.11(16)		1.10	
Anthracene-9-carboxylic acid	12(27)	4.30(38)	3.65(38)	0.15-2.38	4.54-8.32
Benzamide	1(9)	0.64(38)		1.25	
Benzene	2(26)	2.13(16)		0.66-1.49	
	1(16)	2.13(16)		1.10	
n-Butylbenzene	1(28)	4.13(28)		0.15	
Carbon tetrachloride	2(26)	2.64(26)		0.66-1.49	
Chlorobenzene	2(26)	2.84(16)		0.66-1.49	
	1(16)	2.84(16)		1.10	
	1(28)	2.84(16)		0.15	
2-Chlorobiphenyl	1(16)	4.51(16)		1.10	
Chloroform	2(26)	1.97(26)		0.66-1.49	
3-Chlorophenol	1(29)	2.50(29)	8.85(40)	2.80	8.00
1,2:5,6-Dibenzanthracene	14(30)	6.50(30)		0.11-2.38	
1,2-Dichlorobenzene	2(26)	3.38(16)		0.66-1.49	
	1(16)	3.38(16)		1.10	
	1(31)	3.38(16)		0.93	
1,3-Dichlorobenzene	1(16)	3.38(16)		1.10	
1,4-Dichlorobenzene	1(16)	3.39(16)		1.10	
	1(28)	3.39(16)		0.15	
2,2'-Dichlorobiphenyl	1(16)	4.80(16)		1.10	
2,4'-Dichlorobiphenyl	1(16)	5.10(16)		1.10	
1,2-Dichloroethane	1(31)	1.45(41)		0.93	
3,4-Dichlorophenol	2(29)	3.44(42)	7.39(40)	2.80	6.00-8.00
7,12-Dimethylbenzanthracene	13(30)	5.98(30)		0.15-2.38	
1,4-Dimethylbenzene	2(26)	3.15(28)		0.66-1.49	
	1(28)	3.15(28)		0.15	
2,4-Dinitro-*o*-cresol	12(32)	2.85(43)	4.46(32)	0.15-3.04	4.27-8.29
Ethylbenzene	1(16)	3.15(16)		1.10	
Furan	2(26)	1.34(26)		0.66-1.49	
Hexachlorobenzene	1(26)	5.73(44)		0.66	
Hexanoic acid	1(9)	1.90(45)	4.85(46)	4.85	2.80
Methoxychlor	13(13)	5.08(13)		0.13-3.29	

Table 1 (continued)

Chemical	n#	log K_{ow}	pKa	%OC	pH
3-Methylcholanthrene	12(30*)	6.42(30)		0.11-2.38**	
Nitrobenzene	2(26)	1.87(26)		0.66-1.49	
Pentachlorophenol	1(29)	5.04(42)	4.92(40)	3.20	4.70
Pyrene	14(30)	5.09(30)		0.11-2.38	
	12(13)	5.09(30)		0.13-3.29	
Silvex	12(32)	3.41(47)	3.07(32)	0.15-3.04	4.27-8.29**
2,3,7,8-TCDD	1(33)	6.42(48)		0.66	
1,2,3,4-Tetrachlorobenzene	1(28)	4.64(44)		0.15	
1,2,4,5-Tetrachlorobenzene	1(28)	4.72(28)		0.15	
1,1,2,2-Tetrachloroethane	1(31)	2.39(41)		0.93	
Tetrachloroethylene	1(28)	2.60(28)		0.15	
2,3,4,6-Tetrachlorophenol	2(29)	4.42(42)	5.38(40)	1.70-3.20	3.40-4.70
Tetrahydrofuran	2(26)	0.46(26)		0.66-1.49	
1,2,4,5-Tetramethylbenzene	1(28)	4.05(28)		0.15	
Toluene	2(26)	2.71(26)		0.66-1.49	
	1(28)	2.71(26)		0.15	
1,2,3-Trichlorobenzene	1(28)	4.14(44)		0.15	
	1(34)	4.14(44)		4.70	
1,2,4-Trichlorobenzene	1(16)	4.02(16)		1.10	
	1(28)	4.02(16)		0.15	
2,4,4'-Trichlorobiphenyl	1(16)	5.62(16)		1.10	
1,1,1-Trichloroethane	1(31)	2.47(41)		0.93	
2,4,5-Trichlorophenol	1(29)	3.72(49)	7.43(40)	2.80	8.00
1,2,3-Trichloropropane	2(26)	2.01(26)		0.66-1.49	
1,2,3-Trimethylbenzene	1(28)	3.60(28)		0.15	
1,3,5-Trimethylbenzene	1(28)	3.60(28)		0.15	

#number of experimental K_p values; *reference; **range.

Regression analysis of the 229 K_p values obtained from the 53 chemicals under study versus their log K_{ow} and log f_{oc} values (Table 1) yields Eq. 4.

$$\log K_p = 0.96 \log K_{ow} + 1.04 \log f_{oc} - 0.13 \qquad (4)$$

$n = 229$ $s = 0.639$ $r = 0.924$ $F = 660.07$ $p < 0.01\%$

Graphical analysis of the residuals obtained with Eq. 4 shows (Fig. 1) that this model overestimates the K_p values of the acids and underestimates those of the bases. At the

opposite, Fig. 1 reveals that the residuals for the other chemicals under study are well distributed.

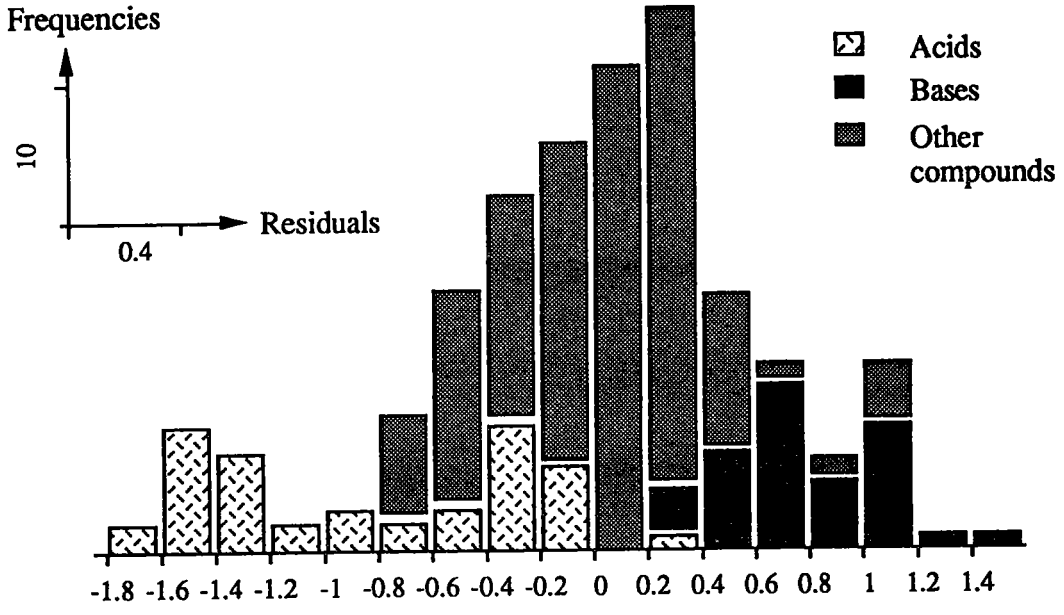

Fig. 1. Graphical analysis of the residuals (log $K_{p\ obs.}$ - log $K_{p\ calc.}$) obtained with Eq. 4.

Our results are not surprising since numerous authors[32, 36, 39, 50-53] have underlined that it was dangerous to neglect the role of pH in the modeling of the adsorption of acids and bases in soils and sediments. Indeed, it is well admitted that most weakly acidic chemicals are in predominantly ionic (i.e. negatively charged) form at the pH of most natural soils, while most weakly basic chemicals are in molecular form. In either case, as natural sorbent pH decreases toward a value equal to the dissociation constant (pKa) of the chemical, sorption tends to increase because at low pH, the acidic chemical has more of the molecular species and the basic chemical has more of the protonated (positive) ionic species.[8] The colloidal surfaces of most natural soils are negatively charged and therefore have an affinity for positively charged molecules, but not much affinity for negatively charged molecules.[8, 54]
Therefore, to optimize the model, it could be interesting to introduce two different correction factors (one for acids and another for bases) allowing to quantify the variations of the concentration of ionic species in the range of soil pH values.
Thus, for acids, the evolution of the anionic species concentration in relation to pH values can be estimated by:[55]

$$CFa = \log \frac{1}{1 + 10^{pH - pKa}} \qquad (5)$$

For bases, the relation between the protonated species concentration and the pH values can be expressed by:[55]

$$CFb = \log \frac{1}{1 + 10^{pKa - pH}} \qquad (6)$$

Introduction of CFa and CFb in Eq. 4 allows to obtain the following model:

$$\log K_p = 0.92 \log K_{ow} + 1.09 \log f_{oc} + 0.33\ CFa - 1.32\ CFb + 0.30 \qquad (7)$$

$n = 229 \qquad s = 0.453 \qquad r = 0.963 \qquad F = 713.57 \qquad p < 0.01\%$

Like Wauchope and coworkers,[56] we have defined acids as the sole chemicals whose neutral (molecular) forms are capable of forming negatively charged ions. Therefore, in Eq. 7, CFa must be taken equal to zero for bases and other compounds since this parameter is null when the concentration of anionic species is zero.[55] In the same way,[56] we have defined bases as the sole chemicals whose neutral forms are able to form positively charged ions. Therefore in Eq. 7, CFb must be taken equal to zero for acids and other compounds since this parameter is null when the concentration of cationic species is zero.[55]
Eq. 7 gives a better distribution of the residuals for the acids and bases (Fig. 2) than Eq. 4 (Fig. 1), but some K_p values for basic chemicals are still underestimated.

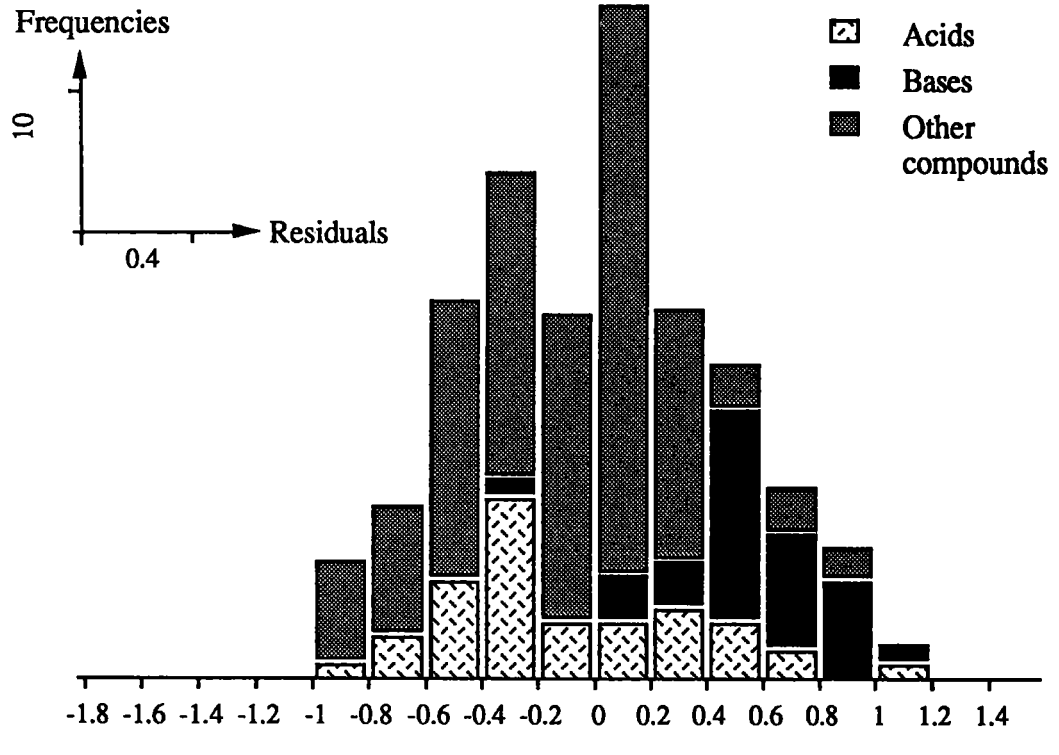

Fig. 2. Graphical analysis of the residuals ($\log K_{p\ obs.} - \log K_{p\ calc.}$) obtained with Eq. 7.

The remaining difference between the adsorption behavior of bases and acids could be

explained by the fact that the adsorption of basic compounds in certain soils (e.g. montmorillonite clay systems) is principally dependent upon the surface acidity and not upon the pH of the bulk solution, while the converse is true for the adsorption of acidic compounds.[50] Bailey *et al.*[50] have estimated that the surface acidity of montmorillonite appears to be 3-4 pH units lower than the pH of bulk solution. Green and Karickhoff[8] have stressed that a reasonable estimate of surface acidity (pHs) is two pH units lower than the bulk suspension pH (i.e. pHs = pH - 2). Under these conditions, we have tried to introduce this correction in our model (Eq. 7) defining the new following variable:

$$CFb' = \log \frac{1}{1 + 10^{pKa - (pH - 2)}} \qquad (8)$$

Introduction of CFb' in Eq. 7 instead of CFb yields Eq. 9.

$$\log K_p = 0.93 \log K_{ow} + 1.09 \log f_{oc} + 0.32\ CFa - 0.55\ CFb' + 0.25 \qquad (9)$$

$n = 229 \qquad s = 0.433 \qquad r = 0.966 \qquad F = 786.07 \qquad p < 0.01\%$

Fig. 3 depicts the high quality of Eq. 9 to describe the 229 Kp values of the training set (Table 1). Note that CFb' (like CFb) must be taken equal to zero for acids and other chemicals since this parameter is null when the concentration of cationic species is zero.

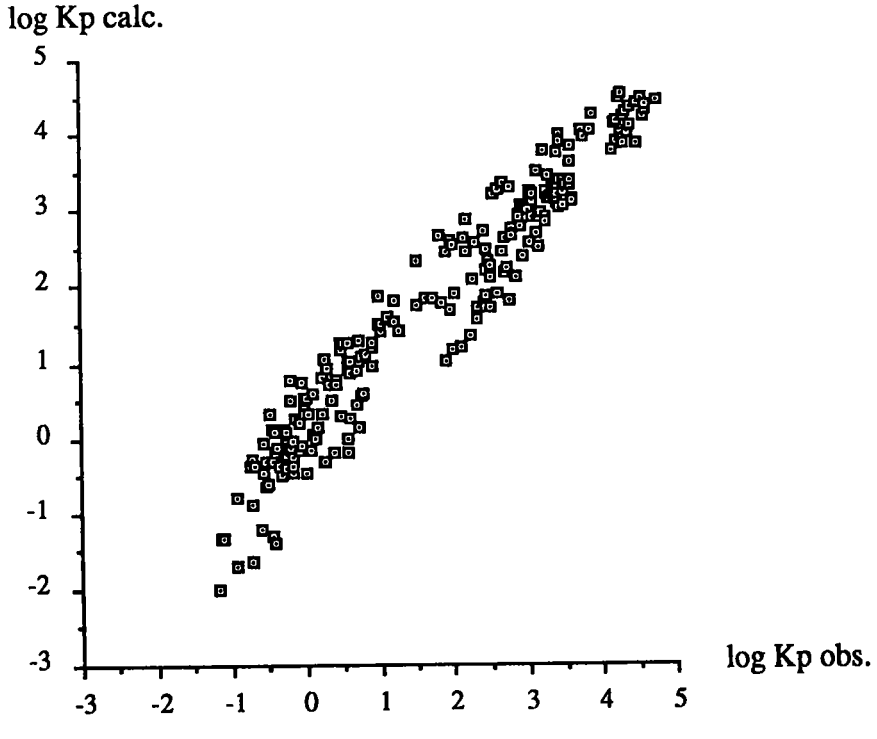

Fig. 3. Observed versus calculated (Eq. 9) K_p values for the training set.

Introduction of CFb' in the model leads to a better distribution of the residuals of basic compounds (Fig. 4).

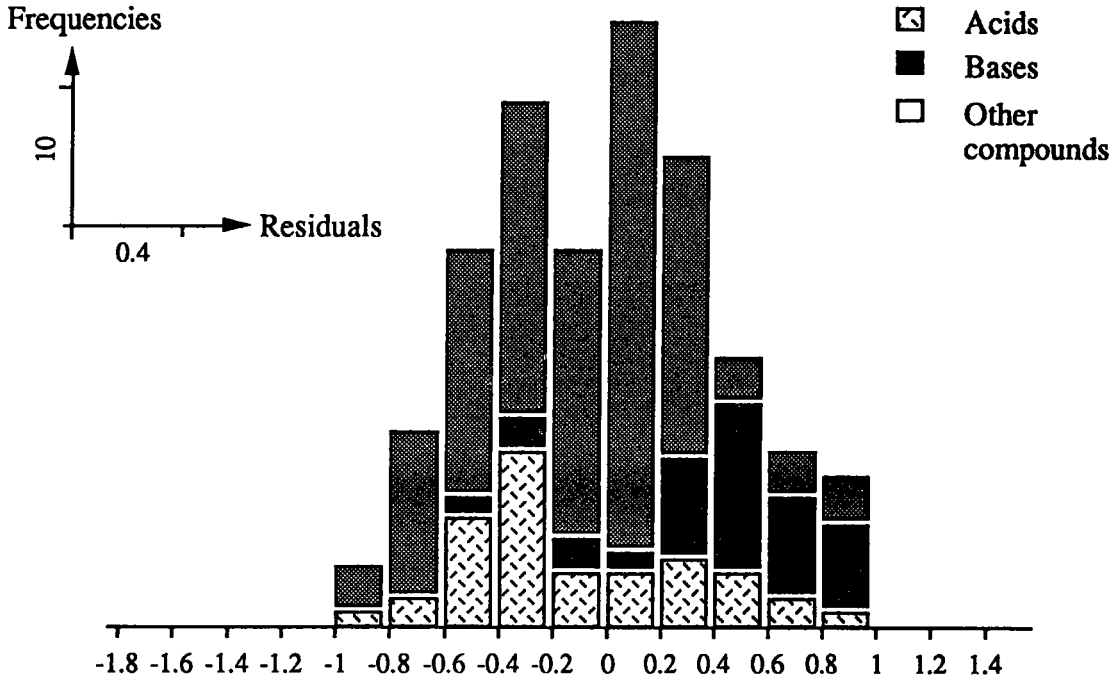

Fig. 4. Graphical analysis of the residuals (log $K_{p\ obs.}$ - log $K_{p\ calc.}$) obtained with Eq. 9.

MODEL VALIDATION

To estimate the predictive power of our final model (Eq. 9), a test set of 500 experimental K_p values for 87 chemicals has been constituted (Table 2). It is important to note that these values did not satisfy all the constraints defined for the selection of the original training set since they were generally obtained from Freundlich isotherms with $0.8 < N < 1.2$ or by one initial concentration.[9, 15, 29, 34, 39, 51, 57-76]

The log K_{ow} and pKa values (Table 2) were obtained from the literature.[4, 15, 16, 29, 38-46, 49, 52, 59, 60, 63, 70, 71, 75-85] Experimental values or data obtained from critical compilations were preferentially selected.

Table 2: Test set.

Chemical	n#	log K_{ow}	pKa	N	%OC	pH
Acetanilide	2(9*)	1.16(38)		0.82-0.84†	1.58-4.85†	
Acridine	1(39)	3.40(38)	5.68(39)	1.02	0.58	7.64
Alachlor	1(57)	2.64(77)		1.01	1.17	

Table 2 (continued)

Chemical	n#	log K_{ow}	pKa	*N*	%OC	pH
Aldicarb	1(15*)	1.08(77)		1$	2.05	
Aldrin	1(15)	5.66(4)		1$	2.05	
Ametryne	34(58)	2.58(78)	4.00(79)	1$	0.35-20.88†	4.50-9.00†
Aniline	1(59)	0.90(38)	4.60(46)	0.83	0.84§	5.40§
Atrazine	4(60)	2.33(77)	1.68(79)	1	0.40-7.60	4.40-8.00
	1(61)	2.33(77)	1.68(79)	0.92	0.43	6.05
	25(62)	2.33(77)	1.68(79)	1$	0.35-2.84	4.30-7.10
Benzamide	1(9)	0.64(38)		0.88	4.85	
Benzoic acid (B.a.)	1(9)	1.87(38)	4.20(46)	0.90	4.85	2.80
B.a. ethyl ester	3(9)	2.64(38)		0.81-0.88†	1.25-4.85	
B.a. methyl ester	3(9)	2.20(38)		0.81-0.85	1.25-4.85	
B.a. phenyl ester	2(9)	3.59(38)		0.91-0.93	1.25-1.58	
4-Bromophenol	1(15)	2.59(15)	9.34(46)	1$	1.46	6.70
Captafol	1(15)	3.83(15)		1$	2.05	
Captan	1(15)	2.54(15)		1$	2.05	
Carbendazim	15(63)	1.52(63)	4.48(63)	1$	0.63-3.47	4.14-7.54
Carbaryl	1(15)	2.32(15)		1$	2.05	
Carbofuran	2(64)	1.63(77)		0.90-0.94	1.60-2.50	
Chlorfenvinphos	1(15)	3.10(15)		1$	2.05	
Chlorobenzene	1(65)	2.84(16)		0.87	4.70	
2-Chlorophenol	1(66)	2.17(43)	8.49(40)	0.80	2.96	5.70
3-Chlorophenol	5(29)	2.50(29)	8.85(40)	0.80	1.70-3.20	3.40-6.00
	3(34)	2.50(29)	8.85(40)	0.85-0.96	2.15-9.05	3.60-5.90
	1(66)	2.50(29)	8.85(40)	0.83	2.96	5.70
Chlorsulfuron	1(67)	2.20(80)	3.60(52)	0.87	1.42	4.60
	23(68)	2.20(80)	3.60(52)	1$	0.95-20.36	5.20-7.90
3-Cresol	1(66)	1.98(38)	10.0(46)	0.87	2.96	5.70
2,4-D	3(9)	2.81(81)	2.64(46)	0.89-1.06	1.25-4.85	2.80-7.10
	19(69)	2.81(81)	2.64(46)	0.82-1.16	0.28-2.73	6.30-8.30
Diazinon	1(15)	3.11(15)		1$	2.05	
Dibenzothiophene	11(70)	4.38(70)		0.88-1.10	0.15-2.38	
2,4-Dichloroaniline	3(34)	2.78(82)	2.05(83)	0.85-1.11	3.54-9.05	3.60-5.90
3,5-Dichloroaniline	1(59)	2.69(59)	2.37(46)	0.91	0.84§	5.40§
1,4-Dichlorobenzene	1(65)	3.39(16)		0.96	2.15	
2,4-Dichlorophenol	3(71)	3.21(42)	7.68(40)	1$	0.20-3.70	4.20-7.40
3,4-Dichlorophenol	5(29)	3.44(42)	7.39(40)	0.80-0.90	0.90-3.20	3.40-7.50
	4(34)	3.44(42)	7.39(40)	0.81-0.94	2.15-9.05	3.60-5.90
Dieldrin	1(15)	4.60(4)		1$	2.05	

Table 2 (continued)

Chemical	n#	log K_{ow}	pKa	*N*	%OC	pH
Dimethoate	1(15*)	0.79(15)		1$	2.05	
N,N-Dimethylaniline	3(9)	2.31(38)	5.15(46)	0.87-0.91†	1.25-4.85†	2.80-7.10†
Diuron	34(58)	2.60(77)		1$	0.35-20.88	
Fenamiphos	1(15)	3.18(15)		1$	2.05	
Folpet	1(15)	3.63(15)		1$	2.05	
Hexachlorobenzene	1(15)	5.73(44)		1$	1.53	
Hexanoic acid	2(9)	1.90(45)	4.85(46)	1.01	1.25-1.58	6.70-7.10
3-Methoxyphenol	1(66)	1.58(49)	9.65(46)	0.89	2.96	5.70
N-Methylaniline	1(9)	1.66(38)	4.85(46)	0.89	4.85	2.80
4-Methylaniline	1(9)	1.39(38)	5.08(38)	0.96	4.85	2.80
4-Methylbenzoic acid	1(9)	2.34(38)	4.36(46)	0.82	4.85	2.80
Metsulfuron-methyl	23(68)	2.20(80)	3.30(80)	1$	0.95-20.36	5.20-7.90
4-Nitroaniline	1(9)	1.39(45)	1.01(46)	0.81	1.25	6.70
4-Nitrobenzoic acid	1(9)	1.89(45)	3.44(46)	1.14	4.85	2.80
2-Nitrophenol	1(66)	1.79(45)	7.22(46)	0.89	2.96	5.70
Parathion	1(15)	3.76(77)		1$	2.05	
	6(72)	3.76(77)		1.02-1.11	0.44-14.28	
2,2',5,5'-PCB	2(73)	6.10(84)		1$	0.16-1.87	
	5(74)	6.10(84)		1$	0.16-1.87	
3,3',4,4'-PCB	5(74)	6.10(84)		1$	0.16-1.87	
2,2',3,4,5'-PCB	2(73)	6.50(84)		1$	0.16-1.87	
2,2',3,5',6-PCB	2(73)	6.40(84)		1$	0.16-1.87	
2,2',3',4,5-PCB	2(73)	6.60(84)		1$	0.16-1.87	
2,2',4,5,5'-PCB	2(73)	6.40(84)		1$	0.16-1.87	
	5(74)	6.40(84)		1$	0.16-1.87	
2,3,3',4',6-PCB	2(73)	6.53(85)		1$	0.16-1.87	
2,3',4,4',5-PCB	2(73)	6.40(84)		1$	0.16-1.87	
2,2',3,4,4',5-PCB	2(73)	7.00(84)		1$	0.16-1.87	
2,2',3,4,5,5'-PCB	2(73)	7.59(85)		1$	0.16-1.87	
2,2',3,4',5',6-PCB	2(73)	6.80(84)		1$	0.16-1.87	
2,2',4,4',5,5'-PCB	2(73)	6.90(84)		1$	0.16-1.87	
	5(74)	6.90(84)		1$	0.16-1.87	
Pentachlorobenzene	2(73)	4.94(41)		1$	0.16-1.87	
Pentachlorophenol	6(29)	5.04(42)	4.92(40)	0.80-0.90	0.90-29.80	3.40-7.50
	4(34)	5.04(42)	4.92(40)	0.82-0.92	2.15-9.05	3.60-5.90
	3(71)	5.04(42)	4.92(40)	1$	0.20-3.70	4.20-7.40
Phenol	1(15)	1.46(15)	9.99(46)	1$	1.46	6.70
Phenylacetic acid	2(9)	1.41(38)	4.31(46)	0.95-1.12	2.80-6.70	1.25-4.85

Table 2 (continued)

Chemical	n#	log K_{ow}	pKa	*N*	%OC	pH
Phorate	1(15*)	3.83(77)		1$	2.05	
Prometone	2(61)	1.94(78)	4.28(79)	0.92-0.99†	0.33-0.43†	6.05-6.30†
	25(62)	1.94(78)	4.28(79)	1$	0.35-2.84	4.30-7.10
Prometryne	25(62)	2.99(78)	4.05(79)	1$	0.35-2.84	4.30-7.10
Propazine	25(62)	3.09(78)	1.85(79)	1$	0.35-2.84	4.30-7.10
Pyridine	1(39)	0.65(38)	5.23(39)	1.04	0.58	7.64
Quinoline	1(39)	2.03(38)	4.92(39)	0.87	0.58	7.64
	2(51)	2.03(38)	4.92(39)	0.84-0.91	0.35-0.58	7.46-7.64
Simazine	1(15)	2.27(78)	1.65(79)	1$	2.05	6.10
	25(62)	2.27(78)	1.65(79)	1$	0.35-2.84	4.30-7.10
2,4,5-T	3(9)	3.36(81)	2.90(75)	0.84-1.14	1.25-4.85	2.80-7.10
	2(75)	3.36(81)	2.90(75)	0.81-0.85	0.46-1.74	5.90-7.70
1,2,3,4-TCB£	2(65)	4.64(44)		0.91-1.13	2.15-4.70	
	2(73)	4.64(44)		1$	0.16-1.87	
1,2,3,5-TCB£	2(73)	4.46(41)		1$	0.16-1.87	
Tetrachloroguaiacol	3(71)	4.45(42)	5.97(71)	1$	0.20-3.70	4.20-7.40
2,3,4,5-TCP&	2(34)	4.82(42)	6.96(40)	0.81-0.82	2.15-3.54	4.80-5.60
2,3,4,6-TCP&	5(29)	4.42(42)	5.38(40)	0.80-0.90	0.90-29.80	4.60-7.50
	3(71)	4.42(42)	5.38(40)	1$	0.20-3.70	4.20-7.40
3,4,5-Trichloroaniline	6(76)	3.49(76)	1.78(83)	1	0.12-6.34	4.50-5.10
1,2,3-Trichlorobenzene	3(34)	4.14(44)		0.96-1.01	2.15-9.05	
	2(73)	4.14(44)		1$	0.16-1.87	
1,2,4-Trichlorobenzene	2(73)	4.02(16)		1$	0.16-1.87	
1,3,5-Trichlorobenzene	2(73)	4.19(44)		1$	0.16-1.87	
4,5,6-Trichloroguaiacol	3(71)	3.74(42)	7.40(71)	1$	0.20-3.70	4.20-7.40
2,4,5-Trichlorophenol	8(29)	3.72(49)	7.43(40)	0.80-0.90	0.90-29.80	3.40-7.50
	4(34)	3.72(49)	7.43(40)	0.81-0.98	2.15-9.05	3.60-5.90
2,4,6-Trichlorophenol	3(71)	3.75(42)	7.42(40)	1$	0.20-3.70	4.20-7.40
Trifluralin	4(60)	5.07(60)		1	0.40-7.60	

number of experimental K_p values

*reference; †range; $single concentration; §ref. 86; £Tetrachlorobenzene; &Tetrachlorophenol.

Comparison of Figs. 5 to 7 shows that Eq. 9 is the most suitable model to describe the sorption behavior of the 87 organic chemicals listed in Table 2.

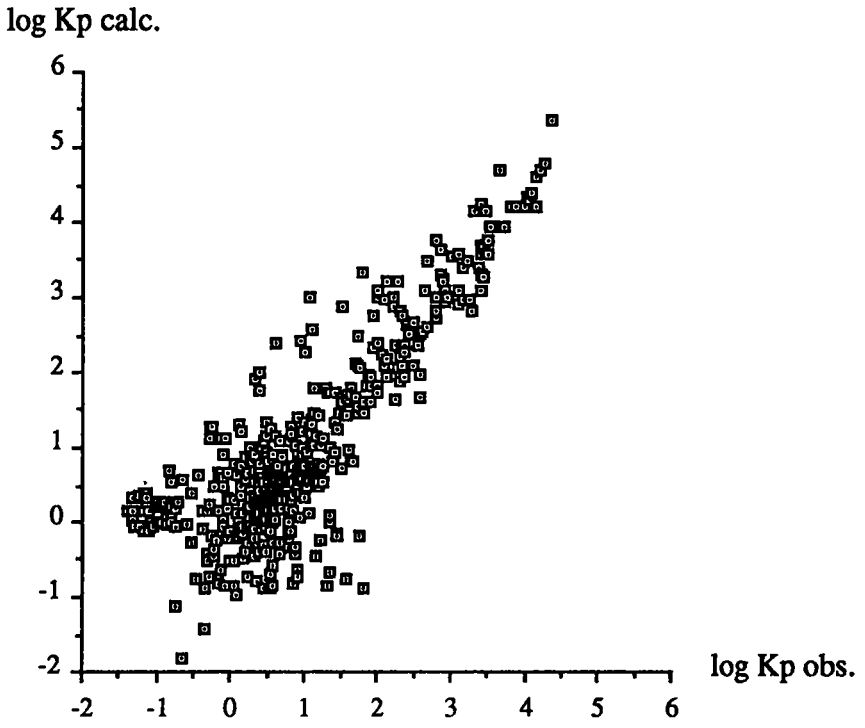

Fig. 5. Observed versus calculated (Eq. 4) K_p values for the test set.

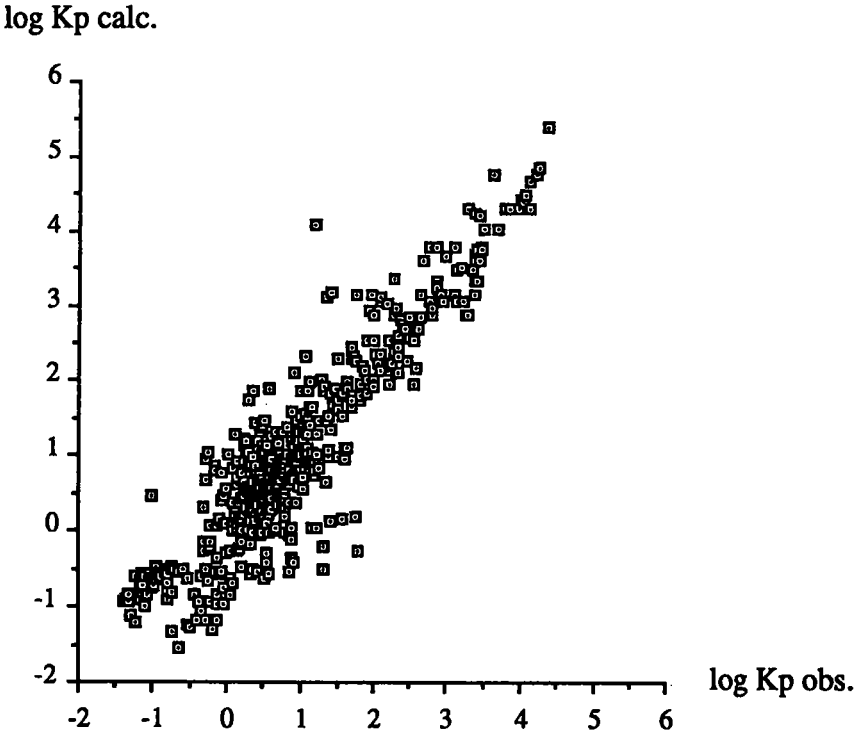

Fig. 6. Observed versus calculated (Eq. 7) K_p values for the test set.

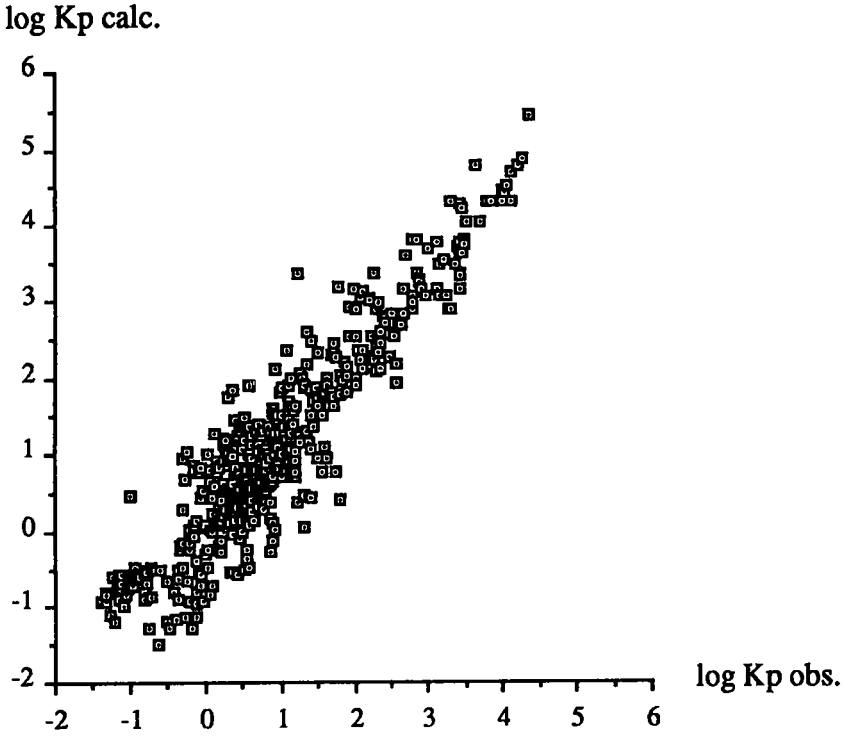

Fig. 7. Observed versus calculated (Eq. 9) K_p values for the test set.

CONCLUSION

Our study shows that it is possible to propose a unique general QSAR equation (Eq. 9) for estimating the sorption behavior of all the organic chemicals which can potentially contaminate the ecosystems. Introduction of Eq. 9 in the environmental fate models (e.g. fugacity models[6, 87]) could be useful to increase the accuracy of their outputs and stretch their domain of application. It could be also interesting to test the usefulness of our correction factors for ionization problems to improve the predictive power of the models based upon linear relationships between soil and/or sediment sorption coefficients and topological descriptors such as molecular connectivity indices.

ACKNOWLEDGEMENTS

We acknowledge with appreciation the comments of Pr. M. Chastrette (Laboratoire de Chimie Organique Physique, University Lyon I, France) and Dr. T. E. McKone (Health and Ecological Assessments Division, Lawrence Livermore National Laboratory, California) which improved this paper.

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87. Devillers, J., Bintein, S., Domine, D., and Karcher, W. CHEMFRANCE: A regional fugacity level III model applied to France. (In preparation).

ARTICLE III

Pergamon

0045-6535(94)00425-0

Chemosphere, Vol. 30, No. 3, pp. 457-476, 1995

0045-6535/95 $9.50+0.00

CHEMFRANCE: A REGIONAL LEVEL III FUGACITY MODEL APPLIED TO FRANCE

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ABSTRACT

CHEMFRANCE, a computer model allowing to estimate the environmental fate of organic chemicals in France, is presented. This multimedia model is represented by six bulk compartments (i.e., air, surface water, soil, bottom sediment, groundwater, coastal water), and by ten subcompartments. The model employs the fugacity concept and requires information on chemical properties (i.e., molecular weight, aqueous solubility, vapor pressure, *n*-octanol/water partition coefficient, dissociation constant, melting point, reaction half-lives) and emission rates of the pollutants. The outputs of the model consist of estimated chemical distribution between environmental media, transport and transformation process rates, and steady state concentrations in one of the twelve defined regions of France, or France as a whole, at a chosen season.

The nature of the model and its underlying assumptions are described. An illustrative example dealing with the modeling of the environmental fate of isobutylene is presented. Aspects of model validation are discussed and recommendations are made for a proper use of CHEMFRANCE.

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INTRODUCTION

Pollutants discharged into the environment are distributed across environmental media (e.g., air, water, soil) and among biota as the result of their physicochemical properties (e.g., aqueous solubility, vapor pressure, *n*-octanol/water partition coefficient (log P), dissociation constant) and the nature of the environment (e.g., climatic parameters).[1, 2] The human mind is not able to take into account simultaneously the above parameters in order to estimate the theoretical distribution of a chemical between the different compartments of the biosphere. Mathematical models, at different levels of complexity can be used to overcome this problem. These models are very attractive since they provide a rapid and inexpensive simulation tool to produce a comprehensive picture of the environmental fate of the organic chemicals.[3, 4] Among them, the level III fugacity models are particularly powerful to estimate the environmental distribution of pollutants in abiotic and biotic media.[4-6] The assessment is based on information relative to emission rates, environmental conditions, and physicochemical and reactive properties of the organic chemicals.

In this paper, we describe a level III computer model (CHEMFRANCE) which can be used to estimate the environmental fate of organic chemicals in France. The country has been divided into twelve regions where the environment is represented by a multimedia system constituted of six bulk compartments (i.e., air, surface water, soil, bottom sediment, groundwater, coastal water). The first four bulk compartments are considered as a combination of subcompartments of varying proportions of pure and particle phases. Equilibrium is assumed to apply within each bulk compartment, but is not assumed between compartments. Expressions for emissions, advective flows, degrading reactions, and interphase transports by diffusive and non-diffusive processes are included in CHEMFRANCE.

The aim of this paper is basically to present the theoretical foundations of CHEMFRANCE and underline the difficulties encountered to construct such a model. For illustrative purposes, the modeling of the environmental fate of isobutylene is presented.

MODEL DESCRIPTION

Regions of CHEMFRANCE

To develop CHEMFRANCE, it was necessary to divide France into a reasonable number of regions of similar hydrogeological, climatic, and ecologic characteristics. These regions were defined after a careful study of the factors susceptible to have an effect on the environmental fate of chemicals in France. Thus, it is obvious that all the economical or political parameters inducing artifactitious divisions (e.g., limits of department, high density population area) were excluded. The factors selected in priority were the drainage basins constituting the French hydrographical network, the climate (i.e., precipitations, temperatures, wind), the nature of the soil, and the different types of vegetation.

Under these conditions, France was divided into the twelve following regions (Figure 1):

Region 1- Bretagne, Pays de Loire
Region 2- Nord, Normandie
Region 3- Bassin de Paris
Region 4- Alsace, Lorraine
Region 5- Vallée du Rhône
Region 6- Massif central
Region 7- Alpes
Region 8- Bassin méditerranéen
Region 9- Aquitaine, Midi-Pyrénées
Region 10- Pyrénées
Region 11- Bordure atlantique
Region 12- Centre
Region 13 being France

Dividing a country into regions is ultimately a matter of judgement, and is almost certain to generate controversy. Therefore, the segmentation presented in Figure 1 has to be regarded as an optimal compromise which can be modified for particular simulation purposes. Indeed, in CHEMFRANCE an option allows a user to define its own regions without any kind of restriction.

Environmental media

The choice of environmental compartment structures requires to identify the acceptable level of model complexity. The modeler should make a balance between the current perceptions of the system and the experimental and environmental data available from the system. In CHEMFRANCE, the environment is rationalized and simplified to a multimedia system constituted of six bulk compartments (i.e., air, surface water, soil, bottom sediment, groundwater, coastal water). The first four bulk compartments (i.e., principal compartments) consist of a combination of subcompartments of varying proportions of pure and particle phases. A brief description of these compartments is given below.

1- Air

The air compartment is divided into two subcompartments (i.e., pure air, air particles). In CHEMFRANCE, chemicals enter the air compartment by local emissions, advective inflow from adjacent regions, and by diffusion (i.e., volatilization) from soil and surface water. The environmental loss processes are advective outflow, reaction, transfer to higher altitude, wet and dry depositions, rain dissolution of gaseous chemicals, and diffusion (i.e., adsorption) to soil and water. An average value of 5 days was selected for the air residence time, in order to calculate the advective flows.[5] The total surface area for each region was calculated from the surface of departments and the fraction of departments included in each region.[7] The air height was reduced to 1000 m, since the depth of the troposphere, into which emissions generally occur and are constrained, is typically around 100 m during the night and 1000 m during the day.[8, 9]

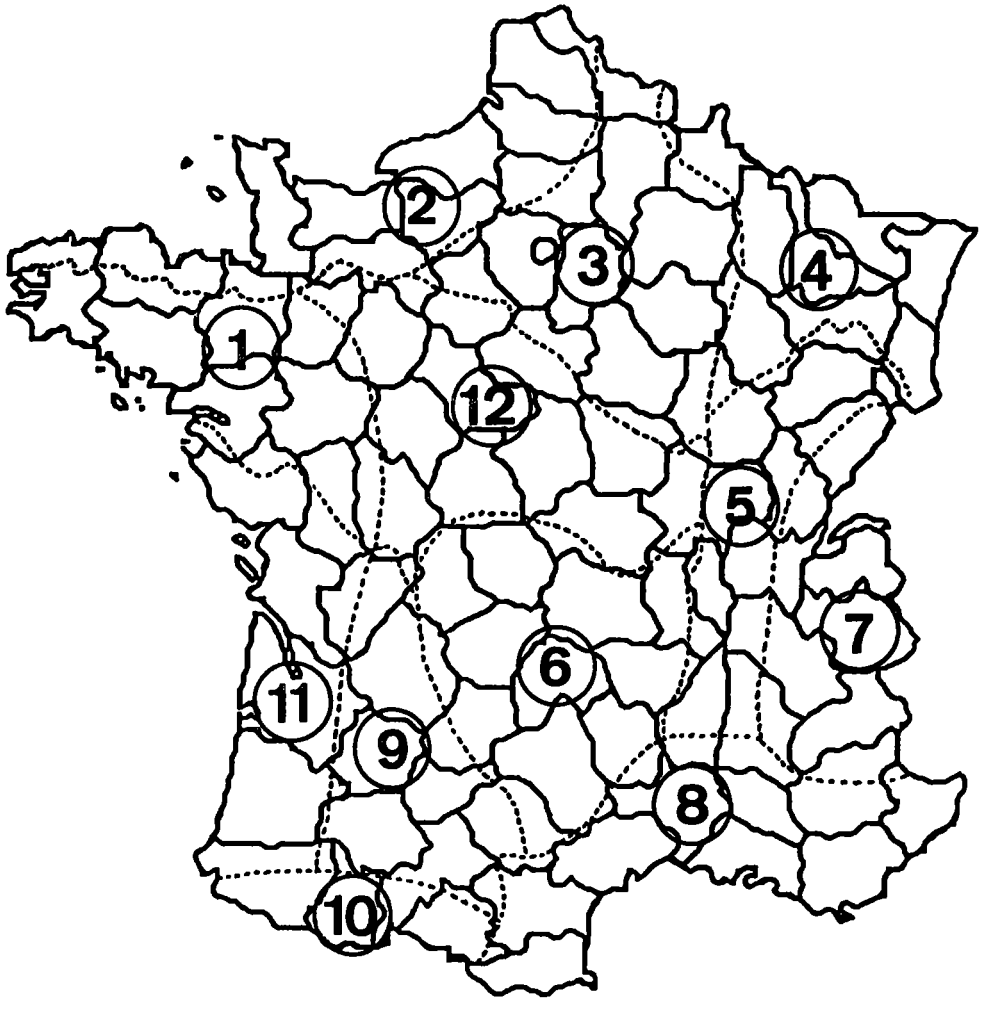

Figure 1: Defined regions of CHEMFRANCE.

2- Surface water

The surface water compartment is composed of pure water, suspended sediment, and biota (only represented by fish). In CHEMFRANCE, pollutants move into this compartment by local emissions, advective inflow from adjacent regions, diffusion from air and sediment, soil and water runoffs, wet and dry depositions, rain dissolution of gaseous chemicals, and sediment resuspension. The removal processes are advective outflow, reaction, diffusion to air and sediment, and deposition. In order to calculate the advective flows, an average value of 500 days was selected for the surface water residence time.[5] This compartment is used to represent lakes, ponds, dams, rivers, and canals. The surface and volume of surface water were estimated from numerous bibliographical references.[10-18] When only the surface area was available, we assumed an average depth of 10 m, 2 m, and 15 m for lakes, ponds, and dams, respectively. The volume fraction of suspended sediment was also estimated for each region.[19, 20] In order to take into account the possible ionization of chemicals, an average pH value of suspended sediment equal to 7 was adopted for all the regions.[21]

3- Soil

The soil compartment consists of three subcompartments (i.e., pure soil, soil water, soil air). Pollutants move into this compartment by local emissions, diffusion from water (i.e., adsorption), wet and dry depositions, and by rain dissolution of gaseous chemicals. Chemicals are assumed to be removed by reaction, diffusion to air (i.e., volatilization), soil and water runoffs, and by leaching to groundwater. Soil was characterized by depth (15 cm), density, air and water content, fraction of organic carbon, and the pH allowing to take into account the ionization of acidic and basic compounds. In CHEMFRANCE, only the last two parameters were adapted to each region. The nature of the soil of the twelve regions was determined from a pedologic map,[22] which allowed to select the predominant soil. The soil was then characterized from the upper layer type (i.e., horizon A_0 or A_1 in pedology).[23-25]

4- Bottom sediment

This compartment is constituted of two subcompartments (i.e., pure sediment, sediment pore water). Chemicals enter this compartment by local emissions, deposition, and by diffusion from water. The environmental loss mechanisms are reaction, diffusion to water, resuspension, and sediment burial. As for the suspended sediment, an average pH value equal to 7 was adopted for all the regions,[21] in order to take into account the possible ionization of chemicals.

5- Groundwater

The groundwater compartment represents the saturated material of the lowest soil horizon. For each region, the volume of groundwater was estimated from the nature, the surface area, the thickness and the porosity of the substratum.[26-35]

6- Coastal water

The coastal water was assumed to extend 1 km offshore with a mean depth of 100 m. A flushing time of 100 h and an advective inflow rate of 500 days were selected for all the regions possessing coasts. Marine biota and sediments were ignored in our model.

Fugacity and basic equations

CHEMFRANCE is a level III fugacity model. The concept of fugacity[36] and its usefulness in environmental modeling[4-6, 37-46] have been clearly described in the seminal book of Mackay.[4] Briefly, fugacity, which means escaping or fleeing tendency, has units of pressure (F in Pa) and can be viewed as the partial pressure which a chemical exerts as it attempts to escape from one phase and migrate to another.[41] Fugacity is linearly related to concentration (C in mol/m^3) through the fugacity capacity (Z in mol/m^3 Pa):

$$C = Z F \qquad (1)$$

The Z values depend on the physicochemical properties of the studied substance, the nature of the phase into which the chemical partitions, and the environmental temperature.
In CHEMFRANCE, the Z values are calculated according to Mackay and Paterson[40] (Tables I and II) except for those related to the bioconcentration of chemicals in fish (BCF) and to the sorption phenomena (Kp).

Table I. Definition of Z values (mol/m^3 Pa) for the subcompartments.

Subcompartment (i,j)	$Z_{(i,j)}$
pure air (1,1)	1/RT
air particles (1,3)	$6\ 10^6\ Z_{(1,1)}/VPL$
pure water (2,2)	1/H
suspended sediment (2,3)	$Kp_{(2,3)}\ \rho_{(2,3)}\ Z_{(2,2)}/1000$
biota (fish) (2,4)	$BCF\ \rho_{(2,4)}\ Z_{(2,2)}/1000$
soil air (3,1)	1/RT
soil water (3,2)	1/H
pure soil (3,3)	$Kp_{(3,3)}\ \rho_{(3,3)}\ Z_{(2,2)}/1000$
sediment pore water (4,2)	1/H
pure sediment (4,3)	$Kp_{(4,3)}\ \rho_{(4,3)}\ Z_{(2,2)}/1000$

R = 8.314 (Pa m^3/mol K); T = environmental temperature (K); VPL* = liquid vapor pressure (Pa); H = VP/S = Henry's law constant (Pa m^3/mol); S£ = solubility in water (mol/m^3); VP£ = vapor pressure (Pa); Kp = sorption coefficient; BCF = bioconcentration factor; $\rho_{(i,j)}$ = density of subcompartment (i,j) (kg/m^3).

* for solids VPL = VP/exp (6.79 (1-MP/T)) in which MP is the melting point (K) of the chemical.

£ temperature dependence is included.[40]

Table II. Definition of Z values (mol/m^3 Pa) for the bulk compartments.

Compartment (i)	$Z_{(i)}$
air (1)	$Z_{(1,1)}+Z_{(1,3)}\,\phi_{(1,3)}$
surface water (2)	$Z_{(2,2)}+Z_{(2,3)}\,\phi_{(2,3)}+Z_{(2,4)}\,\phi_{(2,4)}$
soil (3)	$Z_{(3,3)}\,\phi_{(3,3)}+Z_{(3,1)}\,\phi_{(3,1)}+Z_{(3,2)}\,\phi_{(3,2)}$
bottom sediment (4)	$Z_{(4,3)}\,\phi_{(4,3)}+Z_{(4,2)}\,\phi_{(4,2)}$
groundwater (5)	$Z_{(2,2)} = 1/H$
coastal water (6)	$0.8\,Z_{(2,2)} = 0.8/H$

$\phi_{(i,j)}$ = volume fraction of subcompartment (i,j).

Indeed, to estimate the BCF values in fish a bilinear model[47] (Eq. 2) particularly suitable for very hydrophobic chemicals is used.

$$\log BCF = 0.910 \log P - 1.975 \log (6.8\ 10^{-7} P + 1) - 0.786 \qquad (2)$$

n = 154 s = 0.347 r = 0.950 F = 463.51

The Kp values are estimated from an original model taking into account the possible ionization of basic and acidic chemicals.[48] This model[48] requires to know the log P and pKa values of the chemicals and also the fraction of organic carbon (foc) and pH of the sorbent (soil or sediment).

CHEMFRANCE describes a steady-state system with non-equilibrium distribution between the bulk compartments in which each phase may have a different fugacity.[39] Therefore, intermedia transfer coefficients D (in mol/h Pa) for the various diffusive and non-diffusive processes[40] have to be calculated as displayed in Tables III and IV.

Table III. Calculation of D parameters (mol/h Pa).

Compartment	Process	Individual D
(1)-(2)	diffusion	$D_V = 1/((1/TK_{(1,2)})\,AR_{(2)}\,Z_{(1,1)})+(1/TK_{(2,1)})\,AR_{(2)}\,Z_{(2,2)}))$
	rain	$D_{QW} = AR_{(2)}\,Z_{(2,2)}\,U_Q$
	wet deposition	$D_{DW} = AR_{(2)}\,Z_{(1,3)}\,\phi_{(1,3)}\,U_D$
	dry deposition	$D_{PW} = AR_{(2)}\,Z_{(1,3)}\,\phi_{(1,3)}\,U_P$
(2)-(1)	diffusion	$D_V = 1/((1/TK_{(1,2)})\,AR_{(2)}\,Z_{(1,1)})+(1/TK_{(2,1)})\,AR_{(2)}\,Z_{(2,2)}))$
(1)-(3)	diffusion	$D_S = 1/((1/TK_{(1,3)})\,AR_{(3)}\,Z_{(1,1)})+(Y_3/(AR_{(3)}\,(B_{A3}\,Z_{(1,1)}+B_{W3}\,Z_{(2,2)})))$
	rain	$D_{QS} = AR_{(3)}\,Z_{(2,2)}\,U_Q$
	wet deposition	$D_{DS} = AR_{(3)}\,Z_{(1,3)}\,\phi_{(1,3)}\,U_D$
	dry deposition	$D_{PS} = AR_{(3)}\,Z_{(1,3)}\,\phi_{(1,3)}\,U_P$
(3)-(1)	diffusion	$D_S = 1/((1/TK_{(1,3)})\,AR_{(3)}\,Z_{(1,1)})+(Y_3/(AR_{(3)}\,(B_{A3}\,Z_{(1,1)}+B_{W3}\,Z_{(2,2)})))$
(3)-(2)	water runoff	$D_{WW} = AR_{(3)}\,Z_{(2,2)}\,U_{WW}$
	soil runoff	$D_{SW} = AR_{(3)}\,Z_{(3,3)}\,U_{SW}$

Table III. (Continued)

Compartment	Process	Individual D
(2)-(4)	diffusion	$D_Y = 1/((1/TK_{(2,4)}\ AR_{(4)}\ Z_{(2,2)})+(Y_4/B_{W4}\ AR_{(4)}\ Z_{(2,2)}))$
	deposition	$D_{DX} = AR_{(4)}\ Z_{(2,3)}\ U_{DX}$
(4)-(2)	diffusion	$D_Y = 1/((1/TK_{(2,4)}\ AR_{(4)}\ Z_{(2,2)})+(Y_4/B_{W4}\ AR_{(4)}\ Z_{(2,2)}))$
	resuspension	$D_{RX} = AR_{(4)}\ Z_{(4,3)}\ U_{RX}$
D parameters for advective, pseudo-advective and reaction processes		
advection (i = 1 to 2)		$D_{A(i)} = Z_{(i)}\ G_{A(i)} = Z_{(i)}\ V_{(i)}/\tau_{(i)}$
transfer to higher altitude		$D_{ST} = Z_{(1)}\ U_{ST}\ AR_{(1)}$
leaching from soil		$D_L = AR_{(3)}\ Z_{(2,2)}\ U_L$
advective flow from coastal water		$D_{CW} = Z_{(6)}\ V_{(6)}/\tau_{CW}$
advective flow to coastal water		$D_{A(6)} = D_{A(2)}$
sediment burial		$D_{BX} = AR_{(4)}\ Z_{(4,3)}\ U_{BX}$
reaction (i = 1 to 4)		$D_{R(i)} = V_{(i)}\ Z_{(i)}\ k_{(i)}$

$AR_{(i)}$ = area of compartment i and $V_{(i)}$ = volume of compartment i.

Table IV. Total D value ($DT_{(i)}$) for the principal compartments.

$DT_{(1)} = D_{(1,2)}+D_{(1,3)}+D_{A(1)}+D_{R(1)}+D_{ST}$
$DT_{(2)} = D_{(2,1)}+D_{(2,4)}+D_{A(2)}+D_{R(2)}$
$DT_{(3)} = D_{(3,1)}+D_{(3,2)}+D_{R(3)}+D_L$
$DT_{(4)} = D_{(4,2)}+D_{R(4)}+D_{BX}$

$D_{(i,j)} = \sum$ individual $D_{(i,j)}$ of Table III.

Equations for calculation of the D values (Tables III and IV) require to use the transport velocity parameters described in Table V.

Table V. Assumed transport parameters.

Parameter	Symbol	Value	Unit
air-side mass transfer coefficient over water	$TK_{(1,2)}$	3	m/h
water-side mass transfer coefficient	$TK_{(2,1)}$	0.03	m/h
rain rate	U_Q	$12\ U_{QM}/(24*365)$	m/h
rain rate	U_{QM}	Region dependent	m/month
wet deposition velocity	U_D	$U_Q\ Q$	m/h
scavenging ratio	Q	200000	no unit
dry deposition velocity	U_P	10.8	m/h
air-side mass transfer coefficient over soil	$TK_{(1,3)}$	1	m/h

Table V. (Continued)

Parameter	Symbol	Value	Unit
diffusion path length in soil	Y_3	0.05	m
effective diffusivity in soil air	B_{A3}	BMA $(\phi_{(3,1)})^{3.33}/(1-\phi_{(3,3)})^2$	m^2/h
molecular diffusivity in air	BMA	0.04	m^2/h
effective diffusivity in soil water	B_{W3}	BMW $(\phi_{(3,2)})^{3.33}/(1-\phi_{(3,3)})^2$	m^2/h
molecular diffusivity in water	BMW	$4\ 10^{-6}$	m^2/h
water runoff rate from soil	U_{WW}	$12\ U_{WWM}/(24*365)$	m/h
velocity of water runoff from soil	U_{WWM}	$0.4\ U_{QM}$	m/month
solids runoff rate from soil	U_{SW}	$2\ 10^{-4}/(24*365)$	m/h
water-side mass transfer coefficient over sediment	$TK_{(2,4)}$	0.01	m/h
diffusion path length in sediment	Y_4	$5\ 10^{-3}$	m
effective diffusivity in sediment pore water	B_{W4}	BMW $(\phi_{(4,2)})^{1.33}$	m^2/h
sediment deposition rate	U_{DX}	$4\ 10^{-4}/(24*365)$	m/h
sediment resuspension rate	U_{RX}	$1\ 10^{-4}/(24*365)$	m/h
transfer to higher altitude	U_{ST}	$90/(24*365)$	m/h
leaching rate from soil to groundwater	U_L	$0.4\ U_Q$	m/h
flushing time for coastal water	τ_{CW}	100	h
air residence time	$\tau_{(1)}$	120	h
water residence time	$\tau_{(2)}$	12000	h
sediment burial rate	U_{BX}	$U_{DX}-U_{RX} = (3\ 10^{-4}/(24*365))$	m/h

For the four principal compartments, the previous calculations (Tables I to IV) allow to setup steady state mass balance equations (Table VI), which incorporate emissions, transfers between adjacent phases, reaction, and advection. The solutions for the four unknown fugacity values (Table VI) can be easily obtained by a matrix inversion technique such as the Gaussian elimination.

Table VI. Mass balance equations.

Compartment	Equation
air	$E_{(1)}+G_{A(1)}\,CB_{(1)}+F_{(2)}\,D_{(2,1)}+F_{(3)}\,D_{(3,1)} = F_{(1)}\,DT_{(1)}$
surface water	$E_{(2)}+G_{A(2)}\,CB_{(2)}+F_{(1)}\,D_{(1,2)}+F_{(3)}\,D_{(3,2)}+F_{(4)}\,D_{(4,2)} = F_{(2)}\,DT_{(2)}$
soil	$E_{(3)}+F_{(1)}\,D_{(1,3)} = F_{(3)}\,DT_{(3)}$
bottom sediment	$E_{(4)}+F_{(2)}\,D_{(2,4)} = F_{(4)}\,DT_{(4)}$

$CB_{(i)}$ = background inflow concentration (mol/m^3) of adjacent region in compartment i and $E_{(i)}$ = emission (mol/m^3) in compartment i.

In order to estimate the fugacity in the two remaining bulk phases (i.e., groundwater, coastal water), we use fugacity values relative to the principal phases:

Groundwater $F_{(5)} = F_{(3)}$ (3)

Coastal water $F_{(6)} = F_{(2)} D_{A(6)}/D_{CW}$ (4)

Eq. (3) assumes that the groundwater and the soil compartments are in equilibrium. This assumption is based on the relatively prolonged contact between the soil water and the surface soil during infiltration.[40] Eq. (4) allows to calculate the fugacity of the coastal water from a consideration of the advective inflow rate and the flushing time using a simple dilution calculation.[40]

Fugacity values of the subcompartments are obtained from those of the principal compartments, since equilibrium partitioning is assumed to apply within each of the four principal compartments (i.e., $F_{(i)} = F_{(i,j)}$). This implies that the time required to reach equilibrium within a bulk phase is short compared to the time required to reach equilibrium between bulk phases.[40]

CHEMFRANCE allows one to obtain a considerable amount of information which is summarized in Table VII.

Table VII. Some output information obtained with CHEMFRANCE.

Output	Equation	Unit
concentration	$C_{(i)} = F_{(i)} Z_{(i)}$	mol/m^3
amount	$M_{(i)} = V_{(i)} C_{(i)}$	mol
diffusive flux between two phases	$Nd_{(i,j)} = D_{(i,j)} (F_{(i)} - F_{(j)})$	mol/h
non-diffusive flux between phases	$Nnd_{(i)} = D_{(i)} F_{(i)}$	mol/h
first-order reaction process in a phase	$Nk_{(i)} = DR_{(i)} F_{(i)}$	mol/h
net flux between two phases	$Nf_{(i,j)} = D_{(i,j)} F_{(i)} - D_{(j,i)} F_{(j)}$	mol/h
persistence time	$TP = \frac{\sum M_{(i)}}{\sum DR_{(i)} F_{(i)}}$	h
residence time	$TR = \frac{\sum M_{(i)}}{\sum DA_{(i)} \frac{CB_{(i)}}{Z_{(i)}} + \sum E_{(i)}}$	h

i and j represent compartments.

Environmental parameters

The monthly mean precipitations and temperatures were determined from maps[49] and data given locality by locality.[50] Table VIII summarizes the environmental parameters for which no region dependence was included. The values of the remaining parameters (i.e., area and volume of the compartments, coastal length, monthly mean precipitation and temperature for the four seasons, fraction of organic carbon content and pH of soil, volume fraction of suspended sediment) were selected for each region.

Table VIII. Values of constant environmental parameters selected for the twelve regions of CHEMFRANCE*.

Parameter	Selected value
fraction of organic carbon content of suspended sediment	$foc_{(2,3)} = 0.2$
fraction of organic carbon content of pure sediment	$foc_{(4,3)} = 0.04$
pH of suspended sediment	$pH_{(2,3)} = 7$
pH of pure sediment	$pH_{(4,3)} = 7$
volume fraction of air particles	$\phi_{(1,3)} = 2\ 10^{-11}$
volume fraction of biota	$\phi_{(2,4)} = 1\ 10^{-6}$
volume fraction of soil air	$\phi_{(3,1)} = 0.2$
volume fraction of soil water	$\phi_{(3,2)} = 0.3$
volume fraction of sediment pore water	$\phi_{(4,2)} = 0.7$
density of pure air and soil air	$\rho_{(1,1)} = \rho_{(3,1)} = 1.2$ kg/m^3
density of air particles and suspended sediment	$\rho_{(1,3)} = \rho_{(2,3)} = 1500$ kg/m^3
density of pure soil and pure sediment	$\rho_{(3,3)} = \rho_{(4,3)} = 2400$ kg/m^3
density of pure water, biota, soil water, and sediment pore water	$\rho_{(2,2)} = \rho_{(2,4)} = \rho_{(3,2)} = \rho_{(4,2)} = 1000$ kg/m^3
height of air	$DEP_{(1)} = 1000$ m
depth of soil	$DEP_{(3)} = 0.15$ m
depth of sediment	$DEP_{(3)} = 0.03$ m
depth of coastal water	$DEP_{(6)} = 100$ m

* all these values can be changed by the user, as well as all those selected for each region.

CASE STUDY: ISOBUTYLENE

Isobutylene [CAS RN 115-11-7] has become an important starting material for the manufacture of polymers and chemicals. There are many patents describing the use of isobutylene or its derivatives to produce insecticides, antioxidants, elastomers, additives for lubricating oils, adhesives, sealants, and caulking compounds.[51, 52] The estimated Western Europe isobutylene consumption in 1984 was 1640 10^3 t/y.[53] The main sources for the commercial production of isobutylene are catalytic or thermal cracking (730 10^3 t/y in Western Europe) and steam cracking (920 10^3 t/y in Western Europe). There are other processes available for the production of isobutylene but they are more site or manufacturer specific (e.g., dehydration of *tert*-butanol, 50 10^3 t/y in Western Europe).[51, 53] Environmental contaminations of isobutylene principally occur during industrial processes of production and use as well as during fuel combustions (stationary and mobile sources).[54-57] To illustrate the usefulness of CHEMFRANCE as simulation tool, we have modeled the environmental fate of isobutylene in France. In our case study, the physicochemical properties required to run CHEMFRANCE were the following:

- Molecular weight: 56.11 g/mol,

- Solubility in water: 263 mg/l at room temperature,[58]
- Vapor pressure: 257.4 kPa at 20°C,[59]
- *n*-Octanol/water partition coefficient (log P): 2.11,[59]
- Melting point: -140 °C,[59]
- Half-life in air: 4 h.[59]

In addition to the six above input data, it was necessary to make the following assumptions:
- due to the lack of information on the degradation processes of isobutylene in the water, soil, and sediment compartments, it was necessary to estimate the half-lives of this chemical in these compartments. As generally assumed, in that case, fictitiously large half-life values are supplied inducing that there is no reaction.[40] In this study, a half-life value of 10^{11} h was arbitrarily selected.
- as no information was available on the amounts of isobutylene released to the environment in France, a scenario was designed from the estimation of isobutylene emissions in the California's South Coast Basin.[55, 60] Thus, considering that in the California's South Coast Basin, an atmospheric emission of 7 10^3 kg/d was measured for a surface area of 60000 km^2, the emissions in the 12 regions of CHEMFRANCE were calculated using the ratio of these two above values and the surface area of the corresponding region. Only the results obtained with region n°8 (i.e., bassin méditerranéen) in summer are presented here.

Thus, the outputs of CHEMFRANCE (Tables IX to XII) clearly show that the concentrations of isobutylene are low in all the compartments. The highest amount (99.99%) is found in the air compartment (Table X). The high percentage found in air is due to the high vapor pressure of this chemical. It therefore exists as a gas at ambient temperature. This high vapor pressure value combined to low log P and high Henry's law constant values induces that the transfers from air to the other compartments are not important. It is noteworthy that the major part of the emissions reacts in air (i.e., 95.4%) and the remaining is advected (i.e., 4.6%) (Table XII). All other reactions and transfer processes are negligible. The individual intermedia transport coefficients (D) are small compared to the reaction ($D_{R(1)}$) and advection ($D_{A(1)}$) values (Table XI). Therefore isobutylene tends to remain in air where it is rapidly degraded or advected. Indeed, its residence and persistence time values are very low (5.51 h and 5.77 h, respectively). From a practical point of view, this means that the outflow to other regions is unlikely due to the rapid degradation of this chemical.

Table IX. Z and F values obtained in region n°8 (summer) for isobutylene.

Compartment	Z (mol/m^3 Pa)	F (Pa)
Bulk compartment		
air	$Z_{(1)} = 4.08\ 10^{-4}$	$F_{(1)} = 1.17\ 10^{-6}$
surface water	$Z_{(2)} = 1.63\ 10^{-5}$	$F_{(2)} = 1.19\ 10^{-6}$
soil	$Z_{(3)} = 2.71\ 10^{-4}$	$F_{(3)} = 1.17\ 10^{-6}$
bottom sediment	$Z_{(4)} = 8.80\ 10^{-5}$	$F_{(4)} = 1.19\ 10^{-6}$
groundwater	$Z_{(5)} = 1.63\ 10^{-5}$	$F_{(5)} = 1.17\ 10^{-6}$
coastal water	$Z_{(6)} = 1.30\ 10^{-5}$	$F_{(6)} = 6.42\ 10^{-10}$

Table IX. (Continued)

Compartment	Z (mol/m^3 Pa)	F (Pa)
Subcompartment		
pure air	$Z_{(1,1)} = 4.08\ 10^{-4}$	$F_{(1,1)} = 1.17\ 10^{-6}$
air particles	$Z_{(1,3)} = 8.27\ 10^{-3}$	$F_{(1,3)} = 1.17\ 10^{-6}$
pure water	$Z_{(2,2)} = 1.63\ 10^{-5}$	$F_{(2,2)} = 1.19\ 10^{-6}$
suspended sediment	$Z_{(2,3)} = 7.98\ 10^{-4}$	$F_{(2,3)} = 1.19\ 10^{-6}$
biota (fish)	$Z_{(2,4)} = 2.17\ 10^{-4}$	$F_{(2,4)} = 1.19\ 10^{-6}$
soil air	$Z_{(3,1)} = 4.08\ 10^{-4}$	$F_{(3,1)} = 1.17\ 10^{-6}$
soil water	$Z_{(3,2)} = 1.63\ 10^{-5}$	$F_{(3,2)} = 1.17\ 10^{-6}$
pure soil	$Z_{(3,3)} = 3.70\ 10^{-4}$	$F_{(3,3)} = 1.17\ 10^{-6}$
sediment pore water	$Z_{(4,2)} = 1.63\ 10^{-5}$	$F_{(4,2)} = 1.19\ 10^{-6}$
pure sediment	$Z_{(4,3)} = 2.55\ 10^{-4}$	$F_{(4,3)} = 1.19\ 10^{-6}$

Table X. Chemical fate of isobutylene.

Compartment	Percentage	Amount moles	Concentrations mol/m^3	mg/kg	µg/m^3
Bulk compartment					
air	99.99	$24.36\ 10^{3}$	$4.77\ 10^{-10}$	$2.23\ 10^{-5}$	$2.68\ 10^{-2}$
surface water	0.00	$7.95\ 10^{-2}$	$1.94\ 10^{-11}$	$1.09\ 10^{-9}$	$1.09\ 10^{-3}$
soil	0.01	2.38	$3.18\ 10^{-10}$	$1.19\ 10^{-8}$	$1.78\ 10^{-2}$
bottom sediment	0.00	$3.58\ 10^{-3}$	$1.05\ 10^{-10}$	$4.15\ 10^{-9}$	$5.89\ 10^{-3}$
groundwater	0.00	0.88	$1.91\ 10^{-11}$	$1.07\ 10^{-9}$	$1.07\ 10^{-3}$
coastal water	0.00	$6.62\ 10^{-4}$	$8.36\ 10^{-15}$	$4.69\ 10^{-13}$	$4.69\ 10^{-7}$
Subcompartment					
pure air	99.99	$24.36\ 10^{3}$	$4.77\ 10^{-10}$	$2.23\ 10^{-5}$	$2.68\ 10^{-2}$
air particles	0.00	$9.88\ 10^{-6}$	$9.68\ 10^{-9}$	$3.62\ 10^{-7}$	0.54
pure water	0.00	$7.95\ 10^{-2}$	$1.94\ 10^{-11}$	$1.09\ 10^{-9}$	$1.09\ 10^{-3}$
suspended sediment	0.00	$3.89\ 10^{-5}$	$9.49\ 10^{-10}$	$3.55\ 10^{-8}$	$5.32\ 10^{-2}$
biota (fish)	0.00	$1.06\ 10^{-6}$	$2.58\ 10^{-10}$	$1.45\ 10^{-8}$	$1.45\ 10^{-2}$
soil air	0.00	0.71	$4.77\ 10^{-10}$	$2.23\ 10^{-5}$	$2.68\ 10^{-2}$
soil water	0.00	$4.29\ 10^{-2}$	$1.91\ 10^{-11}$	$1.07\ 10^{-9}$	$1.07\ 10^{-3}$
pure soil	0.01	1.62	$4.33\ 10^{-10}$	$1.01\ 10^{-8}$	$2.43\ 10^{-2}$
sediment pore water	0.00	$4.64\ 10^{-4}$	$1.94\ 10^{-11}$	$1.09\ 10^{-9}$	$1.09\ 10^{-3}$
pure sediment	0.00	$3.11\ 10^{-3}$	$3.05\ 10^{-10}$	$7.12\ 10^{-9}$	$1.71\ 10^{-2}$

Table XI. D values and transfer rates.

Compartment	Process	Individual D (mol/h Pa)	Transfer rate (mol/h)
(1)-(2)	diffusion	$D_V = 55.483\ 10^1$	$6.50\ 10^{-4}$
	rain	$D_{QW} = 0.760$	$8.90\ 10^{-7}$
	wet deposition	$D_{DW} = 1.543\ 10^{-3}$	$1.81\ 10^{-9}$
	dry deposition	$D_{PW} = 2.028\ 10^{-3}$	$2.37\ 10^{-9}$
(2)-(1)	diffusion	$D_V = 55.483\ 10^1$	$6.60\ 10^{-4}$
(1)-(3)	diffusion	$D_S = 30.171\ 10^4$	0.35
	rain	$D_{QS} = 33.431$	$3.91\ 10^{-5}$
	wet deposition	$D_{DS} = 6.784\ 10^{-2}$	$7.94\ 10^{-8}$
	dry deposition	$D_{PS} = 8.915\ 10^{-2}$	$1.04\ 10^{-7}$
(3)-(1)	diffusion	$D_S = 30.171\ 10^4$	0.35
(3)-(2)	water runoff	$D_{WW} = 13.372$	$1.57\ 10^{-5}$
	soil runoff	$D_{SW} = 0.422$	$4.94\ 10^{-7}$
(2)-(4)	diffusion	$D_Y = 8.774$	$1.04\ 10^{-5}$
	deposition	$D_{DX} = 4.136\ 10^{-2}$	$4.92\ 10^{-8}$
(4)-(2)	diffusion	$D_Y = 8.774$	$1.05\ 10^{-5}$
	resuspension	$D_{RX} = 3.309\ 10^{-3}$	$3.95\ 10^{-9}$
Advective, pseudo-advective and reaction processes			
advection		$D_{A(1)} = 17.36\ 10^7$	$20.32\ 10^1$
		$D_{A(2)} = 5.57$	$6.62\ 10^{-6}$
transfer to higher altitude		$D_{ST} = 21.38\ 10^4$	0.25
leaching from soil		$D_L = 13.37$	$1.57\ 10^{-5}$
advective flow from coastal water		$D_{CW} = 10.32\ 10^3$	
sediment burial		$D_{BX} = 9.93\ 10^{-3}$	$1.18\ 10^{-8}$
reaction		$D_{R(1)} = 36.0518\ 10^8$	$42.20\ 10^2$
		$D_{R(2)} = 4.6317\ 10^{-7}$	$5.51\ 10^{-13}$
		$D_{R(3)} = 1.4089\ 10^{-5}$	$1.65\ 10^{-11}$
		$D_{R(4)} = 2.0772\ 10^{-8}$	$2.48\ 10^{-14}$

Table XII. Summary of 4 principal compartment mass balance (mol/h).

Compartment	Emission	Inflow	Reaction	Outflow	Net flux out to other compts.
air	$44.24\ 10^2$	0.0	$42.20\ 10^2$	$20.32\ 10^1$	$2.23\ 10^{-5}$
surface water	0.0	0.0	$5.51\ 10^{-13}$	$6.62\ 10^{-6}$	$-6.62\ 10^{-6}$
soil	0.0	0.0	$1.65\ 10^{-11}$	0.0	$-1.56\ 10^{-5}$
bottom sediment	0.0	0.0	$2.48\ 10^{-14}$	0.0	$-1.18\ 10^{-8}$
total	$44.24\ 10^2$	0.0	$42.20\ 10^2$	$20.32\ 10^1$	

From the simulation results of the environmental fate of isobutylene with CHEMFRANCE, it appears that this chemical is of minor concern regarding its potential hazards to the environment since it is rapidly degraded in air and it is not accumulated in other media.

In order to test the predictive power of CHEMFRANCE, we have tried to compare the results obtained with CHEMFRANCE to concentration data actually found in the environment. Only concentrations in air were retrieved from the literature. There are listed in Table XIII.

Table XIII. Recorded concentrations of isobutylene in air.

Location, date	Concentration
Slottskogen Park (Sweden, 25/07/90)[61]	0.09 $\mu g/m^3$
Avenue of Göteborg (Sweden, 25/07/90, 20°C)[61]	0.7 $\mu g/m^3$
Avenue of Göteborg near intersection with traffic lights (Sweden, 30/11/89, 0°C)[61]	7.7 $\mu g/m^3$
Avenue of Göteborg near intersection with traffic lights (Sweden, 7/05/90, 20°C)[61]	3.2 $\mu g/m^3$
Bridge 5 m above motorway approach to Göteborg (Sweden, 17/11/89, 0°C)[61]	1.5 $\mu g/m^3$
Motorway 10 km south of Göteborg (Sweden, 9/05/90, 10°C)[61]	0.7 $\mu g/m^3$
Inside parking garage near cars leaving in the morning (Sweden, 23/05/90, 15°C)[61]	7.5 $\mu g/m^3$
Service station during refueling. No petrol vapor recovery (Sweden, 7/06/88, 22°C)[62]	1300 $\mu g/m^3$
Service station during refueling. No petrol vapor recovery (Sweden, 22/06/88, 15°C)[62]	700 $\mu g/m^3$
Service station during refueling. Petrol vapor recovery (Sweden, 10/06/88, 21°C)[62]	10 $\mu g/m^3$
Service station. Ambient air. Petrol vapor recovery (Sweden, 15/06/88, 22°C)[62]	9 $\mu g/m^3$
Fos-Berre basin* (France, 17/09/87)[63]	0.058 $\mu g/m^3$

* Located in the region n°8 of CHEMFRANCE.

Table XIII shows that if we consider locations relatively far from sources of emission, the concentrations recorded in air (Slottskogen park: 0.09 $\mu g/m^3$; Fos-Berre basin: 0.058 $\mu g/m^3$) are in accordance with our results (0.0268 $\mu g/m^3$ in Table X). However, note that the concentrations recorded near the emission sources are significantly higher (Table XIII).

From the simulations performed on isobutylene and those carried out on *o*-cresol and atrazine (to be published), it appears that CHEMFRANCE is particularly suitable to estimate the environmental fate of organic chemicals in France. However, it is obvious that to be validated, CHEMFRANCE has to be tested more thoroughly against other substances of widely differing physicochemical properties, reactivity and transport characteristics. The principal difficulties in accomplishing this task are the lack or the variability of emission data, environmental concentration data, reaction rate constants, and physicochemical properties.[5, 64]

CHEMFRANCE is basically a simulation tool for predicting the environmental fate behavior of new or existing chemicals for which there is insufficient environmental experience. To reach this goal, the predefined options of CHEMFRANCE easily allow to test different

scenarios. In addition, as CHEMFRANCE is totally open and flexible, the users can modify numerous parameters (e.g., compartment volumes and areas, densities, climatic parameters) in order to more easily interpret the different outputs or adapt CHEMFRANCE to local and global situations.

ACKNOWLEDGEMENTS

This research which was initiated by A. Chancrogne in the frame of her MSc (1991) constitutes a part of the PhD of S. Bintein. It was sponsored by the European Community and by the French Ministry of the Environment. The authors wish to acknowledge the critical and constructive review by Dr. T. E. McKone (Health and Ecological Assessments Division, Lawrence Livermore National Laboratory, California). The elaboration of CHEMFRANCE would not have been possible without all the published and unpublished information provided by Pr. D. Mackay (Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada) on his fugacity models and more specifically on CHEMCAN which has constituted an invaluable methodological framework for our research. His comments on our manuscript were also helpful.
A first version of CHEMFRANCE was presented in the OECD Workshop on the Application of Simple Models for Environmental Exposure Assessment (Berlin, 11th-13th December 1991). As the version presented in this paper is radically different from that actually distributed via the different OECD Secretariats, it is preferable to contact CTIS to obtain this up-to-date version of CHEMFRANCE.

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ARTICLE IV

Pergamon

PII: S0045-6535(96)00140-3

Chemosphere, Vol. 32, No. 12, pp. 2427–2440, 1996

0045-6535/96 $15.00+0.00

EVALUATING THE ENVIRONMENTAL FATE OF LINDANE IN FRANCE

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(Received in Germany 31 January 1996; accepted 18 March 1996)

ABSTRACT

Lindane, a highly persistent and lipophilic pesticide, is still used in large quantities. This chemical can be found with appreciable concentrations in biota, atmosphere, and in other environmental compartments in the adsorbed form. This information provided a basis for assessing the simulation performances of CHEMFRANCE, a regional level III fugacity model allowing to generate environmental behavior profile of organic chemicals in France. The comparison between the estimated environmental fate and field and laboratory observations suggests that this fugacity model can be used to determine the processes that control the environmental fate of lindane in France. CHEMFRANCE also provides accurate estimates of environmental compartment contaminations. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Lindane, the gamma isomer of hexachlorocyclohexane (γ-HCH) is an organochlorine insecticide. Like DDT, lindane was at first praised as almost a perfect insecticide, being relatively cheap to manufacture, strikingly effective against a wide range of insects and some animal ectoparasites and yet apparently safe to man and warm-blooded animals.[1] However, lindane is notoriously persistent in the environment and possesses a lipophilic character which strongly favors its bioaccumulation. In addition, its use has led to the indiscriminate killing of beneficial as well as harmful insects and, increasingly, to the development of insect resistance.[2,3] Despite restrictions and banishments in several countries, large amounts of lindane are still applied each year for crop protection.[4] Nowadays, the world and French consumptions of lindane are estimated to be 720 000 t/year[4] and 1 600 t/year,[5] respectively.

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The huge use of lindane and its long persistence pose serious environmental problems. Significant concentrations of γ-HCH have been found in surface waters, soils, plants, animals, and food.[6-13] Moreover, due to of its vapor pressure, γ-HCH is released to the atmosphere through spray applications[4] and volatilization from contaminated surfaces and then disseminated to adjacent or more distant regions.[14-18] Due to its economic and environmental concerns, numerous publications dealing with the environmental fate and hazards of lindane are available. This information was used for deriving the environmental fate profile of this chemical and then comparing experimental results with those obtained with CHEMFRANCE, a regional level III fugacity model allowing to simulate the environmental distribution of organic chemicals in France.[19]

LITERATURE DATA ANALYSIS

PHYSICOCHEMICAL PROPERTIES

An analysis of the literature allowed the selection of the following values:
- Molecular weight: 290.85 g/mol,
- Solubility in water: 7.52 mg/l at 25°C,[20]
- Vapor pressure: 4.1 10^{-3} Pa at 25°C,[20]
- *n*-Octanol/water partition coefficient (log P): 3.85,[21]
- Melting point: 112.5°C.[22]

ENVIRONMENTAL BEHAVIOR

Degradation

The structure of lindane constituted entirely of C-C, C-H, and C-Cl bonds induces a high chemical stability in normal environmental conditions. Its degradation products are principally volatile chemicals. In marine systems and soils, one of its main metabolites, γ-pentachlorocyclohex-1-ene (γ-PCCH), is readily transferred to the atmosphere.[23-25] However, there are some divergences in the literature on the part of γ-PCCH in the volatilization process of lindane. Samuel and Pillai[24] reported a percentage slightly superior to ten. Conversely, Cliath and Spencer[26] found that two thirds to three fourths of the volatilized material was lost as γ-PCCH from a calcareous soil treated with lindane. Another principal metabolic product is γ-3,4,5,6-tetrachlorocyclohex-1-ene (γ-TCCH) identified in treated soils[24,27] and in aquatic sediments.[23] Mineralization producing CO_2[24,28] and bioisomerization of γ-HCH to α, β, and δ-HCH in soils[29] are other processes of degradation of lindane. Some aquatic microorganisms can also convert lindane to α-HCH.[23,25]

The degradation profile of lindane can be depicted by the following reaction half-lives:
- Half-life in soil: 2888 h (mean value calculated from data of Isnard and Lambert[5]),
- Half-life in sediment: 1188 h (mean value calculated from data of Isnard and Lambert[5]),
- Half-life in water: 1848 h (mean value calculated from data of Isnard and Lambert[5]),
- Half-life in air: 17000 h (in temperate climatic zones).[30]

Levels of contamination in the different compartments of the environment

Soil contamination

The soil concentrations in lindane depend on the method of application (e.g.; spray application, seed treatment), soil composition, and climatic conditions.[24] Five to six months after its soil application, the amount of lindane present in the top surface soil was estimated to be around 25% of the initial amount.[29] Another field study carried out at Delhi (India) revealed that the lindane concentration dropped to ~15% of the initial concentration one year after treatment.[31] Studies of the partitioning of γ-HCH in soils revealed low contamination of soil water.[24,28] The disappearance of lindane in soils depends principally on volatilization, plant adsorption, and degradation.[24,28,29]

Surface water contamination

Lindane has been detected at relatively low concentrations (i.e.; generally $<<10^3$ ng/l) in surface waters in numerous countries.[7,12,13,17,32,33] In accordance with its low solubility, significant sorption in sediment and suspended sediment has been demonstrated.[12,13,32] Investigations on the lindane contamination of estuarine and sea waters in Europe showed lower contaminations than those reported in freshwater. In French estuaries, concentrations between 5 and 50 ng/l have been reported.[7] In the Scheldt estuaries located in southwest Netherlands and northwest Belgium, lindane was detected in June 1986 with dissolved concentrations ranging from 17 to 125 ng/l (median concentration of 82 ng/l) and with particulate concentrations ranging from 0.3 to 6.0 ng/g (median concentration of 2.5 ng/g).[34] A survey of the lindane contamination in the Baltic Sea and the North Sea reported concentrations in water samples varying between 1.0 to 7.7 ng/l.[25]

Groundwater contamination

Despite the persistent character of lindane, the risk of groundwater contamination is reduced due to its significant sorption in soils.[31] In U.S. surveys concerning groundwater contamination, lindane was seldom detected.[22] In France, between 1977 and 1990, lindane was detected in 11.6% of the 1314 groundwater samples from Calvados department with concentrations greater than 0.02 µg/l, but only in 1% with concentrations above 0.05 µg/l and 0.3% in concentrations superior to 0.1 µg/l.[35]

Atmospheric contamination

Numerous studies have reported the presence of lindane in air and rain samples. The presence of lindane in the atmospheric environment can be explained by spray droplet drift-off during its application and its volatilization from sprayed plants and soils.[24,26,28] Volatilization of incorporated lindane in soil contributes to a smaller extent to the atmospheric contamination.[4] The mean atmospheric concentration of lindane in Paris (France) was 1.5 10^{-3} ng/l from July 1989 to July 1990.[18] In Paris and adjacent areas, mean concentrations in rain samples in the range of 100-150 ng/l were recorded during 1988.[36] In Bavaria (Germany), rainwater samples had average concentrations between 11 and 17 ng/l in suburban stations and between 12 and 22 ng/l in rural stations in winter and summer, respectively.[15] In Jacksonville and Springfield (U.S.), mean air exposure estimates were 224 and 38 ng/day, respectively.[37] γ-HCH was detected in river and estuarine air from eastern and southern Asia and Oceania at concentrations ranging from 5.5 ng/l to 4.0 10^{6} ng/l.[13] Moreover, the presence of lindane in atmosphere and precipitations from sites remote from industrial and human activities indicates that long-range atmospheric transport of this pesticide occurs.[14,38] For illustrative purposes, at Enewetak Atoll in the North Pacific Ocean, lindane was found in concentrations ranging from 0.006 10^{-3} to 0.021 10^{-3} ng/l and from 0.34 to 1.59 ng/l in the atmosphere and bulk precipitation, respectively.[14]

Food and biota contamination

The air and dietary exposures of lindane were considered to be the dominant public exposure pathways.[22,37,39] Due to its high persistence and lipophilic character, lindane enters into the food chain and accumulates in animals and vegetals. Numerous studies reported high levels of γ-HCH in plant biomass,[9,10,40] invertebrates,[7,9,11,41] vertebrates,[11,12,41-44] and food.[8] However, despite this contamination, neither the limit of maximum residues, nor the acceptable daily intake were exceeded in recent years in France.[8,44]

MODELING STRATEGY

Besides the physicochemical properties and degradation half-life values listed in the previous section, information dealing with emissions was also necessary to run CHEMFRANCE.[45] In France, lindane is essentially used in corn crops.[46] The amounts of lindane applied on these crops in each of the 12 regions of CHEMFRANCE were estimated from the surface of corn crops treated (i.e.; 27% with lindane alone, 3.5% in association with chlorpyrifos), the area of this cultivation in the 12 regions, and the applied doses (i.e.; 1.35 kg of active matter/ha for lindane alone, 0.79 kg of active matter/ha when in association with chlorpyrifos).[35] With the above information, the quantities of lindane applied on corn crops in the 12 defined regions of CHEMFRANCE in 1990 could be estimated. However, in order to take into account the application of lindane on other tillages (e.g.; sugar-beet, colza, seed-treatment),

and as veterinary treatment, we assumed that these uses corresponded to 30% of the lindane applied on corn crops. These calculations yielded global releases summarized in Table I.

Table I. Estimated total emission rates of lindane for the regions of CHEMFRANCE.

Region	Emission (kg/y)
1 (Bretagne, Pays de Loire)	355530
2 (Nord, Normandie)	224380
3 (Bassin de Paris)	135380
4 (Alsace, Lorraine)	116370
5 (Vallée du Rhône)	71530
6 (Massif central)	75340
7 (Alpes)	49450
8 (Bassin méditerranéen)	11600
9 (Aquitaine, Midi-Pyrénées)	161030
10 (Pyrénées)	57360
11 (Bordure atlantique)	240260
12 (Centre)	147670
France	1645900

Spring was the season chosen to run CHEMFRANCE, since it is the period of year during which the agricultural applications of lindane occur.
The emission processes were simulated from four different scenarios.[45] The first considered a total emission of lindane into the soil compartment (scenario A), which can be related to a direct incorporation of lindane in soil from seed-treatment. Scenario B took into account accidental pollutions occurring in surface waters and the release via effluents at manufacturing sites (90% in soil and 10% in water). Due to the relative volatility of lindane, significant quantities may be released into the atmosphere through spray applications.[4] Therefore, a scenario C was designed to consider in addition to a soil emission (87%) a loss of 13%[47] into the air compartment. Last, scenario D summarized all the previous assumptions (i.e.; 77% in soil, 10% in surface water, 13% in air).

SIMULATION RESULTS AND COMPARISON WITH LABORATORY AND FIELD OBSERVATIONS

Table II gives the average percentages corresponding to the removal processes obtained for the twelve defined regions of CHEMFRANCE. In all cases, lindane disappearance is principally governed by reaction in soil. Moreover, due to its long persistence time determined by CHEMFRANCE (i.e.; ~180 days), it can be concluded that the greater part of lindane applied on soil remains in this compartment, in which it biodegrades slowly. This is in accordance with experimental studies.[28] When only seed-treatment applications have been assumed (i.e.; scenarios A and B), the dissipation of lindane by advective processes for the air

compartment is low. However, in case of spray applications (i.e.; scenarios C and D), ~9% of the applied lindane is transported to adjacent regions. Furthermore, as lindane is relatively stable in air, the risk of contamination by atmospheric transports must not be neglected. To a lower degree, the advective process in water must be taken into account when emission of lindane in water occurs (i.e.; scenarios B and D). The above conclusions can be linked to the presence of lindane with significant atmospheric concentrations (i.e.; ~10 to 100 pg/m^3) in non-treated areas (e.g.; Arctic and Antarctic zones).[14,48,49]

Field studies clearly demonstrated the low groundwater contamination by lindane.[22] Thus, leaching to groundwater represents only about 0.35% of the emissions (Table II). This percentage is close to the results obtained in a field experiment (i.e.; 1% within 15 days of lindane application[27]).

Table II. Average percentages of each removal process obtained from the four scenarios.

Removal process	Scenario A	Scenario B	Scenario C	Scenario D
air advection	0.05	0.31	8.79	9.04
water advection	0.07	1.40	0.08	1.40
reaction in air	$2\ 10^{-4}$	$2\ 10^{-3}$	0.04	0.04
reaction in water	0.31	6.28	0.33	6.31
reaction in soil	99.07	89.29	90.28	80.50
reaction in sediment	0.11	2.35	0.12	2.36
transfer to higher altitude	$6\ 10^{-5}$	$4\ 10^{-4}$	0.01	0.01
leaching to groundwater	0.39	0.35	0.35	0.32
sediment burial	$7\ 10^{-4}$	0.02	$8\ 10^{-4}$	0.02

Granier[36] reported a mean runoff rate equal to 48 µg/m^2/y in the region of Paris. This rate is ten-fold superior to those calculated by CHEMFRANCE (i.e.; 4.9 to 6.1 µg/m^2/year). Nevertheless, the calculated percentages of loss by runoff of the applied lindane (i.e.; 0.23 to 0.28%) are in accordance with the mean percentage (i.e.; <0.2%) obtained in a field survey.[46]

In scenarios C and D, more than 20% of the atmospheric emissions of lindane are deposited by rain and in lower proportions by wet and dry depositions (93%, 4%, and 3% of the total atmospheric fallout, respectively). These results agree with the percentages observed during a study performed near Paris in 1988.[36] Indeed, Granier[36] found 94%, 5%, and 1% for rain, wet, and dry depositions, respectively. In the same study, a mean flux of total atmospheric fallout equal to 77 µg/m^2/y was reported. This value is similar to those obtained in scenarios C and D (i.e.; 65 and 67 µg/m^2/y, respectively). In the same way, Granier[36] observed a dry deposition rate of 0.92 µg/m^2/y. This is in agreement with our results derived from scenarios C and D (i.e.; 2.01 and 2.08 µg/m^2/y, respectively).

There are some discrepancies in the literature on the part of the volatilization process in the environmental fate of lindane. Firstly, the percentages of γ-HCH detected in the volatilized organics in field studies varied between 0% (i.e.; not detected) and >85%.[24,28] This large variation can be attributed to the fact that it is difficult to know whether it is the lindane itself

that volatilized or its degradation products which possess higher vapor pressures. Secondly, the variations of experimental conditions (e.g.; temperature) induce large fluctuations in the percentage of volatilized lindane.[24,28,50,51] In this context, it is very difficult to compare the transfer of lindane in the air compartment obtained with CHEMFRANCE (i.e.; ~0.1% of the applied lindane) to field and laboratory observations.

The transfer rates of lindane between the sediment and water compartments are dominated by the sorption process and by sediment deposition. This leads to the accumulation of lindane in the bottom sediment. The other transfer rates (i.e.; sediment resuspension, diffusion from air to soil and water) between the four principal compartments (i.e.; air, surface water, soil, bottom sediment) are negligible in all the scenarios.

Figure 1 summarizes the concentrations of lindane found in the six bulk compartments for the different regions of CHEMFRANCE. Observed concentrations in surface water, groundwater, air, rain, and fish as well as those derived from the four different scenarios are reported in Tables III and IV.

The surface water concentrations obtained in scenarios A and C are generally in accordance with the maximum actual concentrations (Table III). However, the results of scenarios B and D greatly exceed field observations. This discrepancy could be due to an overestimation of the percentage of lindane emitted in the water, which could be closer to 1% than to 10% of the total emission of lindane.

The groundwater concentrations measured in regions 9 and 10 are superior to the simulated concentrations (Table III). Nevertheless, a study performed between 1977 and 1990 in the department of Calvados (region 2) revealed that from 1314 groundwater samples, only 1.3% presented a concentration larger than 50 ng/l.[35] This maximum is in accordance with our results for this region (i.e.; 54-67 ng/l).

Very few data are available on lindane contamination in French coastal and sea waters. Marchand[7] reported concentrations in coastal waters ranging between <1 to 5 ng/l, which are slightly superior to the maximum concentration obtained with CHEMFRANCE (i.e.; 0.85 ng/l).

The atmospheric concentrations derived from scenarios C and D assuming emissions in the air compartment are relatively near to those observed in the region of Paris (Table III).

By means of an equation published by Mackay and coworkers,[20] the concentrations in rain for region 3 were calculated from the air concentrations obtained with CHEMFRANCE. For scenarios A and B, the calculated rain concentrations are lower than those observed in Paris.[36] Conversely, scenarios C and D generate values close to the actual data (Table III).

The fish concentrations obtained in scenarios A and C are in accordance with the actual concentrations (Table IV). However, the results obtained with scenarios B and D greatly exceed field observations (Table IV). This overestimation confirms the assumption that the percentage of lindane emitted in the water compartment is probably closer to 1%.

The concentration of residues of lindane detected in a soil historically treated[29] is in accordance with the soil concentrations derived by CHEMFRANCE (i.e.; ~6 10^{-3} mg/kg).

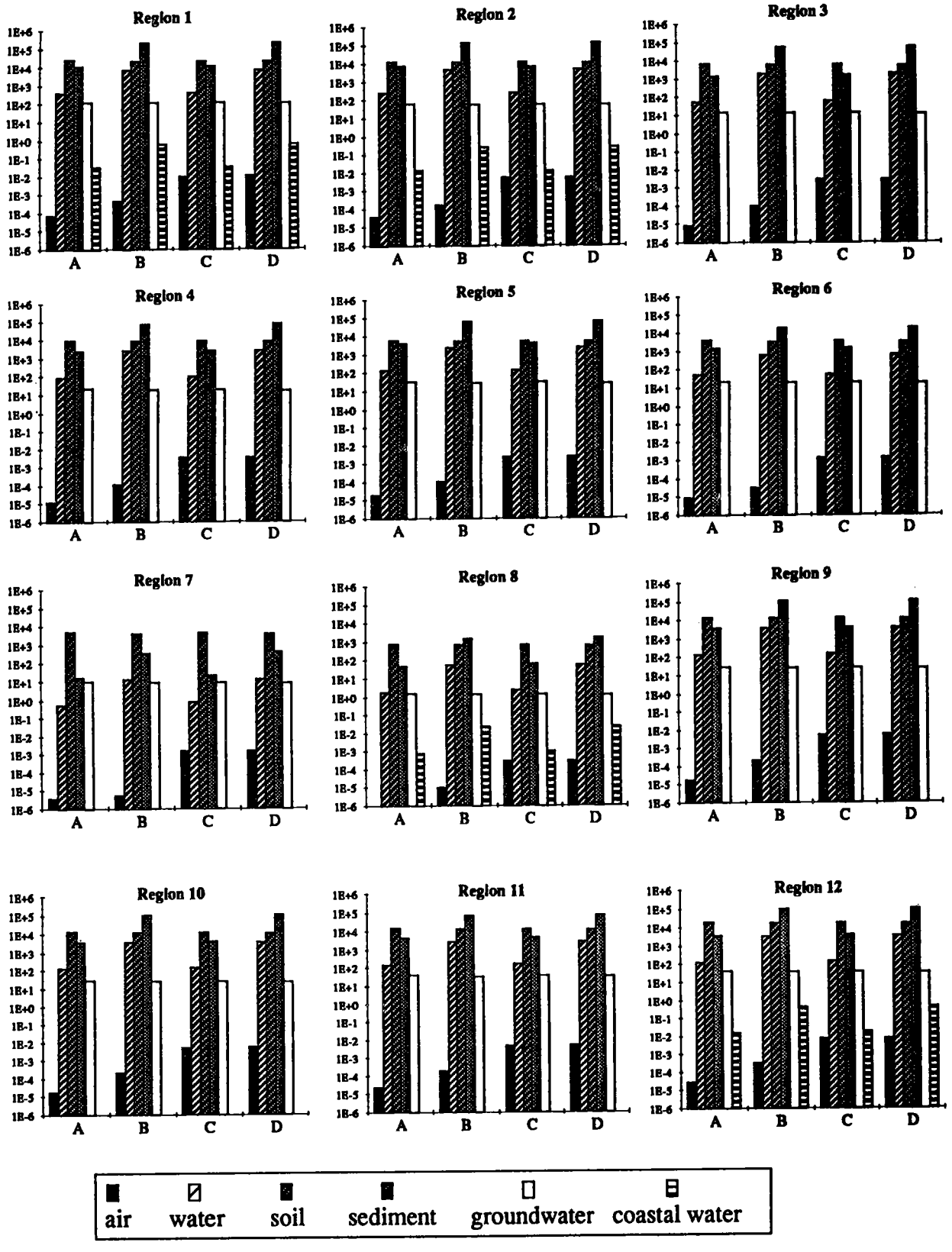

Figure 1. Lindane concentrations (ng/l) for the bulk compartments calculated with CHEMFRANCE for the twelve defined regions and the four scenarios (see text).

Table III. Comparison between field and predicted (scenarios A-D) concentrations (ng/l).

Date, region of CHEMFRANCE	Actual concentration mean&	maximum	Reference	Predicted concentration A	B	C	D
Surface water compartment							
7 rivers (05/1980 to 07/1981), region 1	78.0 (n = 141)	450	35	390.1	7200	387.3	7197
4 rivers (17/04/1990 to 24/07/1990), region 1	95.2 (n = 39)	400	35	390.1	7200	387.3	7197
4 rivers (17/04/1991 to 24/07/1991), region 1	56.1 (n = 27)	400	35	390.1	7200	387.3	7197
12 rivers (04/1991 to 11/1991), region 1	16.6 (n = 75)	70	35	390.1	7200	387.3	7197
1 river (17/04/1990 to 24/07/1990), region 2	48 (n = 10)	103	35	270.8	4999	260.7	4989
1 river (17/04/1991 to 24/07/1991), region 2	41.3 (n = 7)	153	35	270.8	4999	260.7	4989
2 rivers (04/1991 to 11/1991), region 2	73.8 (n = 8)	200	35	270.8	4999	260.7	4989
Yonne river (01/1988 to 03/1991), region 3	22 (n = 3)	36	43	53.35	1908	56.48	1911
Seine barrage (26/03/90 to 19/11/90), region 3	13.6 (n = 46)	29	35	53.35	1908	56.48	1911
29 rivers (summer 1990), region 9	37.2 (n = 46)	550	35	137.0	3707	143.6	3713
17 rivers (summer 1990), region 11	63.2 (n = 24)	550	35	127.3	3444	142.5	3459
Groundwater compartment							
(05/1978 to 12/1987), region 1	9.5 (n = 16)	31	35	122.0	110.0	110.5	98.46
(summer 1990), region 9	183.8 (n = 14)	1125	35	28.60	25.78	26.07	23.25
(summer 1990), region 10	92 (n = 6)	213	35	38.77	34.97	35.85	32.05
Air compartment							
air (05/1988 to 07/1989), Creteil, region 3	2.1 10-3*	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (05/1988 to 07/1989), Paris, region 3	1.7 10-3*	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1986), Paris, region 3	1.4 10-3$	not given	16	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1987), Paris, region 3	1.4 10-3$	not given	16	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (07/1989 to 07/1990), Paris, region 3	1.5 10-3$	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1986 to 1990), in spring at Paris, region 3	2.7 10-3£ (n = 7)	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1986 to 1990), in summer at Paris, region 3	1.4 10-3£ (n = 6)	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1986 to 1990), in fall at Paris, region 3	1.3 10-3£ (n = 7)	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
air (1986 to 1990), in winter at Paris, region 3	0.7 10-3£ (n = 5)	not given	18	8.96 10-6	97.1 10-6	2.82 10-3	2.91 10-3
rain (1988), region of Paris, region 3	130 (n = 6)	150	36	0.34	3.71	107.7	111.2
rain (1986), region of Paris, region 3	39 (n = ?)	90	36	0.34	3.71	107.7	111.2
rain (1986), Paris, region 3	29 (n = ?)	40	36	0.34	3.71	107.7	111.2
rain (1986), region of Paris, region 3	28 (n = ?)	70	36	0.34	3.71	107.7	111.2

& n = number of values; * mean monthly concentration; $ mean annual concentration; £ mean seasonal concentration

Table IV. Comparison between field and predicted (scenarios A-D) fish concentrations in region 3 (μg/kg wet weight).

Species, date, location	Actual concentration mean&	maximum	Ref.	Predicted concentration A	B	C	D
Roach, (04/1991 to 05/1991), Seine river	29.25 (n = 7)	97.5	42	26.2	940	27.8	940
Roach, (04/1991 to 05/1991), Yonne river	11.25 (n = ?)	not given	42	26.2	940	27.8	940
Roach, (04/1991 to 05/1991), Marne river	12.25 (n = ?)	not given	42	26.2	940	27.8	940
Roach, (10/1991), Seine river	13.5 (n = ?)	not given	43	26.2	940	27.8	940
Perch, (10/1991), Seine river	15.0 (n = ?)	not given	43	26.2	940	27.8	940

& n = number of values

The field bioconcentration factors of lindane in fish[46] ranging between 435 and 758 are on the same order of magnitude as that derived by the QSAR equation[52] (i.e.; ~500) included in CHEMFRANCE.

In the air compartment, lindane is principally present in pure air (i.e.; 99.3%), and only a low quantity is bound to the air particles (i.e.; 0.7%). This percentage of lindane associated with air particles is in agreement with field measurements in the Lake Ontario area indicating low particulate-associated fractions of lindane (i.e.; generally <1%).[53]

The great tendency of lindane to be sorbed[31] explains the high percentage (i.e.; >99%) of lindane bound to solid components in the soil and sediment compartments of CHEMFRANCE. This sorption capacity also induces an accumulation in the suspended sediments,[32] as depicted by the sorption coefficient of lindane in this subcompartment (i.e.; ~2000) obtained by the QSAR model[54] used in CHEMFRANCE.

CONCLUSION

The literature data analysis on the environmental fate and hazards of lindane reveals its high potential for accumulation in biota and its capacity to be bound to the solid components of abiotic media. In addition to the risk of human contamination from food, inhalation exposure cannot be neglected due to potential atmospheric contamination through volatilization and spray applications. Surface waters, as well as the marine compartment, are only weakly contaminated by lindane. Indeed, runoff, water advection, and atmospheric deposition processes are not considered as major fate pathways and therefore lead to relatively low amounts of lindane being present in these compartments. The weak groundwater concentrations are linked to the slow leaching process. The similarity between the actual environmental fate profile of lindane and that obtained from CHEMFRANCE underlines the relevance of this fugacity model in simulating the environmental fate of this pesticide. From these results and those recently obtained,[45] it appears that CHEMFRANCE is a useful tool for estimating the environmental fate of organic chemicals in France. Information on the availability of this computer program can be obtained from the authors.

ACKNOWLEDGMENTS

The authors are grateful to Dr. D.M. Kane (Health and Welfare, Ottawa, Canada) for his comments. This study was granted by the French Ministry of the Environment.

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ARTICLE V

Pergamon

PII: S0045-6535(96)00145-2

Chemosphere, Vol. 32, No. 12, pp. 2441–2456, 1996

0045-6535/96 $15.00+0.00

EVALUATING THE ENVIRONMENTAL FATE OF ATRAZINE IN FRANCE

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(Received in Germany 31 January 1996; accepted 18 March 1996)

ABSTRACT

Atrazine is used in large quantities in U.S. and European countries as a weed-control agent. As a result, numerous data on its environmental fate and hazards have been published. Analysis of the literature shows that this herbicide can be found with appreciable concentrations in groundwaters, rivers, lakes, and estuaries. This contamination principally results from leaching and runoff processes. Atrazine can also pollute fog and rain due to its release into the atmosphere through spray applications. This large amount of information constitutes a very attractive basis for assessing the simulation performances of environmental fate models. In this context, CHEMFRANCE, a regional fugacity model level III which calculates the environmental distribution of organic chemicals in twelve defined regions of France has been used to estimate the environmental fate of atrazine. The calculated values are comparable with field and laboratory results. Therefore, CHEMFRANCE can be considered as a useful tool for simulating the environmental fate of this agrochemical.

INTRODUCTION

Atrazine is a selective pre- and post-emergent weed-control agent for corn and millet cultivations. It is also used in asparagus, forestry, grassland, grass crops, sugarcane, sorghum, and pineapple.[1] In addition, atrazine is employed at higher rates as a nonselective herbicide for general weed control (e.g.; along roads and railroads).[2] The world consumption of atrazine is estimated to be ~70000 t/year (90% for corn cultivations).[3] In France, large amounts of atrazine are applied each year (e.g.; 5000 t in 1986 used in pre-emergence on 3 10^6 ha of corn crops).[4]

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Due to the agricultural and non-agricultural applications, subsequent surface runoff,[5-7] and leaching to groundwater,[8] the environment is widely contaminated by this chemical. Atrazine causes considerable pollution in the groundwater and surface water in France and all over the world.[9-14] Furthermore, atrazine can also pollute fog and rain due to its release into the atmosphere through spray applications.[10,14-18] Due to its economic and environmental concerns, numerous publications dealing with the environmental fate and hazards of atrazine are available. This bibliography provides a comprehensive understanding of the processes governing the fate and hazards of this chemical.

In contrast, it is well recognized that for estimating the environmental fate of chemicals, models at different levels of complexity represent very attractive tools when experimental results are scarce. Among them, the level III fugacity models are particularly powerful for estimating the environmental distribution of pollutants in biotic and abiotic media.[19] In this context, CHEMFRANCE, a level III fugacity computer model was developed to simulate the environmental fate of organic chemicals in France.[20] The assessment is based on information in connection with environmental parameters, emission rates, and physicochemical and reactive properties of the organic chemicals. However, the main problem with these types of models is to determine if the simulation results are realistic. Under these conditions, the aim of this paper was first to review the large amount of bibliography available on atrazine in order to derive the environmental fate profile of this agrochemical and then to compare field and laboratory results with those obtained with CHEMFRANCE. This exercise is required in order to underline the usefulness and limitations of CHEMFRANCE in the estimation of the environmental behavior of the organic chemicals in France.

LITERATURE DATA ANALYSIS

PHYSICOCHEMICAL PROPERTIES

The estimation of the environmental distribution of a pesticide highly depends on its basic physicochemical properties.[21] For atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine, CAS RN 1912-24-9), the physicochemical data found in the literature are numerous and an appreciable variability is observed. Therefore, great care must be taken in their selection. Indeed, it was shown that the physicochemical properties of the molecules significantly influence the results obtained with the fugacity models.[22,23] An extensive bibliographical survey permitted the selection of the following physicochemical properties:

- Molecular weight: 215.69 g/mol,
- Solubility in water: 30 mg/l at 20°C,[24]
- Vapor pressure: 4 10^{-5} Pa at 20°C,[24]
- *n*-Octanol/water partition coefficient (log P): 2.34,[24]
- Melting point: 174°C,[25]
- pKa: 1.70.[24]

ENVIRONMENTAL BEHAVIOR

Degradation

In its pure state, atrazine is relatively stable and may be stored for a period of several years.[2] In the environment, its transformation begins immediately after application[26] and follows three main pathways. The first deals with hydrolysis of the chlorine-carbon bond inducing the formation of hydroxyatrazine which is one of the main degradation products in both the soil and the aquatic systems.[8,27-30] Note that this hydrolysis yielding hydroxyatrazine is considered as a major step in the deactivation process of the herbicide.[29,31] The second is a *N*-dealkylation of carbon no. 4 and/or no. 6 which gives rise to deethylated atrazine, deisopropylated atrazine, and 2-chloro-4,6-diaminotriazine.[8,28-30,32] Both deethylated atrazine and deisopropylated atrazine are phytotoxic degradation products,[32] but 2-chloro-4,6-diaminotriazine has been shown to be nonphytotoxic in oat bioassays.[29] Nevertheless, atrazine is significantly more toxic than its degradation products towards *Chlorella pyrenoidosa, Scenedesmus quadricauda, Anabaena inaequalis, A. cylindrica,* and *A. variabilis.*[33] The third degradation process corresponds to the splitting of the triazine ring usually caused by microorganisms.[2]

The reported rates of decomposition in the various media of the environment are extremely variable.[2] In soil, the persistence of atrazine is influenced by a large number of physical, chemical, and biological factors.[26,27,34-36] In aquatic systems, the rate of hydrolytic and photolytic decomposition is affected by the chemical composition of the water.[2,26] When released into the atmosphere, reactions with photochemically produced hydroxyl radicals may be important.[37] Therefore, as stated above, the data concerning the environmental degradation of atrazine are numerous and variable. The degradation behavior of atrazine can be summarized by means of the following values of reaction half-lives:

- Half-life in soil: 1440 h,[38]
- Half-life in sediment: 420 h,[39]
- Half-life in water: 180 h,[39]
- Half-life in air: 19 h.[39]

The above values were selected from a perusal of the literature. However, they must only be regarded as a compromise to summarize the degradation profile of this chemical. Undoubtedly, there is considerable variation in these half-lives from place-to-place and from time-to-time, for example with temperature.

Levels of contamination in the different compartments of the environment

Soil contamination

The atrazine soil concentrations depend on agricultural and non-agricultural practices, soil composition, and climatic conditions.[14] The recommended application level of atrazine in corn crops in the European community (EC) (i.e.; 1.5 kg of active ingredient per hectare)

corresponds to a concentration of 0.5 µg/g of dry soil.[14] Pesticides added to soils are subject to sorption and to several chemical and biological degradation mechanisms that promote reduction of pesticide concentrations in the soil. One year after its soil application, the amount of atrazine present in the top surface soil is estimated to be around 8 to 20% of the initial level solution.[14]

Surface water contamination

Numerous reports and publications have been written on the level of atrazine contamination of surface waters in various European countries and in North America.[9-14.16.40] The concentration of atrazine in water strongly depends upon the seasons, with maximum concentrations during the period when crops are planted. Table I gives the upper peak values in surface waters encountered during studies carried out between 1989 and 1991 in European countries.[3.12] However, the mean level in each case is far lower than the maximum concentration. In U.S. rivers, atrazine concentrations between 0 and 87 µg/l have been found.[2] In aquatic systems, atrazine is taken up by nearly all members of the aquatic biocenoses, but in many cases, it is also quickly eliminated.[2] In France, a study performed in four rivers of Brittany highly contaminated by atrazine revealed no detectable concentration of atrazine in fish.[41] Only few investigations on the atrazine contamination of estuarine and sea waters in Europe have been carried out.[40.42-44] It is worth noting that these studies reported significant concentrations of atrazine in estuarine Mediterranean waters (e.g.; 17 10^{-3} to 0.386 µg/l in the Rhone Delta),[40] in the Baltic and North Sea (e.g.; 1 10^{-3} to 0.11 µg/l in German Bight),[43] and in British estuarine rivers.[42]

Table I. Maximum atrazine concentrations in surface waters (1989-1991).[3.12]

Country	Concentration
Belgium	3.7 µg/l
Denmark	0.42 µg/l
France	7.5 µg/l
Germany	0.42 µg/l
Italy	2 µg/l
Luxembourg	0.6 µg/l
The Netherlands	9.4 µg/l
UK	
- England	10 µg/l
- Scotland	4.23 µg/l
- Wales	0.17 µg/l

Groundwater contamination

When applied on soils, pesticides migrate through the other environmental compartments by several processes such as volatilization, leaching, and runoff. The risk of groundwater

contaminations from vertical transports is ultimately determined by the balance between the rates of chemical sorption and degradation in soil profile.[45] Atrazine is only moderately sorbed in soil systems and is relatively persistent.[24,36,46] Indeed, one year after its application, atrazine residues are still found in soil.[14,32] Therefore, this herbicide can potentially contaminate groundwaters.[47] Thus, in the numerous sampling programs concerning groundwater contamination of various western European countries, atrazine was one of the most frequently detected pesticides.[12,14] Nevertheless, the concentrations recorded were generally lower than those found in surface water samples. In some cases the measured concentrations were greater that the EC limit (i.e.; 0.1 µg/l). This is clearly illustrated in Table II which shows that more than 30% of the French population is exposed to concentrations above the admissible limit. For comparison purposes, in the United States, during a national survey on the pesticides in drinking water wells, recorded atrazine concentrations ranged between 0.18 and 1.04 µg/l.[2]

Table II. Distribution of the French population as a function of maximum and mean atrazine concentrations (µg/l) in the water supplies (before any treatment) in 1990.[12]

max. conc.	**<0.1**	**0.1-0.2**	**0.2-0.5**	**0.5-1.0**	**1.0-2.0**	**>2.0**
% of population	66.3	15.5	14.2	2.4	0.9	0.7
mean conc.	**<0.1**	**0.1-0.2**	**0.2-0.5**	**0.5-1.0**	**1.0-2.0**	**>2.0**
% of population	77.8	11.6	7.5	2.3	0.5	0.3

Atmospheric contamination

Despite the low rates of atrazine volatilization,[48,49] several studies have reported the presence of this herbicide in air, rain, snow, and fog samples. The presence of atrazine in the atmospheric environment could be due to spray droplet drift-off during its application or wind erosion of soil particles and wettable powder formulations from treated areas.[14] Atrazine volatilization, favored by the increasing moisture of soil surface, contributes to a smaller extent to the atmospheric contamination.[14,50]

Thus, for example, in the United States, concentrations in fog from 270 to 820 ng/l were recorded.[15] In air samples, concentrations between <0.2 10^{-3} and 3.4 10^{-3} ng/l were measured.[15] In rain, the 1.0 µg/l level is frequently exceeded.[16,17] In Maryland, the mean concentration of atrazine in air samples was 3.7 10^{-3} ng/l in summer and 0.026 10^{-3} ng/l in winter 1982.[16] In France, concentrations of atrazine between <5 ng/l and 140 ng/l were found in rain water samples collected in Paris in 1991.[18] In the same study, this herbicide was only detected in the vapor phase between April and June at concentrations of ca. 0.05 10^{-3} ng/l.[18] In eastern France, concentrations in rain samples from 2300 to 3170 ng/l were recorded.[14] In Switzerland, the analysis of rain and snow samples revealed concentrations between 0 and 600 ng/l.[10] It is interesting to note that most of these studies showed that the concentrations of atrazine were strongly dependent upon the seasons.

CHEMFRANCE

DESCRIPTION

The complete description of CHEMFRANCE with all equations, definition of the regions, and so on can be found in a previous publication.[20] Briefly, in CHEMFRANCE, France has been divided into twelve regions of homogeneous hydrogeological, climatic, and ecologic characteristics. The environment is represented by a multimedia system constituted of six bulk compartments (i.e.; air, surface water, soil, bottom sediment, groundwater, coastal water). The first four bulk compartments are considered to be a combination of subcompartments of varying proportions of pure and particle phases. CHEMFRANCE is based on a level III fugacity model for which equilibrium within each bulk compartment is considered, but not between compartments. Expressions for emissions, advective flows, degrading reactions, and interphase transports by diffusive and non-diffusive processes are included. As input, the model requires information on the physicochemical properties (i.e.; molecular weight, aqueous solubility, vapor pressure, *n*-octanol/water partition coefficient, dissociation constant, melting point), reaction half-lives, and emission rates of the studied chemical. The output of the model principally consists of the estimated chemical distribution between environmental media, transport and transformation process rates, and steady-state concentrations in France or in a particular French region (Figure 1) at a defined season.

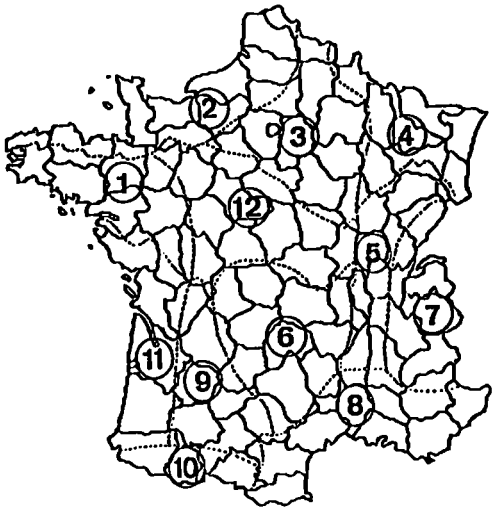

Figure 1. Defined regions of CHEMFRANCE.

MODELING STRATEGY

With the physicochemical properties and degradation half-life values listed in the previous section, almost all information necessary to run CHEMFRANCE is available. Indeed, only the

estimations of the amounts applied in each of the twelve defined regions of CHEMFRANCE (Figure 1) are missing as well as the definition of the media in which the release occurs. For obtaining the former information, some assumptions have to be made. In addition, numerous data dealing with the surface of treated crops, the applied dose, the number of treatments per year, and the percentage of active ingredient included in the formulations have to be collected. Thus, in France, atrazine is essentially used for pre- and post-emergence weed control in corn crops.[4] In 1991, corn crops represented 19.1% (i.e.; 3444082 ha) of French cultivated lands.[51] This indicates that an estimation of the total release of atrazine in France can be obtained principally from its application in corn crops. In addition, this shows that the release of atrazine into the environment principally occurs in spring and this was the season chosen to run CHEMFRANCE. A sample survey performed by the BVA institute on the use of weed control on corn crops in France in 1990 resulted in the following information on atrazine:

- Mean % of ha of corn crops treated: 99%,
- Mean number of treatment per year: 1.87,
- Mean % of ha of corn crops treated with atrazine alone: 36.9%,
- Mean % of ha of corn crops treated with atrazine associated with simazine: 2.6%,
- Mean % of ha of corn crops treated with atrazine associated with other active ingredients (e.g.; pendimethalin, cyanazine, metolachlor, alachlor, pyridate): 13.5%.

The survey also gave the mean dose applied for each formulation. The percentages of active ingredient of atrazine contained in these formulations were retrieved from a phytosanitary index[52] and the estimations of corn crop surfaces corresponding to the defined regions of CHEMFRANCE were estimated from the data given department by department.[53] With the above information, the amounts of atrazine applied on corn crops in the twelve defined regions of CHEMFRANCE in 1990 were estimated. In order to take into account the application of atrazine on other crops, and also on non-agricultural areas, we assumed that the use of atrazine as weed control in corn crops represented 90% of its total consumption.[3] These calculations yielded the global release in 1990 for the twelve regions of CHEMFRANCE (Table III). It is interesting to compare this estimation with the data related to the importations of atrazine in France between 1973 and 1991 (Figure 2).

The emission processes were simulated from four different scenarios. The first considered a total emission of atrazine into the soil compartment (scenario A). Scenario B took into account accidental pollutions occurring in surface waters (e.g.; cleaning tank near river) and the release via effluents at manufacturing sites. Therefore, in this scenario, emissions of 90% into the soil and 10% into the surface water compartment were assumed. The commercial formulations of atrazine usually involve spray applications on agricultural or non-agricultural areas which allow the dissemination of fine droplets providing a uniform distribution of a small volume over a large area. Through spray applications, significant quantities of atrazine may be released into the atmosphere.[14,54] Therefore, the third scenario (scenario C) was designed to also consider a loss of 1% into the air compartment of the atrazine applied on soil. The last scenario (scenario D) summarized all the previous assumptions (i.e.; 89% in soil, 10% in surface water, 1% in air).

Table III. Estimated total emission rates of atrazine for the twelve defined regions of CHEMFRANCE.

Region*	Emission (kg/y)
1	913130
2	576290
3	347700
4	298870
5	183720
6	193490
7	127010
8	29790
9	413590
10	147320
11	617080
12	510220
France	4358210

* For location, see Figure 1.

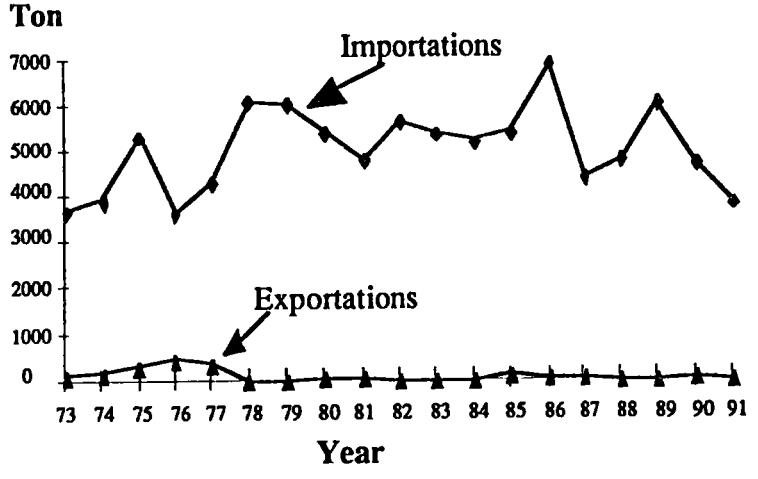

Figure 2. Importations and exportations of atrazine between 1973 and 1991 in France.

SIMULATION RESULTS AND COMPARISON WITH LABORATORY AND FIELD OBSERVATIONS

Table IV gives the average percentages corresponding to the removal processes obtained for the twelve defined regions of CHEMFRANCE. In all cases, atrazine is principally removed from the system by reaction in soil. This is in accordance with experimental studies.[54,55] As expected, the reaction in water significantly increases when emissions of atrazine in water compartment are simulated (i.e.; scenarios B and D). The dissipation of atrazine by advective processes for the air and water compartments is low. Furthermore, as atrazine is relatively rapidly degraded in air and water, the risk of contamination of adjacent regions is minor. However, this transport must not be neglected since it was suggested that this type of contamination was the major reason for the presence of atrazine in non-treated areas (e.g.; mountain lake).[10]

Field and laboratory studies clearly demonstrated the risk of groundwater contaminations by atrazine from vertical transports. Our results reveal that about 5% of the emissions leach to groundwater (Table IV). This percentage is close to the results obtained in a laboratory experiment in which 5.64% of the emissions are subjected to the leaching process.[8] However, it must be emphasized that the pollution of groundwater is principally due to the chlorinated metabolites of atrazine and more specifically deethylated atrazine, rather than atrazine. Indeed, a lysimeter study showed that atrazine represented only 10% of the leached compounds.[56]

Table IV. Average percentages of each removal process obtained from the four scenarios.

Removal process	Scenario A	Scenario B	Scenario C	Scenario D
air advection	$6\ 10^{-5}$	$5\ 10^{-5}$	$6\ 10^{-3}$	$6\ 10^{-3}$
water advection	0.12	0.31	0.12	0.31
reaction in air	$2\ 10^{-4}$	$4\ 10^{-5}$	0.03	0.03
reaction in water	5.34	14.45	5.35	14.46
reaction in soil	88.98	80.09	88.94	80.05
reaction in sediment	0.08	0.22	0.08	0.22
transfer to higher altitude	$7\ 10^{-8}$	$6\ 10^{-8}$	$7\ 10^{-6}$	$5\ 10^{-7}$
leaching to groundwater	5.48	4.93	5.48	4.93
sediment burial	$2\ 10^{-4}$	$4\ 10^{-4}$	$2\ 10^{-4}$	$4\ 10^{-4}$

The calculated percentage of loss of atrazine by runoff (i.e.; 5.54%) is in accordance with the mean percentage (i.e.; 3.19%) obtained in field analyses.[7] This shows the importance of horizontal transports in the contamination of the surface waters by atrazine. Despite the importance of the runoff process, the rain deposition of dissolved atrazine leading to low contamination levels cannot be neglected. In addition, from the results obtained with scenarios C and D, we can observe that more than 90% of the atmospheric emissions of atrazine are deposited by rain on the soil and water compartments. The wet and dry deposition processes are negligible. In the same way, the transfers of atrazine from soil and water to the air compartment are very weak. Schiavon and coworkers[56] reported volatilization data ranging between 0.017% and 60% of applied dose and selected the values of 0.05% and 0.08%.[49] These values agree with the average percentage of volatilized atrazine obtained in our four scenarios (i.e.; 0.02%). This confirms the minor influence of this process in the environmental fate of atrazine. The transfer rates of atrazine between the sediment and water compartments are dominated by the sorption process. This induces the accumulation of atrazine in the bottom sediment. The other transfer rates (i.e.; sediment resuspension, diffusion from air to soil and water) between the four principal compartments (i.e.; air, surface water, soil, bottom sediment) are negligible in all the scenarios.

Figure 3 summarizes the concentrations in the six bulk compartments for the twelve defined regions of CHEMFRANCE. It shows the relatively low differences between the four scenarios, except for the air compartment, in which the contamination significantly increases for scenarios C and D. Observed concentrations in air, surface water, and groundwater as well as those derived from the different simulation scenarios are reported in Table V.

The high surface water and groundwater concentrations obtained in all the simulations (Figure 3) are in accordance with atrazine field data (Table V). Nevertheless, the results obtained for the groundwater compartment are of lesser quality. No data are available for the French sea water contamination by this herbicide. Therefore, our results are not directly comparable with field data. Nevertheless, it is interesting to note that the study dealing with the contamination of the German Bight (North Sea) reported concentrations of atrazine between $<<1$ to 110 ng/l,[43] which greatly exceed our results corresponding to the same area (i.e.; $6.18\ 10^{-2}$ to 0.15 ng/l).

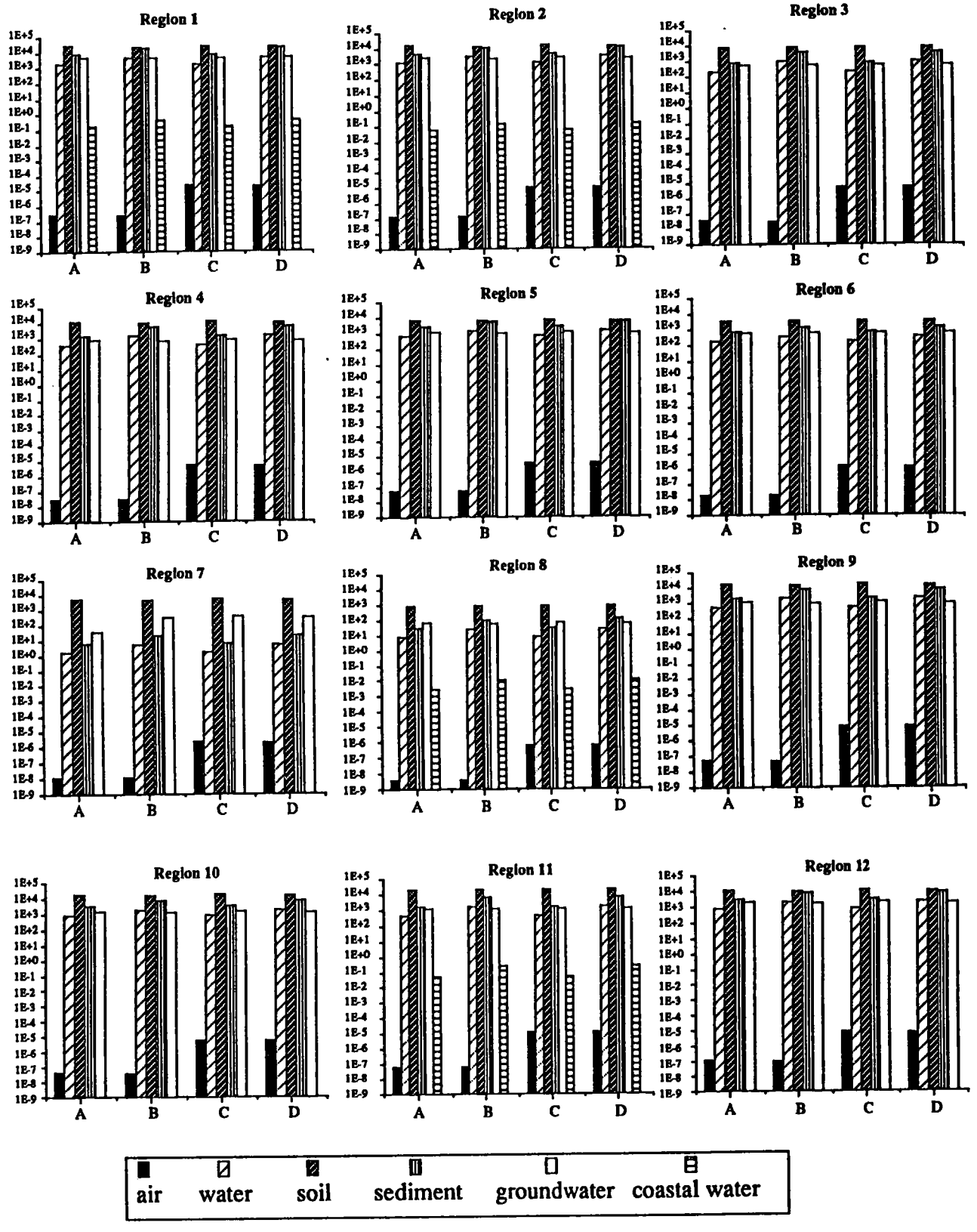

Figure 3. Atrazine concentrations (ng/l) for the bulk compartments calculated with CHEMFRANCE for the twelve defined regions and the four scenarios (see text).

Table V. Comparison between field and predicted (scenarios A-D) concentrations (ng/l).

Date, region of CHEMFRANCE	Actual concentration		Reference	Predicted concentration			
	mean[$]	maximum		A	B	C	D
Surface water compartment							
4 rivers (17/04/1990 to 24/07/1990), region 1	2149 (n = 40)	7460	41	1949	4711	1950	4712
4 rivers (17/04/1991 to 24/07/1991), region 1	984 (n = 26)	3050	41	1949	4711	1950	4712
12 rivers (04/1991 to 11/1991), region 1	210 (n = 75)	750	41	1949	4711	1950	4712
1 river (17/04/1990 to 24/07/1990), region 2	1747 (n = 10)	6030	41	1236	2989	1237	2989
1 river (17/04/1991 to 24/07/1991), region 2	788 (n = 7)	2500	41	1236	2989	1237	2989
2 rivers (04/1991 to 11/1991), region 2	1206 (n = 8)	2400	41	1236	2989	1237	2989
Seine barrage, region 3	98 (n = 46)	260	41	195.1	951.2	195.5	951.6
9 rivers (04/07/1989 to 28/08/1989), region 3	360 (n = 106)	1550	41	195.1	951.2	195.5	951.6
Seine river (July 1987), region 3	810 (n = 1)		13	195.1	951.2	195.5	951.6
Marne river (July 1987), region 3	60 (n = 1)		13	195.1	951.2	195.5	951.6
1 river (18/03/1991 to 16/03/1992), region 4	159 (n = 51)	340	41	375.8	1308	376.4	1309
29 rivers (summer 1990), region 9	165 (n = 47)	710	41	593.5	2066	594.4	2067
Rhone delta (10/1990 to 03/1994), region 9	17-386[£]		40	593.5	2066	594.4	2067
Rhone river, 7 stations (10/1990), region 9	12-33[£]		44	593.5	2066	594.4	2067
15 rivers (summer 1990), region 11	277 (n = 24)	1000	41	460.6	1856	462.0	1858
Groundwater compartment							
(July 1987), region 1	60 (n = 1)		13	4614	4153	4612	4151
(July 1987), region 3	95 (n = 1)		13	565.7	509.1	565.4	508.8
(November 1987), region 3	225 (n = 1)		13	565.7	509.1	565.4	508.8
(07/1990 to 09/1990), region 4	182 (n = 39)	856	41	774.4	697.0	774.2	696.7
(November 1987), region 4	90 (n = 1)		13	774.4	697.0	774.2	696.7
(summer 1990), region 9	174 (n = 18)	630	41	1093	984.0	1093	983.6
(summer 1990), region 10	238 (n = 6)	430	41	1408	1267	1407	1266
(summer 1990), region 11	86.6 (n = 3)	130	41	1276	1148	1275	1148
(July 1987), region 11	110 (n = 1)		13	1276	1148	1275	1148
(April 1989), region 12	200 (n = 1)		13	1937	1743	1936	1742
Air compartment							
air (04/1991 to 06/1991), region 3	$5\ 10^{-5}$ (n = ?)	not given	18	$3.66\ 10^{-8}$	$3.40\ 10^{-8}$	$6.38\ 10^{-6}$	$5.74\ 10^{-6}$
rain (03/1991 to 12/1991), region 3	<5-140[£]		18	0.08	0.07	13.98	12.56

[$] n = number of values; [£] range

The calculated concentrations in the air compartment are relatively lower than those observed in the environment (Figure 3 and Table V). By means of an equation published by Mackay and coworkers[57], the concentrations in rain for region 3 were calculated from the air concentrations obtained with CHEMFRANCE. For scenarios A and B, the calculated rain concentrations are lower than those observed in Paris between March and December 1991 (Table V).[18] At the opposite, for scenarios C and D, the generated values are relatively closer to the actual data (Table V).

The calculated soil concentrations are lower than those expected after an application (i.e.; 0.5 µg/g) at the rate recommended by the EC. However, these results agree with those observed in a soil historically treated (i.e.; 0.025 µg/g) but before any further treatment.[30]

The mass distribution obtained in the soil compartment (i.e.; 96.7% in the solid components and 3.3% in the water and air contained in the pore of the soil) is near this reported by Tasli.[58] Indeed, in her study, 96% of the amount included in the soil is sorbed in the soil solids and 4% is dissolved in the soil water. In the same way, the results obtained for the sediment compartment indicate that 89% of the atrazine is sorbed and 11% dissolved. Huckins *et al.*,[48] in a microcosm study, found a slightly smaller percentage (i.e.; 86.1%) although the organic carbon content of their studied sediment (i.e.; 7.28%) was higher than this considered in CHEMFRANCE (i.e.; 4%). In the water compartment, ca. 99.9% of the total atrazine content of this compartment is dissolved in pure water, 0.07% is sorbed in the suspended sediment, and 0.002% is accumulated in biota (i.e.; fish). Field studies gave similar results (i.e.; 99.5% and 0.5% of atrazine in the dissolved and particulate river matter, respectively).[11] The mass distributions obtained for the air compartment cannot be compared with experimental results. In the air compartment, atrazine is principally present in pure air (i.e.; 89.2%), and only a low quantity is bound to the air particles (i.e.; 10.8%).

CONCLUSION

From the survey of literature data available on the environmental fate and hazards of atrazine, it appears that this chemical presents a high contamination potential for water systems, since leaching and runoff processes have been identified as major fate pathways. The results derived with CHEMFRANCE are in accordance with those obtained in laboratory or field experiments. Therefore, CHEMFRANCE can be considered as a useful tool for simulating the environmental fate of this agrochemical in France. In addition, CHEMFRANCE provides a concise environmental fate profile of atrazine while literature data on this herbicide are numerous and variable, and therefore, difficult to interpret. This underlines the usefulness of environmental fate models for confirming results of fields and laboratory studies but also to provide a comprehensive summary of the processes involved in the environmental fate of chemicals.

An interesting characteristic of models is that they allow the user to quickly test several hypotheses through different scenarios. Thus, in our study, four scenarios assuming different emission profiles were studied. By taking into account the accidental pollutions occurring in surface water and the releases into the atmosphere through spray applications (scenario D) gave

the most satisfactory results. However, many other scenarios integrating variations in seasons, quantities, and so on could have been tested. In the same way, it should be noted that models can be coupled with sensitivity and uncertainty analyses in order to test the influence of all input parameters and assumptions on the outputs.

ACKNOWLEDGMENTS

The authors are grateful to Pr. D. Mackay (Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada) for his thoughtful comments. This study was granted by the French Ministry of the Environment.

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ARTICLE VI

Modeling the Environmental Fate of Atrazine

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Mathematical simulation models of fate and transport of chemicals have been identified by researchers and regulators as potentially valuable tools for improving the understanding of the environmental behavior of chemicals which may be released to the environment as a consequence of routine (i.e.; normal manufacturing, use, disposal) and non-routine (e.g.; accidental spill) events. In this context, CHEMFRANCE, a regional fugacity model level III, which calculates the environmental distribution of organic chemicals in 12 defined regions of France, or France as a whole, has been designed. The aim of this study is to show that CHEMFRANCE provides interesting simulation results for understanding the environmental fate behavior of atrazine.

Organic chemicals may be released into the compartments of the biosphere as a result of their normal manufacture, formulation, use, and disposal or as a result of their accidental spill. Therefore, it is essential to develop both a qualitative and quantitative understanding of their environmental fate behavior (*1*). These insights, along with information on their possible adverse effects towards organisms occupying different trophic levels in the ecosystems, enable the risk to human health and the environment to be assessed. To achieve this understanding, the physicochemical properties of the organic compounds and emission patterns must be combined with the characteristics of the environment into which they are released in order to predict how advective and inter-compartment transport and transformation processes will affect their environmental distribution. However, because the environmental fate behavior of a chemical is always the result of numerous complex and interacting processes, the use of models is highly recommended. Among them, the Mackay-type multimedia models have shown their efficiency for estimating the environmental fate profile of numerous organic chemicals at a global or regional scale (*1-4*). In this context, CHEMFRANCE, a level III fugacity computer model, has been designed for simulating the environmental fate of organic chemicals in France (*5*). In this paper, we show the usefulness of CHEMFRANCE for simulating the environmental fate behavior of atrazine. Indeed, in France this herbicide is of environmental concern since it is widely used for control of certain annual broadleaf and grass weeds in corn, and to a lesser extent, other crops and landscaping (*6*).

Model Description

In CHEMFRANCE, France has been divided into twelve regions of homogeneous hydrogeological, climatic, and ecologic characteristics (Figure 1). The environment is represented by a multimedia system constituted of six bulk compartments (i.e.; air, surface water, soil, bottom sediment, groundwater, coastal water) presenting various characteristics summarized in Table I. The first four bulk compartments (Table I) are considered to be a combination of subcompartments of varying proportions of pure and particle phases. CHEMFRANCE is based on a level III fugacity model for which equilibrium within each bulk compartment is considered, but not between compartments. Expressions for emissions, advective flows, degrading reactions, and interphase transports by diffusive and non-diffusive processes are included. As input, CHEMFRANCE requires the molecular weight, aqueous solubility, vapor pressure, log P, pKa, melting point, reaction half-lives, and emission rates of the studied chemical. The outputs of CHEMFRANCE principally consist of the estimated chemical distribution between environmental media, transport and transformation process rates, and steady-state concentrations in France or in a particular French region (Figure 1) at a defined season. A more complete description of CHEMFRANCE can be found in a recent publication (*5*).

Data on Atrazine and Simulation Scenarios

The physicochemical data and reaction half-lives selected for running CHEMFRANCE were the following:
- molecular weight: 215.69 g/mol,
- solubility in water: 30 mg/l at 20°C (*7*),
- vapor pressure: 4 10^{-5} Pa at 20°C (*7*),
- *n*-octanol/water partition coefficient (log P): 2.34 (*7*),
- melting point: 174°C (*8*),
- pKa: 1.70 (*7*),
- half-life in soil: 1440 h (*9*),
- half-life in sediment: 420 h (*2*),
- half-life in water: 180 h (*2*),
- half-life in air: 19 h (*2*).

With the above physicochemical properties and degradation half-life values, almost all information necessary to run CHEMFRANCE is available. Indeed, only the estimations of the amounts applied in each of the twelve defined regions of CHEMFRANCE (Figure 1) are missing as well as the definition of the compartment in which the release occurs. For obtaining the former information, some assumptions have to be made. In addition, numerous data dealing with the surface of treated crops, the applied dose, the number of treatments per year, and the percentage of active ingredient included in the formulations have to be collected. Thus, in France, atrazine is essentially used for pre- and post-emergence weed control in corn crops (*6*). In 1991, corn crops represented 19.1% (i.e.; 3444082 ha) of French cultivated lands (*10*). This indicates that an estimation of the total release of atrazine in France can be obtained principally from its application in corn crops. In addition, this shows that the release of atrazine into the environment principally occurs in spring and this was the season chosen to run CHEMFRANCE. A sample survey performed by the BVA institute on the use of weed control on corn crops in France in 1990 resulted in the following information on atrazine:
- mean % of ha of corn crops treated: 99%,
- mean number of treatments per year: 1.87,
- mean % of ha of corn crops treated with atrazine alone: 36.9%,
- mean % of ha of corn crops treated with atrazine associated with simazine: 2.6%,
- mean % of ha of corn crops treated with atrazine associated with other active ingredients (e.g.; pendimethalin, cyanazine, metolachlor, alachlor, pyridate): 13.5%.

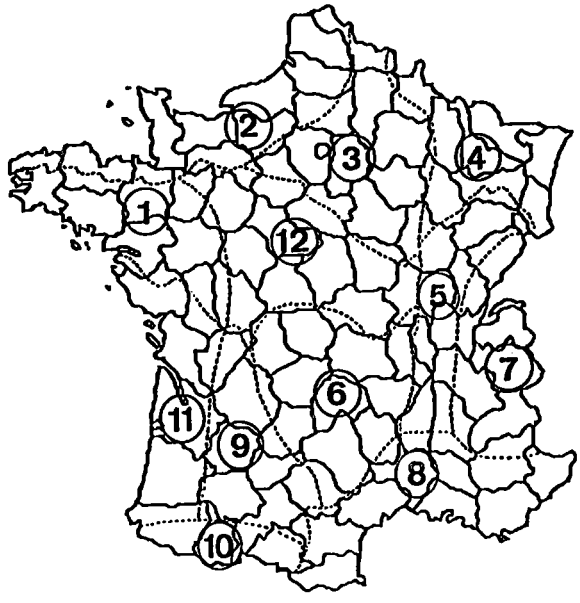

Figure 1. Defined regions of CHEMFRANCE

Table I. Principal characteristics of the bulk compartments in CHEMFRANCE

Compartment	Region-dependent characteristics*	Fixed model characteristics
Air	Total surface area	Residence time (5 d); Height (1000 m); Vf** of aerosols ($2\ 10^{-11}$); Pure air (1.2 kg/m^3) and aerosol density (1500 kg/m^3)
Water	Surface; Volume; Vf of Ss$^{\text{£}}$	Residence time (500 d); OC$^{\$}$ of Ss (20%); pH of Ss (7); Vf of biota ($1\ 10^{-6}$); Pure water and biota density (1000 kg/m^3); Ss density (1500 kg/m^3)
Soil	Surface; OC; pH	Depth (15 cm); Vf of air (0.2) and water (0.3); Pure soil density (2400 kg/m^3)
Sediment		Depth (3 cm); OC (4%); pH (7); Vf of water (0.7); Pure sediment density (2400 kg/m^3)
Groundwater	Volume	
Coastal water	Volume; Length	Depth (100 m)

*Monthly mean precipitations and temperatures for the four seasons are also region-dependent.

**Volume fraction; $^{\text{£}}$Suspended sediment; $^{\$}$% of organic carbon content.

The BVA survey also gave the mean dose applied for each formulation. The percentages of active ingredient of atrazine contained in these formulations and the estimations of corn crop surfaces corresponding to the 12 regions of CHEMFRANCE were retrieved from literature (*11, 12*). With the above information, the amounts of atrazine applied on corn crops in the 12 regions of CHEMFRANCE in 1990 were estimated. In order to take into account the application of atrazine on other crops, and also on non-agricultural areas, we assumed that the use of atrazine as weed control in corn crops represented 90% of its total consumption (*13*). These calculations yielded the global release in 1990 for the 12 regions of CHEMFRANCE (Table II).

Table II. Estimated total emission rates of atrazine for the 12 defined regions of CHEMFRANCE

Region*	Emission (kg/y)
1	913130
2	576290
3	347700
4	298870
5	183720
6	193490
7	127010
8	29790
9	413590
10	147320
11	617080
12	510220
France	4358210

*For location see Figure 1.

The emission processes were simulated from four different scenarios. The first considered a total emission of atrazine into the soil compartment (scenario A). Scenario B took into account accidental pollutions occurring in surface waters (e.g.; cleaning tank near river) and the release via effluents at manufacturing sites. Therefore, in this scenario, emissions of 90% into the soil and 10% into the surface water compartment were assumed. The commercial formulations of atrazine usually involve spray applications inducing the release of significant quantities into the atmosphere (*14, 15*). Therefore, the third scenario (scenario C) was designed to also consider a loss of 1% into the air compartment of the atrazine applied on soil. The last scenario (scenario D) summarized all the previous assumptions (i.e.; 89% in soil, 10% in surface water, 1% in air).

Simulation Results and Comparison with Laboratory and Field Observations

Table III gives the average percentages corresponding to the removal processes obtained for the 12 defined regions of CHEMFRANCE. In all cases, atrazine is principally removed from the system by reaction in soil. This is in accordance with experimental studies (*15, 16*). As expected, the reaction in water significantly increases when emissions of atrazine in water compartment are simulated (i.e.; scenarios B and D). The dissipation of atrazine by advective processes for the air and water compartments is low. Furthermore, as atrazine is relatively rapidly degraded in air and water, the risk of contamination of adjacent regions is minor. However, this transport must not be neglected since it was suggested that this type of contamination was the major reason for the presence of atrazine in non-treated areas (e.g.; mountain lake) (*17*).

Table III. Average percentages of each removal process obtained from the four scenarios

Removal process	Scenario A	Scenario B	Scenario C	Scenario D
Air advection	<<0.01	<<0.01	<<0.01	<<0.01
Water advection	0.12	0.31	0.12	0.31
Reaction in air	<<0.01	<<0.01	0.03	0.03
Reaction in water	5.34	14.45	5.35	14.46
Reaction in soil	88.98	80.09	88.94	80.05
Reaction in sediment	0.08	0.22	0.08	0.22
Transfer to higher altitude	<<0.01	<<0.01	<<0.01	<<0.01
Leaching to groundwater	5.48	4.93	5.48	4.93
Sediment burial	<<0.01	<<0.01	<<0.01	<<0.01

Table III shows that about 5% of the emissions leach to groundwater. This percentage is close to the results obtained in a laboratory experiment in which 5.64% of the emissions were subjected to the leaching process (*18*). However, it must be emphasized that the pollution of groundwater is principally due to the chlorinated metabolites of atrazine and more specifically deethylated atrazine, rather than atrazine. Indeed, a lysimeter study showed that atrazine represented only 10% of the leached compounds (*19*).

The calculated percentage of loss of atrazine by runoff (i.e.; 5.54%) is in accordance with the mean percentage (i.e.; 3.19%) obtained in field analyses (*20*). This shows the importance of horizontal transports in the contamination of the surface waters by atrazine. Despite the importance of the runoff process, the rain deposition of dissolved atrazine leading to low contamination levels cannot be neglected. In addition, from the results obtained with scenarios C and D, we can observe that more than 90% of the atmospheric emissions of atrazine are deposited by rain on the soil and water compartments. The wet and dry deposition processes are negligible. In the same way, the transfers of atrazine from soil and water to the air compartment are very weak. Schiavon and coworkers (*19*) reported volatilization data ranging between 0.017% and 60% of applied dose and selected the values of 0.05% and 0.08% (*21*). These values agree with the average percentage of volatilized atrazine obtained in our four scenarios (i.e.; 0.02%). This confirms the minor influence of this process in the environmental fate of atrazine. The transfer rates of atrazine between the sediment and water compartments are dominated by the sorption process. This induces the accumulation of atrazine in the bottom sediment. The other transfer rates (i.e.; sediment resuspension, diffusion from air to soil and water) between the four principal compartments (i.e.; air, surface water, soil, bottom sediment) are negligible in all the scenarios.

When the concentrations in atrazine in the six bulk compartments for the 12 defined regions of CHEMFRANCE are calculated, relatively low differences between the four scenarios are observed, except for the air compartment, in which the contamination significantly increases for scenarios C and D. Only the results obtained for the least and the most contaminated regions are given in Tables IV and V, respectively. Observed concentrations in air, surface water, and groundwater as well as those derived from the different simulation scenarios are reported in Table VI. The high surface water and groundwater concentrations obtained in all the simulations are generally in accordance with atrazine field data (Table VI). Nevertheless, the results obtained for the groundwater compartment are of lesser quality. No data are available for the French sea water contamination by atrazine. Therefore, our results are not directly comparable with field data. Nevertheless, it is interesting to note that the study dealing with the contamination of the German Bight (North Sea) reported concentrations of atrazine between <<1 and 110 ng/l (*22*), which greatly exceed our results corresponding to the same area (i.e.; 6.18 10^{-2} to 0.15 ng/l).

Table IV. Concentrations (ng/l) obtained with the four scenarios for region 8

Compartment	Scenario A	Scenario B	Scenario C	Scenario D
Air	$4.21\ 10^{-9}$	$3.89\ 10^{-9}$	$6.04\ 10^{-7}$	$5.44\ 10^{-7}$
Water	7.14	27.24	7.18	27.28
Soil	879.4	791.4	878.8	791.2
Sediment	27.67	105.6	27.83	105.8
Groundwater	59.88	53.89	59.84	53.87
Coastal water	$3.08\ 10^{-3}$	$1.18\ 10^{-2}$	$3.10\ 10^{-3}$	$1.18\ 10^{-2}$

Table V. Concentrations (ng/l) obtained with the four scenarios for region 1

Compartment	Scenario A	Scenario B	Scenario C	Scenario D
Air	$2.79\ 10^{-7}$	$2.55\ 10^{-7}$	$2.08\ 10^{-5}$	$1.88\ 10^{-5}$
Water	1949	4711	1950	4712
Soil	27920	25130	27910	25120
Sediment	7554	18260	7559	18270
Groundwater	4614	4153	4612	4151
Coastal water	0.16	0.39	0.16	0.39

The calculated concentrations in the air compartment are relatively lower than those observed in the environment (Table VI). By means of an equation published by Mackay and coworkers (*23*), the concentrations in rain for region 3 were calculated from the air concentrations obtained with CHEMFRANCE. For scenarios A and B, the calculated rain concentrations are lower than those observed in Paris between March and December 1991 (Table VI) (*24*). At the opposite, for scenarios C and D, the simulated values are relatively closer to the actual data (Table VI). The calculated soil concentrations are lower than those expected after an application (i.e.; 0.5 µg/g) at the rate recommended by the EC. However, these results agree with this observed in a soil historically treated (i.e.; 0.025 µg/g) but before any further treatment (*25*).

The mass distribution obtained in the soil compartment (i.e.; 96.7% in the solid components and 3.3% in the water and air contained in the pore of the soil) is near this reported by Tasli (*26*). Indeed, in her study, 96% of the amount included in the soil is sorbed in the soil solids and 4% is dissolved in the soil water. In the same way, the results obtained for the sediment compartment indicate that 89% of the atrazine is sorbed and 11% dissolved. Huckins and coworkers (*27*) in a microcosm study, found a slightly smaller percentage (i.e.; 86.1%) although the organic carbon content of their studied sediment (i.e.; 7.28%) was higher than this considered in CHEMFRANCE (i.e.; 4%). In the water compartment, ca. 99.9% of the total atrazine content of this compartment is dissolved in pure water, 0.07% is sorbed in the suspended sediment, and 0.002% is accumulated in biota (i.e.; fish). Field studies gave similar results (i.e.; 99.5% and 0.5% of atrazine in the dissolved and particulate river matter, respectively) (*28*). The mass distributions obtained for the air compartment cannot be compared with experimental results. In the air compartment, atrazine is principally present in pure air (i.e.; 89.2%), and only a low quantity is bound to the air particles (i.e.; 10.8%).

Table VI. Comparison between field and predicted (scenarios A-D) concentrations (ng/l)

Date, region of CHEMFRANCE	Actual concentration		Ref.	Predicted concentration			
	mean[$]	maximum		A	B	C	D
Surface water compartment							
4 rivers (17/04/1990 to 24/07/1990), region 1	2149 (n = 40)	7460	*29*	1949	4711	1950	4712
4 rivers (17/04/1991 to 24/07/1991), region 1	984 (n = 26)	3050	*29*	1949	4711	1950	4712
12 rivers (04/1991 to 11/1991), region 1	210 (n = 75)	750	*29*	1949	4711	1950	4712
1 river (17/04/1990 to 24/07/1990), region 2	1747 (n = 10)	6030	*29*	1236	2989	1237	2989
1 river (17/04/1991 to 24/07/1991), region 2	788 (n = 7)	2500	*29*	1236	2989	1237	2989
2 rivers (04/1991 to 11/1991), region 2	1206 (n = 8)	2400	*29*	1236	2989	1237	2989
Seine barrage, region 3	98 (n = 46)	260	*29*	195.1	951.2	195.5	951.6
9 rivers (04/07/1989 to 28/08/1989), region 3	360 (n = 106)	1550	*29*	195.1	951.2	195.5	951.6
Seine river (July 1987), region 3	810 (n = 1)		*30*	195.1	951.2	195.5	951.6
Marne river (July 1987), region 3	60 (n = 1)		*30*	195.1	951.2	195.5	951.6
1 river (18/03/1991 to 16/03/1992), region 4	159 (n = 51)	340	*29*	375.8	1308	376.4	1309
29 rivers (summer 1990), region 9	165 (n = 47)	710	*29*	593.5	2066	594.4	2067
Rhone delta (10/1990 to 03/1994), region 9	17-386[£]		*31*	593.5	2066	594.4	2067
Rhone river, 7 stations (10/1990), region 9	12-33[£]		*32*	593.5	2066	594.4	2067
15 rivers (summer 1990), region 11	277 (n = 24)	1000	*29*	460.6	1856	462.0	1858
Groundwater compartment							
(July 1987), region 1	60 (n = 1)		*30*	4614	4153	4612	4151
(July 1987), region 3	95 (n = 1)		*30*	565.7	509.1	565.4	508.8
(November 1987), region 3	225 (n = 1)		*30*	565.7	509.1	565.4	508.8
(07/1990 to 09/1990), region 4	182 (n = 39)	856	*29*	774.4	697.0	774.2	696.7
(November 1987), region 4	90 (n = 1)		*30*	774.4	697.0	774.2	696.7
(summer 1990), region 9	174 (n = 18)	630	*29*	1093	984.0	1093	983.6
(summer 1990), region 10	238 (n = 6)	430	*29*	1408	1267	1407	1266
(summer 1990), region 11	86.6 (n = 3)	130	*29*	1276	1148	1275	1148
(July 1987), region 11	110 (n = 1)		*30*	1276	1148	1275	1148
(April 1989), region 12	200 (n = 1)		*30*	1937	1743	1936	1742
Air compartment							
air (04/1991 to 06/1991), region 3	$5\ 10^{-5}$ (n = ?)	not given	*24*	$3.66\ 10^{-8}$	$3.40\ 10^{-8}$	$6.38\ 10^{-6}$	$5.74\ 10^{-6}$
rain (03/1991 to 12/1991), region 3	<5-140[£]		*24*	0.08	0.07	13.98	12.56

[$]n = number of values; [£]range

The correct use of a model requires to perform a sensitivity analysis showing how variations in the different model input parameters affect the outputs. In our study, a survey of the literature showed that the half-life of atrazine in soil widely varied according to the experimental and environmental conditions (Table VII). Similar observations were reported by Solomon and coworkers (*33*) for the half-lives of atrazine in water and sediments.

Table VII. Soil atrazine half-life ($T_{1/2}$) values obtained in literature

Experimental and environmental conditions	Ref.	$T_{1/2}$ (d)
Laboratory		
Loam, clay-sandy*; T°: 5; SMC: 7%	*34*	240.5
Loam, clay-sandy*; T°: 15; SMC: 7%	*34*	122.6
Loam, clay-sandy*; T°: 25; SMC: 7%	*34*	62.3
Loam, clay-sandy*; T°: 32; SMC: 7%	*34*	51.0
Loam, clay-sandy*; T°: 25; SMC: 4%	*34*	99.5
Loam, clay-sandy*; T°: 25; SMC: 10%	*34*	58.5
Loam, clay-sandy*; T°: 25; SMC: 13%	*34*	57.2
Loam-sandy$; T°: 5; SMC: 7%	*34*	271.0
Loam-sandy$; T°: 15; SMC: 7%	*34*	111.8
Loam-sandy$; T°: 25; SMC: 7%	*34*	65.7
Loam-sandy$; T°: 32; SMC: 7%	*34*	49.6
Loam-sandy$; T°: 25; SMC: 4%	*34*	78.5
Loam-sandy$; T°: 25; SMC: 10%	*34*	56.9
Loamy£; T°: 4; SMC: 17%	*34*	215.8
Loamy£; T°: 15; SMC: 17%	*34*	81.7
Loamy£; T°: 24; SMC: 17%	*34*	49.8
Loamy£; T°: 34; SMC: 17%	*34*	28.8
Loamy£; T°: 24; SMC: 5%	*34*	265.2
Loamy£; T°: 24; SMC: 10%	*34*	96.5
Loamy£; T°: 24; SMC: 15%	*34*	60.9
Loamy£; T°: 24; SMC: 20%	*34*	55.3
pH: 4.8; OM: 1.8; Cy: 10.5; St: 12.4; Sd: 77.1; T°: 22; H: 40; C_0: 10	*35*	53
pH: 6.5; OM: 3.8; Cy: 8.9; St: 7.3; Sd: 83.8; T°: 22; H: 40; C_0: 10	*35*	113
Fine sandy medium sand; pH: 7.7; OC: 0.1; H: 30; C_0: 3	*8*	90
Very coarse sand-fine sand; pH: 7.3; OC: 4.3; H: 42; C_0: 3	*8*	43
Very coarse sandy fine sand; pH: 7.4; OC: 1.5; H: 39; C_0: 3	*8*	50
Fine sand-medium sand; pH: 7.7; OC: 0.6; H: 38; C_0: 3	*8*	47
Silt loam+; H: 80; AR: 2.20	*36*	20/21
Sandy clay loam§; pH: 5.7; OM: 2.7; Cy: 22; St: 26; Sd: 52; W: 0.224	*37*	41
Loam§; pH: 6.2; OM: 2.7; Cy: 26; St: 34; Sd: 40; W: 0.293	*37*	69
Sandy clay loam§; pH: 6.2; OM: 1.7; Cy: 28; St: 26; Sd: 46; W: 0.269	*37*	69
Sandy clay loam§; pH: 6.2; OM: 1.6; Cy: 26; St: 28; Sd: 46; W: 0.245	*37*	231
Sandy clay loam§; pH: 6.2; OM: 1.6; Cy: 26; St: 28; Sd: 46; W: 0.545	*37*	87
Fine loam; pH: 5.9; OM: 1.1; Cy: 6; SMC: 15.8%; T°: 21; H: 80; C_0: 5	*38*	59.6
Sandy loam; pH: 5.5; OC: 0.91; Cy: 17; St: 14; Sd: 69; H: 60; W: 0.17	*39*	330
Silty loam; pH: 6.4; OC: 0.91; Cy: 32; St: 52; Sd: 16; H: 100; W: 0.5	*39*	385
Sandy loam&; SMC: 3%; C_0: 10	*40*	36.7
Sandy loam&; SMC: 6%; C_0: 10	*40*	34.6
Sandy loam&; SMC: 12%; C_0: 10	*40*	26.6
Sandy loam&; SMC: 6%; C_0: 1	*40*	64.0
Loamy-sand#; SMC: 1%; C_0: 10	*40*	32.1
Loamy-sand#; SMC: 2%; C_0: 10	*40*	26.5
Loamy-sand#; SMC: 4%; C_0: 10	*40*	22.9
Loamy-sand#; SMC: 2%; C_0: 1	*40*	51.9

Table VII *(continued)*

Experimental and environmental conditions	Ref.	$T_{1/2}$ (d)
Field		
Silt loam; pH: 5.1-5.5; AR: 2.8; No-till corn crop	*41*	60/72
Riparian zone; AR: 2.2; Depth: 90 cm; Poplar tree plot	*15*	16
Silt loam[@]; AR: 3.2; Depth: 3 cm	*36*	14
Fine sandy loam[§§]; pH: 5.0; AR: 1.12	*42*	9/15
Fine sandy loam[§§]; pH: 6.0; AR: 1.12	*42*	12/19
Fine sandy loam[§§]; pH: 7.0; AR: 1.12	*42*	15/23
Fine sandy loam[§§]; pH: 5.0; AR: 2.24	*42*	16/20
Fine sandy loam[§§]; pH: 6.0; AR: 2.24	*42*	18/23
Fine sandy loam[§§]; pH: 7.0; AR: 2.24	*42*	20/26
Fine sandy loam[§§]; pH: 5.0; AR: 3.36	*42*	17/22
Fine sandy loam[§§]; pH: 6.0; AR: 3.36	*42*	19/25
Fine sandy loam[§§]; pH: 7.0; AR: 3.36	*42*	21/28
Silt loam[&&]; pH: 5.0; AR: 1.12	*42*	18/19
Silt loam[&&]; pH: 6.0; AR: 1.12	*42*	27/28
Silt loam[&&]; pH: 7.0; AR: 1.12	*42*	36/37
Silt loam[&&]; pH: 5.0; AR: 2.24	*42*	22/27
Silt loam[&&]; pH: 6.0; AR: 2.24	*42*	28/34
Silt loam[&&]; pH: 7.0; AR: 2.24	*42*	36/41
Silt loam[&&]; pH: 5.0; AR: 3.36	*42*	25/27
Silt loam[&&]; pH: 6.0; AR: 3.36	*42*	31/33
Silt loam[&&]; pH: 7.0; AR: 3.36	*42*	37/39
Sandy loam[##]; pH: 5.0; AR: 1.12	*42*	6
Sandy loam[##]; pH: 6.0; AR: 1.12	*42*	8
Sandy loam[##]; pH: 7.0; AR: 1.12	*42*	10
Sandy loam[##]; pH: 5.0; AR: 2.24	*42*	7/10
Sandy loam[##]; pH: 6.0; AR: 2.24	*42*	9/12
Sandy loam[##]; pH: 7.0; AR: 2.24	*42*	10/14
Sandy loam[##]; pH: 5.0; AR: 3.36	*42*	8/10
Sandy loam[##]; pH: 6.0; AR: 3.36	*42*	9/12
Sandy loam[##]; pH: 7.0; AR: 3.36	*42*	11/13
Riparian zone; AR: 1; Depth: 2 cm	*8*	48

[*]pH: 8.6; OM: 1.22; Field capacity at -5 kPa: 17.4%; Bulk density: 1.3 g/cm^3
[$]pH: 8.5; OM: 1.23; Field capacity at -5 kPa: 10.6%; Bulk density: 1.2 g/cm^3
[£]pH: 7.8; OM: 0.93; Field capacity at -5 kPa: 20.4%; Bulk density: 1.4 g/cm^3
[+]pH: 5.3-5.6; OC: 0.29-0.50; Cy: 13.8-15.7; St: 76.2-80.7; Sd: 5.5-8.2; T°: 25
[§]T°: 25; AR: 1.86; C_0: 5
[&]pH: 6.05; OC: 0.43; CEC: 5.95 cmol/kg; Cy: 7.05; St: 25.84; Sd: 67.11; T°: 25
[#]pH: 6.30; OC: 0.33; CEC: 0.45 cmol/kg; Cy: 4.47; St: 13.52; Sd: 82.01; T°: 25
[@]pH: 5.3-5.5; OC: 0.43-0.50; Cy: 14.8-15.6; St: 78.4-80.7; Sd: 3.7-6.5
[§§]OM: 0.9; Cy: 6; St: 31; Sd: 63; CEC: 3.8 meq/100 g; No-till corn plot; Depth: 9 cm
[&&]OM: 1.6; Cy: 24; St: 58; Sd: 18; CEC: 8.3 meq/100 g; No-till corn plot; Depth: 9 cm
[##]OM: 1.0; Cy: 12; St: 24; Sd: 64; CEC: 5.4 meq/100 g; No-till corn plot; Depth: 9 cm
T°: Temperature (°C); SMC: Soil moisture content; OM: % Organic matter; Cy: % Clay; St: % Silt; Sd: % Sand; H: % of water holding capacity; C_0: Nominal initial concentration (mg/kg); OC: % Organic carbon; AR: application rate (kg/ha); W: Water content (g/g); CEC: Cation exchange capacity

Simulation experiments were performed in order to test the influence of soil half-life on the outputs calculated by CHEMFRANCE. Region 1 was selected due to its agricultural interest and scenario D was adopted since it represents a summary of the other scenarios. Five runs were performed with a starting value of 6 d and an increment of 95 d. The simulation results are displayed in Figure 2 and Tables VIII and IX. Figure 2 shows that the half-life in soil principally influences water and soil reactions and the leaching and runoff processes.

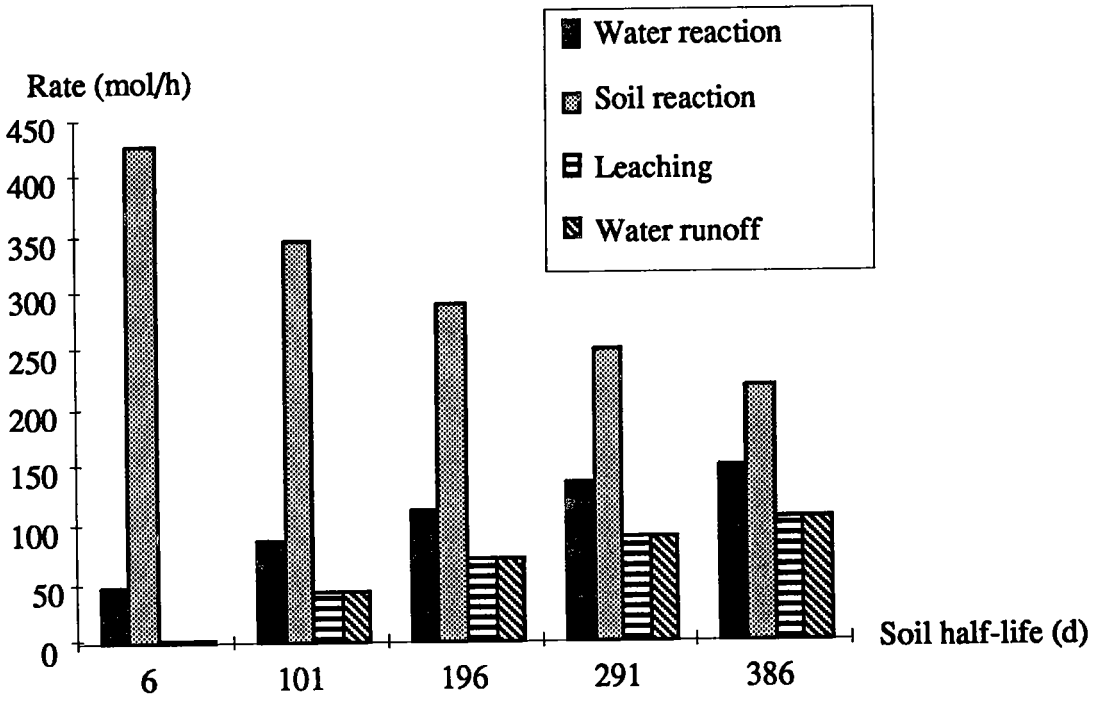

Figure 2. Influence of soil half-life on CHEMFRANCE outputs

It is obvious that changes in soil half-life values induce other variations than those displayed in Figure 2. Thus, Table VIII clearly shows that soil and water runoff, leaching, and soil volatilization are the most subject to variations. Water runoff and leaching are the most significant due to their magnitude. They induce an increase of the groundwater and surface water concentrations in atrazine (Table IX).

Our study shows that the results obtained with CHEMFRANCE for atrazine are in accordance with those obtained in laboratory or field experiments. This underlines the usefulness of the environmental fate models for confirming results of field and laboratory studies but also to provide a comprehensive summary of the processes involved in the environmental fate of chemicals. This is particularly interesting for atrazine since this herbicide is of environmental concern in France.
An interesting characteristic of CHEMFRANCE is that it allows the user to quickly test several hypotheses through different scenarios. Sensitivity and uncertainty analyses can also be performed in order to test the influence of all input parameters and assumptions on the outputs.

Table VIII. Influence of the soil half-life on the removal and transfer processes

Multiplicative factor*	Process	Range (mol/h)[$]
0.51	Soil reaction	$4.283\ 10^{2}$-$2.204\ 10^{2}$
1.04	Rain deposition on water	$3.41\ 10^{-2}$-$3.56\ 10^{-2}$
1.04	Rain deposition on soil	4.60-4.80
1.04	Dry deposition on soil	$5.01\ 10^{-3}$-$5.23\ 10^{-3}$
1.04	Wet deposition on water	$5.66\ 10^{-5}$-$5.91\ 10^{-5}$
1.04	Wet deposition on soil	$7.63\ 10^{-3}$-$7.97\ 10^{-3}$
1.04	Air advection	$3.6\ 10^{-2}$-$3.76\ 10^{-2}$
1.04	Diffusion air/water	$8.52\ 10^{-5}$-$8.90\ 10^{-5}$
1.04	Diffusion air/soil	$3.78\ 10^{-3}$-$3.95\ 10^{-3}$
1.05	Dry deposition on water	$3.72\ 10^{-5}$-$3.89\ 10^{-5}$
1.05	Transfer to higher altitude	$4.44\ 10^{-5}$-$4.64\ 10^{-5}$
3.01	Sediment reaction	0.94-2.83
3.02	Sediment burial	$1.93\ 10^{-3}$-$5.82\ 10^{-3}$
3.02	Water volatilization	$1\ 10^{-3}$-$3.02\ 10^{-3}$
3.02	Sediment desorption	1.39-4.20
3.02	Sediment resuspension	$6.42\ 10^{-4}$-$1.94\ 10^{-3}$
3.02	Water reaction	49.6-149.9
3.03	Sediment adsorption	2.31-6.99
3.03	Water advection	1.07-3.24
3.03	Sediment deposition	$1.54\ 10^{-2}$-$4.67\ 10^{-2}$
33.07	Soil runoff	$2.57\ 10^{-2}$-0.85
33.14	Leaching	3.22-106.7
33.14	Water runoff	3.22-106.7
33.18	Soil volatilization	$6.63\ 10^{-3}$-0.22

*Ratio between the rate of the process at the highest and this at the lowest half-life value. Only the processes with a ratio different from one have been included.
[$]Obtained with the lowest and the highest half-life, respectively.

Table IX. Influence of the soil half-life on the concentration in atrazine

Compartment	Multiplicative factor*	Concentration range (ng/l)[$]
Air	1.04	$2.060\ 10^{-5}$-$2.150\ 10^{-5}$
Water	3.02	3.15810^{3}-$9.540\ 10^{3}$
Soil	33.11	$2.848\ 10^{3}$-$9.431\ 10^{4}$
Sediment	3.02	$1.224\ 10^{4}$-$3.697\ 10^{4}$
Groundwater	33.10	$4.707\ 10^{2}$-$1.558\ 10^{4}$
Coastal water	3.04	0.26-0.79

*Ratio between the concentration at the highest and this at the lowest half-life value.
[$]Concentration obtained with the lowest and the highest half-life, respectively.

Acknowledgment

This study was granted by the French Ministry of the Environment.

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ARTICLE VII

COMPARISON OF BCF MODELS BASED ON LOG P

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ABSTRACT

Seven linear and nonlinear BCF models based on log P have been compared in order to estimate their accuracy, predictive power, and domain of application. This comparison was performed from a data set constituted of 436 experimental BCF values recorded for 227 chemicals. We showed that for chemicals with log P<6, the different models yielded equivalent results. At the opposite, for highly hydrophobic chemicals (log P>6), the bilinear model log BCF = 0.91 log P - 1.975 log (6.8 10^{-7} P + 1) - 0.786 (n = 154; r = 0.95; s = 0.347; F = 463.5) was superior to the other studied models.

INTRODUCTION

Numerous attempts have been made for modeling the accumulation of organic chemicals by fish since the experimental determination of this important biological activity is a time-consuming and costly exercise. The most widely used method consists in correlating laboratory bioconcentration factors (BCFs) determined in fish and *n*-octanol/water partition coefficients (log P). Bioconcentration can be defined as the result of the uptake, distribution, and elimination of a chemical in a fish due to water-borne exposure (Barron, 1990), whereas bioaccumulation includes all routes of exposure, and biomagnification deals with accumulation via food chains. Numerous test guidelines for the experimental determination of BCF in fish are available (e.g., OECD, ASTM). BCF is determined as the concentration of the chemical in whole fish at steady state divided by the concentration of the chemical in water during the exposure period and/or as the ratio between the uptake (k_1) and depuration (k_2) rate constants assuming first order kinetics. The accumulation of an organic compound in a fish basically depends on its hydrophobicity. Therefore, log P is the physicochemical descriptor of choice for modeling bioconcentration. As a result, numerous BCF QSAR equations derived from log P are available in the literature and there is a need for the evaluation of their domain of application. Under these conditions, the aim of this study was to compare different BCF/log P models in order to estimate their accuracy, predictive power, and domain of application.

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MODEL SELECTION

The selection of the BCF/log P models was principally based on their occurrence of citation in the scientific literature and official reports (e.g., ECETOC, 1995; EEC, 1995). Thus, seven equations were selected. Their main characteristics are given below.

Equation no. 1 (Veith *et al.*, 1979)

$\log BCF = 0.85 \log P - 0.70$

n = 55 r = 0.95 s = not given F = not given

Fathead minnows (*Pimephales promelas*) were used as test species.

Equation no. 2 (Veith *et al.*, 1980)

$\log BCF = 0.76 \log P - 0.23$

n = 84 r (?) = 0.95 s = not given F = not given

Bioconcentration data were measured on *Pimephales promelas* and *Lepomis macrochirus.*

Equation no. 3 (Mackay, 1982)

$\log BCF = 1.00 \log P - 1.32$

n = 44 (?) r = 0.97 s = 0.25 F = not given

The model was designed from bioconcentration data relating to several fish species.

Equation no. 4 (Isnard and Lambert, 1988)

$\log BCF = 0.80 \log P - 0.52$

n = 107 r = 0.904 s = 0.51 F = not given

The model was obtained from bioconcentration data relating to several fish species.

Equation no. 5 (Nendza, 1991)

$\log BCF = 0.99 \log P - 1.47 \log (4.97\ 10^{-8} P + 1) + 0.0135$

n = 132

The above empirical model (without statistical parameters) was designed from bioconcentration data relating to several fish species and expressed as percentage of lipid content.

Equation no. 6 (Bintein *et al.*, 1993)

$\log BCF = 0.91 \log P - 1.975 \log (6.8\ 10^{-7} P + 1) - 0.786$

n = 154 r = 0.95 s = 0.347 F = 463.51

The equation was derived from bioconcentration data measured on five families of freshwater fish (i.e., Salmonidae, Cyprinidae, Centrarchidae, Poeciliidae, Cyprinodontidae).

Equation no. 7 (Connell and Hawker, 1988)

$\log BCF = 6.9\ 10^{-3} (\log P)^4 - 0.185 (\log P)^3 + 1.55 (\log P)^2 - 4.18 \log P + 4.79$

The model was designed from bioconcentration data relating to several fish species. No statistical parameters were given.

BCF AND LOG P VALUES DATABASE CONSTITUTION

Experimental BCF Data

To properly compare the accuracy, the predictive power, and the domain of application of the seven selected models, it would have been necessary to use new experimental BCF data specifically measured for this comparative study. However, for reasons of time and cost, this solution could not obviously be envisioned and only data retrieved from the literature were employed. This induced methodological problems. Indeed, there are relatively few experimental bioconcentration data towards fish and they have widely been used to derive QSAR models including those compared in this study. Under these conditions, in the present study, we can consider that a bias was systematically introduced when one of the BCF values used for the comparison exercise was included in the training set(s) of the studied models. However, this bias became lesser if this value was used in the derivation of all the seven models. In the same way, it is obvious that the models designed from a small number of compounds were penalized compared with those derived from large numbers of molecules. Indeed, the values selected in our study were more likely to be in the training sets of models derived from a large number of molecules than in those for which the training set was of a reduced size. To overcome these problems, rather than selecting a sole BCF value per molecule, when possible, a set of coherent experimental BCF data was compiled in order to provide bioconcentration profiles for a given molecule. This allowed to partly solve the problems stressed above and also to take into account the influence of the experimental protocols.

The experimental BCF values used in our comparative study are listed in Tables I and II. They only concern freshwater fish. They do not originate from data compilations but were all retrieved from the original publications. Only data obtained after a steady-state was reached (i.e., ratio between concentration in fish and concentration in water) or by the kinetic method (i.e., ratio between first-order uptake and elimination rate constants) were retained. Data for which contamination by food and/or presence of adsorbent was observed were not selected. The apparent BCF values were selected for the experiments using radiolabelled compounds. Data expressed as lipid content are indicated in Tables I and II. Table I only contains the experimental results obtained from tests performed under flow-through conditions (342 values) while Table II lists those obtained under static and semi-static conditions (94 values). The lipid content values were selected from the values given or recommended by the authors, otherwise the generally accepted estimate of 5 % was adopted (e.g., Connell and Hawker, 1988). In many instances, confirmation of the lipid content was obtained directly from the authors. When this compilation was performed, the BCF data being obviously out-of-line with those generally found in the literature were removed. For the sake of homogeneity, if one or more values appeared out-of-line in a publication, all the data contained in this paper were removed.

Compilation of log P Values

In order to minimize the influence of the *n*-octanol/water partition coefficient values on the simulation results, the selection of log P data was based on the following criteria. First of all, direct methods involving normalized protocols were privileged. In addition, when several data were available, the selection was performed in order to obtain a coherent database for all the studied molecules. Indeed, a coherency between the selected log P values and the chemical structures of the molecules was maintained. Last, as far as possible, the log P selections made by the different authors who derived the models to be compared were also taken into account. The selected log P values for the 227 studied chemicals are shown in Tables I and II.

RESULTS AND DISCUSSION

The obtained results are listed in Tables I to III and displayed in Figures 1 to 14. Thus, in the last column of Tables I and II, the seven models have been classified according to their decreasing predictive power estimated on the basis of the residuals. The first cited model (on the left-hand side) is the one which yields the lowest residual value (absolute value). At the opposite, the last model cited (on the right-hand side) presents the highest residual value. Thus, for example, for acenaphthene (i.e., first chemical of Table I), our comparative study shows that the most accurate model is that of Nendza (1991), followed by that designed by Mackay (1982), that of Isnard and Lambert (1988), Veith *et al.* (1979), Connell and Hawker (1988), Veith *et al.* (1980) and finally, the least accurate model to estimate the BCF of acenaphthene is Eq. (6) (Bintein *et al.*, 1993). The tendency of each model to under- or overestimate the BCF of the studied molecules is a critical feature to inspect. Thus, in Tables I and II, for each entry, the model numbers for which the predicted value is superior to the observed BCF are underlined. The analysis of the classifications obtained for the 227 studied chemicals (Tables I and II) shows that for chemicals with log P values inferior to 6, the seven models are broadly equivalent. At the opposite, for molecules presenting a log P value superior to 6, the nonlinear equations (6) and (7) bear better predictive performances. Among them, the bilinear model of Bintein *et al.* (1993) is the most often classified first. For some chemicals (e.g., permethrin), the use of different experimental protocols does not change the classification of the model performances while for some others (e.g., fenitrothion, fenthion), the classification can be completely modified. However, it is noteworthy that these classifications must be interpreted with care since the different residual values can be relatively weak or very high. Thus, for example, the residual values (i.e., log $BCF_{obs.}$ - log $BCF_{calc.}$) which give the classification 5, 3, 4, 1, 7, 2, 6 obtained for acenaphthene (Table I) are the following: 0.00, -0.01, -0.03, -0.04, -0.12, -0.16, and -0.19. At the opposite, the residual values yielding the classification 6, 7, 2, 4, 1, 5, 3 for octachlorodibenzo-*p*-dioxin (Table I, last value for this chemical) are the following: 0.08, -1.00, -2.18, -2.19, -2.39, -2.47, and -2.91. In the former case, it can be advanced that all the models are able to produce satisfactory estimations for the BCF of acenaphthene. Therefore, the information provided by the classification is useless. However, for octachlorodibenzo-*p*-dioxin, the classification is far more significant. Indeed, it is obvious that Eq. (6) (Bintein *et al.*, 1993) is the most suitable for predicting the bioconcentration of this chemical in fish. As inspection of Tables I and II does not provide information on the magnitude of the differences observed between the studied models, the classification was completed by a graphical study of the residuals obtained with each of the seven studied models. For this purpose, the residuals were plotted versus the log P values (Figures 1 to 14). Inspection of these figures confirms the equivalence of the different models for chemicals having log P values inferior to 6. The comparison of these different figures also confirms that for highly hydrophobic chemicals, the nonlinear equations (6) and (7) provide better simulations. In addition, Figures 1 to 14 allow a better estimation of the effect of the different experimental protocols on the results of the BCF simulations since for a same chemical (i.e., same log P value), the residuals corresponding to different protocols appear on a same vertical line. Thus, for example, in Figures 1, 3, 5, and 7, it is possible to stress that the BCF values calculated by the linear models for octachlorodibenzo-*p*-dioxin are always largely superior to those experimentally observed. The same remark can be made for the bilinear equation (5) (Figure 9). At the opposite, for the nonlinear equations (6) and (7) (Figures 11 and 13), the results show a higher variability. It is particularly interesting to note that according to the selected experimental BCF values, Eq. (6) (Bintein *et al.*, 1993) can have a tendency to underestimate or at the opposite to overestimate the bioconcentration of

Table I *n*-octanol/water partition coefficients (log P), bioconcentration data (log BCF) obtained under flow-through conditions and classification of the seven models.

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Acenaphthene	3.92	2.59	*Lepomis macrochirus*	Veith *et al.* (1980)	5, 3, 4, 1, 7, 2, 6
Acridine	3.45	2.10	*Pimephales promelas*	Southworth *et al.* (1979)	3-5, 7, 1, 4, 6, 2
Acrolein	0.90	2.54	*Lepomis macrochirus*	Veith *et al.* (1980)	7, 2, 4, 1, 6, 5, 3
Benzo[*a*]pyrene	5.97	3.51	*Lepomis macrochirus*	Jimenez *et al.* (1987)	6, 4, 2, 1, 7, 5, 3
Bis(2-chloroethyl)ether	1.12	1.04	*Lepomis macrochirus*	Veith *et al.* (1980)	2, 4, 7, 1, 6, 5, 3
BPMC	2.78	1.41	*Pseudorasbora parva*	Kanazawa (1981)	3-5, 7, 1, 4, 6, 2
Bromacil	2.11	0.51	*Pimephales promelas*	Call *et al.* (1987)	3, 5, 1, 6, 4, 7, 2
5-Bromoindole	3.00	1.15	*Pimephales promelas*	Veith *et al.* (1979)	3-5, 7, 1, 4, 6, 2
4-Bromophenol	2.59	1.56	*Brachydanio rerio*	Butte *et al.* (1987)	4-6, 1, 7, 2, 3, 5
Bromophos	4.88	4.60[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 2, 6, 1, 4, 7, 5
	4.88	4.65[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	6, 3, 2, 7, 1, 5, 4
2-*t*-Butoxy ethanol	0.39	-0.22	*Cyprinus carpio*	Fujiwara *et al.* (1984)	4, 1, 6, 2, 5, 3, 7
Butyl benzyl phthalate	4.05	2.89	*Lepomis macrochirus*	Veith *et al.* (1980)	6, 2-7, 1, 3, 4-5
t-Butyl isopropyl ether	2.14	0.76	*Cyprinus carpio*	Fujiwara *et al.* (1984)	3, 5, 1, 6, 4, 7, 2
t-Butyl methyl ether	1.24	0.18	*Cyprinus carpio*	Fujiwara *et al.* (1984)	6, 1, 5, 3, 4, 2, 7
4-*t*-Butyl phenol	3.31	1.86	*Brachydanio rerio*	Butte *et al.* (1987)	5, 3, 7, 1, 4, 6, 2
Carbaryl	2.31	0.95	*Pseudorasbora parva*	Kanazawa (1981)	3, 5, 1, 6-7, 4, 2
Carbon tetrachloride	2.73	1.48	*Lepomis macrochirus*	Veith *et al.* (1980)	5, 3-7, 1, 4, 6, 2
Chlordane	6.00	4.58	*Pimephales promelas*	Veith *et al.* (1979)	5, 7, 3, 1, 2, 4, 6
α-Chlordane	6.00	4.45	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 1, 2, 4, 6, 3, 5
γ-Chlordane	6.00	4.20	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 4, 2, 1, 7, 3, 5
Chlornitrofen	4.70	3.04	*Pseudorasbora parva*	Kanazawa (1981)	4, 1, 2, 5, 3, 6, 7
2-Chloroaniline	1.93	0.30	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
	1.93	0.57	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
3-Chloroaniline	1.91	-0.10	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
	1.91	0.34	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
4-Chloroaniline	1.88	-0.10	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
	1.88	0.23	*Cyprinus carpio*	Tsuda *et al.* (1993)	3, 5, 1, 6, 4, 2, 7
p-Chlorobiphenyl	4.61	3.54[§]	*Oryzias latipes*	Sugiura *et al.* (1984)	7, 6, 3, 5, 2, 1, 4
Chloroform	1.90	0.78	*Lepomis macrochirus*	Veith *et al.* (1980)	1, 6, 5, 3, 4, 2, 7
2-Chloronitrobenzene	2.52	2.10	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 4, 1, 5, 7, 3
3-Chloronitrobenzene	2.50	1.89	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 4, 1, 5-7, 3
4-Chloronitrobenzene	2.39	2.00	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 4-6, 7, 1, 5, 3
2-Chlorophenol	2.15	2.33	*Lepomis macrochirus*	Veith *et al.* (1980)	2, 7, 4, 6, 1, 5, 3
3-Chlorophenol	2.50	1.25	*Brachydanio rerio*	Butte *et al.* (1987)	3, 5-7, 1, 4, 6, 2
Chlorothion	3.63	2.46[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 4, 1-7, 6, 2, 5
	3.63	2.61[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 4, 1-7, 6, 2, 5
Cresyldiphenyl phosphate	4.51	2.00	*Alburnus alburnus*	Bengtsson *et al.* (1986)	4, 1, 5, 3, 2, 6, 7
	4.51	2.34	*Alburnus alburnus*	Bengtsson *et al.* (1986)	4, 1, 5, 3, 2, 6, 7
4-Cyanophenol	1.60	0.91	*Brachydanio rerio*	Butte *et al.* (1987)	2, 4, 6, 1, 7, 3, 5
Cyanophos	2.71	2.49[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 7, 1, 5, 4, 6, 2
	2.71	2.62[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	7, 1, 5, 4, 6, 3, 2
Cypermethrin	6.05	2.89	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 1, 7, 5, 3
	6.05	2.92	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 1, 7, 5, 3
2,7-DCDD*	6.38	2.56	*Poecilia reticulata*	Gobas and Schrap (1990)	6, 4, 7, 2, 1, 3, 5
p,p'-DDE	5.83	4.71	*Pimephales promelas*	Veith *et al.* (1979)	3, 5, 7, 1, 2, 6, 4
	5.83	4.91	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	5, 3, 7, 1, 2, 6, 4
o,p'-DDT	6.00	4.57	*Pimephales promelas*	Veith *et al.* (1979)	5, 7, 3, 1, 2, 4, 6
p,p'-DDT	6.00	4.47	*Pimephales promelas*	Veith *et al.* (1979)	7, 1, 2, 5, 4, 3, 6
	6.00	4.81	*Oncorhynchus mykiss*	Muir *et al.* (1994)	3, 5, 7, 1, 2, 4, 6
	6.00	4.86	*Oncorhynchus mykiss*	Muir *et al.* (1994)	3, 5, 7, 1, 2, 4, 6
	6.00	4.95	*Oncorhynchus mykiss*	Muir *et al.* (1994)	3, 5, 7, 1, 2, 4, 6
	6.00	4.97	*Oncorhynchus mykiss*	Muir *et al.* (1985)	3, 5, 7, 1, 2, 4, 6
	6.00	4.99	*Oncorhynchus mykiss*	Muir *et al.* (1994)	3, 5, 7, 1, 2, 4, 6
Decachlorobiphenyl	8.27	3.92[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	7, 6, 5, 2, 4, 1, 3
	8.27	4.00[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	7, 5, 6, 2, 4, 1, 3

Table I (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Deltamethrin	6.20	2.62	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 7, 1, 5, 3
	6.20	2.70	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 7, 1, 5, 3
Diazinon	3.81	1.24	*Poecilia reticulata*	Kanazawa (1978)	5, 3, 4, 1, 7, 2, 6
	3.81	1.34	*Oryzias latipes*	Tsuda *et al.* (1995)	5, 3, 4, 1, 7, 2, 6
	3.81	1.41	*Misgurnus anguillicaudatus*	Seguchi and Asaka (1981)	5, 3, 4, 1, 7, 2, 6
	3.81	1.45	*Oryzias latipes*	Tsuda *et al.* (1995)	5, 3, 4, 1, 7, 2, 6
	3.81	1.56	*Cyprinus auratus*	Kanazawa (1978)	5, 3, 4, 1, 7, 2, 6
	3.81	1.80	*Oncorhynchus mykiss*	Seguchi and Asaka (1981)	3, 4, 1, 7, 2, 6, 5
	3.81	1.81	*Cyprinus carpio*	Kanazawa (1978)	5, 3, 4, 1, 7, 2, 6
	3.81	2.08	*Cyprinus carpio*	Seguchi and Asaka (1981)	3, 4, 1, 7, 2, 6, 5
	3.81	2.18	*Pseudorasbora parva*	Kanazawa (1981)	5, 3, 4, 1, 7, 2, 6
	3.81	2.18	*Pseudorasbora parva*	Kanazawa (1978)	5, 3, 4, 1, 7, 2, 6
1,3-Dibromobenzene	3.75	2.82	*Oncorhynchus mykiss*	Oliver and Niimi (1984)	5, 2-6, 7, 1, 4, 3
1,4-Dibromobenzene	3.79	1.96[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	3, 4, 1, 7, 5, 2, 6
4,4'-Dibromobiphenyl	5.72	4.24[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	1-6, 2-7, 3, 4, 5
2,6-Dibromo-4-cyanophenol	2.61	1.67	*Brachydanio rerio*	Butte *et al.* (1987)	2-6, 4, 1, 7, 3, 5
Dicapthon	3.58	2.95[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 1-4-7, 6, 2, 5
	3.58	3.09[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 1-4-7, 6, 2, 5
1,2-Dichlorobenzene	3.43	1.95	*Lepomis macrochirus*	Veith *et al.* (1980)	3-5, 7, 1-4, 6, 2
	3.43	2.43	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 1-4, 7, 3
	3.43	2.75	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 1-4, 7, 3
1,3-Dichlorobenzene	3.53	1.82	*Lepomis macrochirus*	Veith *et al.* (1980)	3-5, 7, 1-4, 6, 2
	3.53	2.62	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 1-4, 7, 3
	3.53	2.87	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 1-4, 7, 3
1,4-Dichlorobenzene	3.44	1.78	*Lepomis macrochirus*	Veith *et al.* (1980)	3-5, 7, 1, 4, 6, 2
	3.44	2.47	*Jordanella floridae*	Smith *et al.* (1990)	2, 5, 6, 4, 1, 7, 3
	3.44	2.57	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 4, 1, 7, 3
	3.44	2.71	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2, 6, 5, 4, 1, 7, 3
	3.44	2.86	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	2, 5, 6, 4, 1, 7, 3
	3.44	2.95	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2, 6, 5, 4, 1, 7, 3
2,5-Dichlorobiphenyl	5.16	4.00	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 3, 6, 1-2, 4
	5.16	4.14[§]	*Carassius auratus*	Bruggeman *et al.* (1981)	7, 3, 6, 1-2, 5, 4
	5.16	4.24[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	7, 3, 6, 1-2, 5, 4
	5.16	4.53	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 3, 6, 1-2, 4
3,5-Dichlorobiphenyl	5.37	3.79	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	4, 2, 1, 6, 3, 7, 5
	5.37	3.82	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2, 1-4, 6, 3, 7, 5
1,2-Dichloroethane	1.45	0.30	*Lepomis macrochirus*	Veith *et al.* (1980)	5, 3, 1-6, 4, 2, 7
4,5-Dichloroguaiacol	3.18	2.03	*Oncorhynchus mykiss*	Niimi *et al.* (1990)	4, 1-5, 6, 7, 2, 3
1,4-Dichloronaphthalene	4.66	3.75	*Oncorhynchus mykiss*	Oliver and Niimi (1984)	5, 7, 6, 3, 2, 1, 4
2,3-Dichloronitrobenzene	3.05	2.16	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 5, 4, 1, 7, 3
2,4-Dichloronitrobenzene	3.05	2.07	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 5, 4, 1, 7, 3
2,5-Dichloronitrobenzene	3.03	2.05	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 5, 4, 1, 7, 3
3,4-Dichloronitrobenzene	3.04	2.07	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 5, 4, 1, 7, 3
3,5-Dichloronitrobenzene	3.09	2.23	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 5, 4, 1, 7, 3
Dichlorvos	1.47	-0.10	*Gnathopogon caerulescens*	Tsuda *et al.* (1992)	3, 5, 1-6, 4, 2, 7
Dieldrin	5.40	3.65	*Pseudorasbora parva*	Kanazawa (1981)	4, 2, 1, 6, 5, 3, 7
Di(2-ethylhexyl)phthalate	7.45	2.19	*Pimephales promelas*	Mayer (1976)	6, 7, 2, 4, 5, 1, 3
	7.45	2.95	*Pimephales promelas*	Mayer (1976)	6, 7, 2, 4, 5, 1, 3
Diethyl phthalate	2.47	2.07	*Lepomis macrochirus*	Veith *et al.* (1980)	2, 4-6, 1, 7, 5, 3
2,4-Dimethylphenol	2.42	2.18	*Lepomis macrochirus*	Veith *et al.* (1980)	2, 4-6, 7, 1, 5, 3
Dimethyl phthalate	1.56	1.76	*Lepomis macrochirus*	Veith *et al.* (1980)	7, 2, 4, 1-6, 5, 3
Diphenylamine	3.42	1.48	*Pimephales promelas*	Veith *et al.* (1979)	3-5, 7, 1, 4, 6, 2
Diuron	2.68	2.16	*Pimephales promelas*	Call *et al.* (1987)	2, 6, 4, 1, 7, 5, 3
	2.68	2.20	*Pimephales promelas*	Call *et al.* (1987)	2, 6, 4, 1, 7, 5, 3
EPN	3.85	3.37	*Pseudorasbora parva*	Kanazawa (1981)	6, 2, 7, 1, 4, 3, 5
Fenitrothion	3.47	1.65	*Oryzias latipes*	Tsuda *et al.* (1995)	3-5, 7, 1, 4, 6, 2
	3.47	1.68	*Oryzias latipes*	Tsuda *et al.* (1995)	3-5, 7, 1, 4, 6, 2
	3.47	3.36[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	4, 1, 6, 7, 5, 2, 3
	3.47	2.39	*Pseudorasbora parva*	Kanazawa (1981)	2-6, 4, 1, 7, 3-5

Table I (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Fenitrothion	3.47	2.48	*Oryzias latipes*	Takimoto *et al.* (1987)	2, 6, 4, 1, 7, 3, 5
	3.47	3.54[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	2, 5, 6, 4, 1, 7, 3
	3.47	2.74	*Oryzias latipes*	Takimoto *et al.* (1984)	5, 2, 6, 4, 1, 7, 3
	3.47	2.75	*Oryzias latipes*	Takimoto *et al.* (1984)	5, 2, 6, 4, 1, 7, 3
Fenthion	4.17	1.96	*Oryzias latipes*	Tsuda *et al.* (1995)	4, 1-5, 3, 2, 7, 6
	4.17	2.02	*Oryzias latipes*	Tsuda *et al.* (1995)	4, 1-5, 3, 2, 7, 6
	4.17	2.68	*Gnathopogon caerulescens*	Tsuda *et al.* (1992)	4, 1-5, 3, 2, 7, 6
	4.17	4.17[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 6, 7, 2, 3, 1, 4
	4.17	4.22[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 6, 7, 2, 3, 1, 4
Fenthion-S2145	3.74	3.65[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	2-6, 5, 7, 1, 4, 3
	3.74	3.84[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 2-6, 7, 1, 4, 3
Fenvalerate	6.20	2.61	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 7, 1, 5, 3
	6.20	2.96	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 4, 2, 7, 1, 5, 3
1,2,3,4,7,8-HCDD[$]	7.79	3.29	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 7, 5, 2, 4, 1, 3
	7.79	3.36	*Oncorhynchus mykiss*	Muir *et al.* (1985)	6, 7, 5, 2, 4, 1, 3
	7.79	3.63	*Pimephales promelas*	Muir *et al.* (1985)	6, 7, 5, 2, 4, 1, 3
	7.79	4.13[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	7, 6, 2, 4, 5, 1, 3
1,2,3,4,6,7,8-HCDD[$]	8.20	2.71	*Pimephales promelas*	Muir *et al.* (1985)	6, 7, 5, 2, 4, 1, 3
	8.20	2.97	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 7, 5, 2, 4, 1, 3
	8.20	3.15	*Oncorhynchus mykiss*	Muir *et al.* (1985)	6, 7, 5, 2, 4, 1, 3
	8.20	3.16	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 7, 5, 2, 4, 1, 3
	8.20	3.75[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	7, 6, 5, 2, 4, 1, 3
1,2,3,4,6,7,8-HCDF[£]	7.92	3.62[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	7, 6, 2, 5, 4, 1, 3
Heptachlor	5.44	3.98	*Pimephales promelas*	Veith *et al.* (1979)	6, 1, 2, 5, 3, 4, 7
Heptachlor epoxide	5.40	4.16	*Pimephales promelas*	Veith *et al.* (1979)	7, 3, 5, 6, 1, 2, 4
Heptachloronorbornene	5.28	4.05	*Pimephales promelas*	Veith *et al.* (1979)	7, 3, 5, 6, 1, 2, 4
Hexabromobenzene	6.07	3.04	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 4, 2, 1, 7, 3, 5
Hexabromobiphenyl**	6.39	4.26	*Pimephales promelas*	Veith *et al.* (1979)	6, 4, 7, 2, 1, 5, 3
2,2',4,4',6,6'-Hexabromobiphenyl	7.20	4.66[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	7, 2-4, 1, 5, 6, 3
Hexabromocyclododecane	5.81	4.26	*Pimephales promelas*	Veith *et al.* (1979)	1, 2-6, 4, 7, 5, 3
Hexachlorobenzene	5.73	3.74	*Oncorhynchus mykiss*	Veith *et al.* (1979)	4, 2, 6, 1, 7, 5, 3
	5.73	4.16[§]	*Oryzias latipes*	Sugiura *et al.* (1984)	6, 1, 2, 4, 7, 5, 3
	5.73	4.21	*Pimephales promelas*	Veith *et al.* (1979)	1, 6, 2, 4-7, 5, 3
	5.73	4.30	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	7, 3, 1, 6, 2, 4, 5
	5.73	4.34	*Lepomis cyanellus*	Veith *et al.* (1979)	7, 5, 3, 1, 6, 2, 4
	5.73	4.43	*Poecilia reticulata*	Schrap and Opperhuizen (1990)	3, 5, 7, 1, 6, 2, 4
2,2',4,4',5,5'-Hexachlorobiphenyl	6.90	4.84	*Oncorhynchus mykiss*	Muir *et al.* (1985)	4, 2, 7, 1, 5, 3, 6
	6.90	5.30[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	1, 5, 3, 2, 4, 7, 6
	6.90	5.65	*Poecilia reticulata*	Opperhuizen and Schrap (1987)	3, 5, 1, 2, 4, 7, 6
1,1,2,3,4,4-Hexachloro-1,3-butadiene	4.78	3.76	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
	4.78	4.23	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
α-Hexachlorocyclohexane	3.80	2.33	*Oncorhynchus mykiss*	Vigano *et al.* (1992)	3, 4, 1, 5-7, 2, 6
	3.80	3.04	*Brachydanio rerio*	Butte *et al.* (1991)	6, 2, 5, 7, 1, 4, 3
	3.80	3.04	*Brachydanio rerio*	Butte *et al.* (1991)	6, 2, 5, 7, 1, 4, 3
	3.80	3.20	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 2, 5, 7, 1, 4, 3
	3.80	3.38	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 2, 5, 7, 1, 4, 3
β-Hexachlorocyclohexane	3.78	3.16	*Brachydanio rerio*	Butte *et al.* (1991)	6, 2, 5, 7, 1, 4, 3
	3.78	3.18	*Brachydanio rerio*	Butte *et al.* (1991)	6, 2, 5, 7, 1, 4, 3
δ-Hexachlorocyclohexane	4.14	2.45	*Oncorhynchus mykiss*	Vigano *et al.* (1992)	5, 4, 1-3, 2, 7, 6
	4.14	3.21	*Brachydanio rerio*	Butte *et al.* (1991)	6, 7, 5, 2, 1-3, 4
	4.14	3.25	*Brachydanio rerio*	Butte *et al.* (1991)	6, 7, 5, 2, 1-3, 4
γ-Hexachlorocyclohexane	3.72	2.16	*Oncorhynchus mykiss*	Vigano *et al.* (1992)	5, 3, 1-4, 7, 2-6
	3.72	2.26	*Pimephales promelas*	Veith *et al.* (1979)	3-5, 1-4, 7, 2-6
	3.72	2.93	*Brachydanio rerio*	Butte *et al.* (1991)	2-6, 5, 7, 1-4, 3
	3.72	2.96	*Brachydanio rerio*	Butte *et al.* (1991)	2-6, 5, 7, 1-4, 3
	3.72	3.08	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2-6, 5, 7, 1-4, 3
	3.72	3.10	*Pseudorasbora parva*	Kanazawa (1981)	2-6, 7, 1-4, 3-5
	3.72	3.30	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2-6, 5, 7, 1-4, 3
	3.72	3.32	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	2-6, 5, 7, 1-4, 3

Table I (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Hexachloroethane	3.93	2.14	*Lepomis macrochirus*	Veith *et al.* (1980)	5, 3, 4, 1, 7, 2, 6
	3.93	2.71	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	7, 2, 1, 6, 4, 3, 5
	3.93	3.08	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 2, 7, 1, 4, 3
Hexachloronorbornadiene	5.28	3.81	*Pimephales promelas*	Veith *et al.* (1979)	1, 2, 6, 4, 5, 3, 7
IBP	3.21	0.60	*Pseudorasbora parva*	Kanazawa (1981)	3-5, 7, 1, 4, 6, 2
Iodofenphos	5.16	4.30[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	4, 1-2, 6, 3, 7, 5
	5.16	4.68[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	4, 1-2, 6, 3, 7, 5
Isophorone	1.67	0.85	*Lepomis macrochirus*	Veith *et al.* (1980)	4, 6, 1, 2, 7, 5, 3
Leptophos	5.88	3.78	*Pseudorasbora parva*	Kanazawa (1981)	4, 6, 2, 1, 7, 5, 3
Methidation	2.42	1.26	*Gnathopogon caerulescens*	Tsuda *et al.* (1992)	1, 7, 5, 3-4-6, 2
Methoxychlor	5.08	3.92	*Pimephales promelas*	Veith *et al.* (1979)	7, 6, 3, 5, 2, 1, 4
2-Methyl-4,6-dinitrophenol	2.13	0.16	*Brachydanio rerio*	Butte *et al.* (1987)	5, 3, 1, 6, 4, 7, 2
Methylisocyanothion	3.58	3.39[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	1-4-7, 3, 6, 2, 5
	3.58	3.53[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	2-6, 5, 1-4-7, 3
Methylparathion	2.94	2.98[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	6, 5, 2, 4, 1, 7, 3
	2.94	3.04[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	2, 6, 5, 4, 1, 7, 3
2-Methylphenol	1.95	1.03	*Brachydanio rerio*	Butte *et al.* (1987)	4, 6, 1, 2, 7, 3, 5
Mirex	6.89	4.26	*Pimephales promelas*	Veith *et al.* (1979)	6-7, 4, 2, 1, 5, 3
	6.89	4.31[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	7, 6, 4, 2, 1, 5, 3
Molinate	3.21	1.41	*Pseudorasbora parva*	Kanazawa (1981)	3-5, 7, 1, 4, 6, 2
Naphthalene	3.36	2.49	*Lepomis macrochirus*	McCarthy and Jimenez (1985)	2, 6, 4, 1, 7, 3-5
	3.36	2.51	*Lepomis macrochirus*	McCarthy and Jimenez (1985)	2, 6, 4, 1, 7, 3-5
3-Nitrophenol	2.00	1.40	*Brachydanio rerio*	Butte *et al.* (1987)	2, 7, 4, 6, 1, 3, 5
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	7.67	4.33[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	7, 5, 6, 2, 4, 1, 3
Octachlorodibenzo-*p*-dioxin	7.59	1.93	*Oncorhynchus mykiss*	Muir *et al.* (1985)	6, 7, 2-5, 4, 1, 3
	7.59	2.59	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 7, 2-5, 4, 1, 3
	7.59	2.67	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 7, 2-5, 4, 1, 3
	7.59	2.85	*Poecilia reticulata*	Gobas and Schrap (1990)	6, 7, 2, 4, 5, 1, 3
	7.59	3.35	*Pimephales promelas*	Muir *et al.* (1985)	6, 7, 2-5, 4, 1, 3
	7.59	3.36[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	6, 7, 2, 4, 1, 5, 3
Octachlorodibenzofuran	7.97	2.77	*Poecilia reticulata*	Gobas and Schrap (1990)	6, 7, 5, 2, 4, 1, 3
	7.97	3.10[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	6, 7, 5, 2, 4, 1, 3
Octachloronaphthalene	6.42	2.52	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 7, 4, 2, 1, 3, 5
Octachlorostyrene	6.29	4.52	*Pimephales promelas*	Veith *et al.* (1979)	4, 2, 7, 1, 6, 5, 3
1,2,3,4,7-PCDD[§§]	7.44	2.91	*Oncorhynchus mykiss*	Muir *et al.* (1985)	6, 7, 2, 4, 5, 1, 3
	7.44	3.16	*Pimephales promelas*	Muir *et al.* (1985)	6, 7, 2, 4, 5, 1, 3
1,2,3,7,8-PCDD[§§]	6.64	4.50[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	7, 4, 2, 6, 1, 3, 5
2,3,4,7,8-PCDF[££]	6.92	4.36[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	7, 6, 4, 2, 1, 3, 5
Pentachloroaniline	5.08	2.56	*Poecilia reticulata*	de Wolf *et al.* (1994)	4, 1, 2, 3, 6, 7, 5
Pentachlorobenzene	5.18	2.94[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	4, 5, 1, 2, 6, 3, 7
	5.18	3.53	*Lepomis macrochirus*	Veith *et al.* (1980)	4, 1, 2, 5-6, 3, 7
	5.18	4.11	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 3, 6, 2, 1, 4
	5.18	4.30	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 3, 6, 2, 1, 4
	5.18	4.36	*Poecilia reticulata*	Schrap and Opperhuizen (1990)	7, 3, 5-6, 2, 1, 4
Pentachloroethane	2.89	1.83	*Lepomis macrochirus*	Veith *et al.* (1980)	6, 4, 1, 2, 7, 3-5
Pentachloronitrobenzene	4.77	2.23	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	4, 1, 2, 3, 6, 7, 5
	4.77	2.38	*Pseudorasbora parva*	Kanazawa (1981)	4, 1, 2, 5, 3, 6, 7
	4.77	2.41	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	4, 1, 2, 3, 6, 5, 7
	4.77	2.77	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	4, 1, 2, 3, 6, 5, 7
Pentachlorophenol	5.01	2.33	*Jordanella floridae*	Smith *et al.* (1990)	4, 1, 2, 3, 6, 7, 5
	5.01	2.58[§]	*Oryzias latipes*	Sugiura *et al.* (1984)	4, 1, 2, 5, 3, 6, 7
	5.01	2.89	*Pimephales promelas*	Veith *et al.* (1979)	4, 1, 2, 5, 3, 6, 7
	5.01	2.99	*Brachydanio rerio*	Butte *et al.* (1987)	4, 1, 5, 2, 3, 6, 7
	5.01	3.23	*Oryzias latipes*	Tachikawa *et al.* (1991)	4, 1, 2, 5, 3, 6, 7
Permethrin	6.50	3.23	*Pimephales promelas*	Spehar *et al.* (1983)	6, 7, 4, 2, 1, 5, 3
	6.50	3.29	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 7, 4, 2, 1, 5, 3
	6.50	3.39	*Oncorhynchus mykiss*	Muir *et al.* (1994)	6, 7, 4, 2, 1, 5, 3

Table I (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Permethrin	6.50	3.49	*Pimephales promelas*	Spehar *et al.* (1983)	6, 7, 4, 2, 1, 5, 3
	6.50	3.52	*Pimephales promelas*	Spehar *et al.* (1983)	6, 7, 4, 2, 1, 5, 3
Phenol	1.46	1.24	*Brachydanio rerio*	Butte *et al.* (1987)	7, 2, 4, 1-6, 3, 5
Phenthoate	3.69	1.56	*Pseudorasbora parva*	Kanazawa (1981)	3-5, 4, 1, 7, 2-6
2-Phenyldodecane	8.19	2.65	*Oncorhynchus mykiss*	Burke *et al.* (1991)	6, 7, 5, 2, 4, 1, 3
N-Phenyl-2-naphthylamine	4.38	2.17	*Pimephales promelas*	Veith *et al.* (1979)	4, 1, 5, 3, 2, 6, 7
Phosmet	2.78	1.56	*Gnathopogon caerulescens*	Tsuda *et al.* (1992)	7, 1-3-5, 4, 6, 2
Ronnel	4.81	4.55[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 2-6, 1, 4-7, 5
	4.81	4.64[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	6, 7, 3, 5, 2, 1, 4
Salithion	2.67	1.88	*Gnathopogon caerulescens*	Tsuda *et al.* (1992)	2, 6, 4, 1, 7, 5, 3
Simetryne	2.54	0.31	*Gnathopogon caerulescens*	Tsuda *et al.* (1988)	3, 5, 7, 1, 4, 6, 2
SV 5	3.00	2.95[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	4, 1-5, 6, 7, 2, 3
	3.00	3.22[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	2, 6, 5, 4, 1, 7, 3
1,2,3,4-TCDD[&]	6.20	2.90	*Poecilia reticulata*	Gobas and Schrap (1990)	6, 4, 2, 7, 1, 3, 5
1,3,6,8-TCDD[&]	6.29	3.20	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 4, 2, 7, 1, 5, 3
	6.29	3.32	*Oncorhynchus mykiss*	Muir *et al.* (1985)	6, 4, 2, 7, 1, 5, 3
	6.29	3.32	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 4, 2, 7, 1, 5, 3
	6.29	3.39	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 4, 2, 7, 1, 5, 3
	6.29	3.57	*Oncorhynchus mykiss*	Servos *et al.* (1989)	6, 4, 2, 7, 1, 5, 3
	6.29	3.76	*Pimephales promelas*	Muir *et al.* (1985)	6, 4, 2, 7, 1, 5, 3
2,3,7,8-TCDD[&]	6.42	4.01[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	6, 7, 4, 2, 1, 3, 5
	6.42	4.56	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	7, 4, 2, 1, 6, 5, 3
	6.42	4.57	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	7, 4, 2, 1, 6, 5, 3
	6.42	4.59	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	7, 4, 2, 1, 5, 6, 3
	6.42	4.93	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	5, 1-3, 2, 4, 7, 6
2,3,7,8-TCDF[&&]	6.53	3.31[§]	*Poecilia reticulata*	Loonen *et al.* (1994)	6, 7, 4, 2, 1, 3, 5
	6.53	3.42	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	6, 7, 4, 2, 1, 5, 3
	6.53	3.65	*Oncorhynchus mykiss*	Mehrle *et al.* (1988)	6, 7, 4, 2, 1, 5, 3
1,2,4,5-Tetrabromobenzene	5.13	3.57	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	4, 1, 2, 3-6, 5, 7
	5.13	3.81	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	3-6, 5, 7, 2, 1, 4
2,2',5,5'-Tetrabromobiphenyl	6.50	4.97[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	1, 5, 3, 2, 4, 7, 6
2,3,4,5-Tetrachloroaniline	4.57	2.10	*Poecilia reticulata*	de Wolf *et al.* (1994)	4, 1, 2, 3, 6, 7, 5
2,3,5,6-Tetrachloroaniline	4.46	2.46	*Poecilia reticulata*	de Wolf *et al.* (1994)	4, 1, 3, 2, 6, 7, 5
1,2,3,4-Tetrachlorobenzene	4.64	3.72	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
	4.64	3.80	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 6, 3, 2, 1, 4
	4.64	3.82	*Poecilia reticulata*	Schrap and Opperhuizen (1990)	7, 6, 3, 2-5, 1, 4
	4.64	3.91	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 6, 3, 2, 1, 4
	4.64	4.08	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
1,2,3,5-Tetrachlorobenzene	4.66	4.40[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	3, 2, 1, 6, 4, 7, 5
	4.66	4.61[†]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 7, 6, 3, 2, 1, 4
	4.66	3.64	*Poecilia reticulata*	de Wolf *et al.* (1994)	7, 5, 6, 3, 2, 1, 4
	4.66	4.81[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 7, 6, 3, 2, 1, 4
	4.66	4.89[†§]	*Poecilia reticulata*	de Bruijn and Hermens (1991)	5, 7, 6, 3, 2, 1, 4
1,2,4,5-Tetrachlorobenzene	4.60	3.61	*Jordanella floridae*	Smith *et al.* (1990)	5, 7, 6, 3, 2, 1, 4
	4.60	3.72	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
	4.60	4.11	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 7, 6, 3, 2, 1, 4
Tetrachlorobenzyltoluene	7.80	3.36	*Brachydanio rerio*	Bouraly and Millischer (1989)	6, 7, 5, 2, 4, 1, 3
2,2',3,3'-Tetrachlorobiphenyl	6.18	4.69	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 1, 3, 2, 5, 4, 6
2,2',5,5'-Tetrachlorobiphenyl	6.09	4.63	*Poecilia reticulata*	Opperhuizen and Schrap (1987)	5, 7, 3, 1, 2, 4, 6
	6.09	4.69[§]	*Carassius auratus*	Bruggeman *et al.* (1981)	3, 7, 5, 1, 2, 4, 6
	6.09	4.84[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	5, 3, 7, 1, 2, 4, 6
	6.09	4.90[§]	*Poecilia reticulata*	Bruggeman *et al.* (1984)	3, 7, 5, 1, 2, 4, 6
	6.09	5.30	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	5, 3, 7, 1, 2, 4, 6
2,3',4',5-Tetrachlorobiphenyl	6.23	4.62[§]	*Carassius auratus*	Bruggeman *et al.* (1981)	1, 5, 7, 2, 4, 3, 6
1,1,2,2-Tetrachloroethane	2.39	0.90	*Lepomis macrochirus*	Veith *et al.* (1980)	3, 5, 1, 7, 4-6, 2
Tetrachloroethylene	2.53	1.69	*Lepomis macrochirus*	Veith *et al.* (1980)	2, 6, 4, 1, 7, 5, 3
Tetrachloroguaiacol	4.45	2.26	*Oncorhynchus mykiss*	Niimi *et al.* (1990)	4, 1, 3, 2, 6, 7, 5
1,2,3,4-Tetrachloronaphthalene	5.75	3.71	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	4, 2, 6, 1, 7, 3, 5

Table I (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
2,3,4,5-Tetrachloronitrobenzene	3.93	1.87	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	3, 4, 1, 7, 2, 6, 5
	3.93	1.90	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	3, 4, 1, 7, 5, 2, 6
2,3,5,6-Tetrachloronitrobenzene	4.38	3.13	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	2, 6, 3, 7, 1, 5, 4
	4.38	3.20	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	5-6-7, 2, 3, 1, 4
	4.38	3.34	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5-6, 2, 3, 1, 4
2,3,5,6-Tetrachlorophenol	4.39	2.15	*Jordanella floridae*	Smith *et al.* (1990)	4, 1, 3, 2, 6, 7, 5
Thiobencarb	3.40	1.82	*Gnathopogon caerulescens*	Tsuda *et al.* (1988)	3-5, 7, 1, 4, 6, 2
	3.40	2.23	*Pseudorasbora parva*	Kanazawa (1981)	4, 1, 6-7, 2, 3-5
Toluene diamine	3.16	1.96	*Pimephales promelas*	Veith *et al.* (1979)	1, 4-7, 3-5, 6, 2
2,4,6-Tribromoanisole	4.48	2.94	*Pimephales promelas*	Veith *et al.* (1979)	4, 1, 5, 3, 2, 6, 7
1,3,5-Tribromobenzene	4.51	3.23[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	2, 3, 5, 6, 1, 7, 4
	4.51	3.70	*Oncorhynchus mykiss*	Oliver and Niimi (1984)	5, 7, 6, 2, 3, 1, 4
	4.51	3.97	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 6, 2, 3, 1, 4
	4.51	4.08	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	7, 5, 6, 2, 3, 1, 4
2,4,6-Tribromobiphenyl	6.03	3.88[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	6, 4, 2, 1, 7, 3, 5
2,4,6-Tribromophenol	4.23	2.71	*Brachydanio rerio*	Butte *et al.* (1987)	5, 4, 1, 3, 2, 6-7
2,3,4-Trichloroaniline	3.68	2.00	*Poecilia reticulata*	de Wolf *et al.* (1993)	3, 4, 1, 7, 6, 2, 5
2,4,5-Trichloroaniline	3.69	2.33	*Poecilia reticulata*	de Wolf *et al.* (1993)	3, 4, 1, 7, 2-6, 5
2,4,6-Trichloroaniline	3.69	2.33	*Poecilia reticulata*	de Wolf *et al.* (1993)	3, 4, 1, 7, 2-6, 5
3,4,5-Trichloroaniline	3.32	2.36	*Poecilia reticulata*	de Wolf *et al.* (1993)	2, 5, 6, 4, 1, 7, 3
1,2,3-Trichlorobenzene	4.14	2.90	*Poecilia reticulata*	de Wolf *et al.* (1993)	2, 7, 6, 1-3, 4, 5
	4.14	3.08	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 7, 2, 1-3, 4
	4.14	3.28	*Poecilia reticulata*	Schrap and Opperhuizen (1990)	6, 7, 2, 1-3, 5, 4
	4.14	3.41	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 7, 2, 1-3, 4
1,2,4-Trichlorobenzene	4.05	2.95	*Oncorhynchus mykiss*	Veith *et al.* (1979)	6, 2-7, 1, 3, 4-5
	4.05	3.11	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 2-7, 1, 3, 4
	4.05	3.31	*Jordanella floridae*	Smith *et al.* (1990)	5, 6, 2-7, 1, 3, 4
	4.05	3.32	*Pimephales promelas*	Veith *et al.* (1979)	6, 2-7, 1, 3, 4-5
	4.05	3.36	*Lepomis cyanellus*	Veith *et al.* (1979)	6, 2-7, 1, 3, 4-5
	4.05	3.36	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 5, 2-7, 1, 3, 4
	4.05	3.51	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 2-7, 1, 3, 4
	4.05	3.57	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	6, 5, 2-7, 1, 3, 4
1,3,5-Trichlorobenzene	4.19	3.26	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 7, 2, 3, 1, 4
	4.19	3.48	*Poecilia reticulata*	Schrap and Opperhuizen (1990)	6, 7, 2, 3, 1-5, 4
	4.19	3.61	*Oncorhynchus mykiss*	Oliver and Niimi (1983)	5, 6, 7, 2, 3, 1, 4
2,2',5-Trichlorobiphenyl	5.60	4.30[§]	*Carassius auratus*	Bruggeman *et al.* (1981)	7, 3, 6, 5, 1, 2, 4
	5.60	4.91	*Oncorhynchus mykiss*	Oliver and Niimi (1985)	5, 7, 3, 6, 1, 2, 4
2,4,5-Trichlorobiphenyl	5.90	3.78[§]	*Poecilia reticulata*	Gobas *et al.* (1989)	4, 6, 2, 1, 7, 3, 5
	5.90	4.15	*Poecilia reticulata*	Gobas and Schrap (1990)	4, 6, 2, 1, 7, 3, 5
2,4',5-Trichlorobiphenyl	5.79	4.63[§]	*Carassius auratus*	Bruggeman *et al.* (1981)	3, 7, 5, 1, 6, 2, 4
1,1,1-Trichloroethane	2.47	0.95	*Lepomis macrochirus*	Veith *et al.* (1980)	3, 5, 7, 1, 4-6, 2
1,1,2-Trichloroethylene	2.42	1.23	*Lepomis macrochirus*	Veith *et al.* (1980)	5, 1-3, 7, 4-6, 2
3,4,5-Trichloroguaiacol	4.11	2.41	*Oncorhynchus mykiss*	Niimi *et al.* (1990)	4, 1-3, 2, 7, 6, 5
4,5,6-Trichloroguaiacol	3.74	1.97	*Oncorhynchus mykiss*	Niimi *et al.* (1990)	3, 4, 1, 7, 2-6, 5
2,3,4-Trichloronitrobenzene	3.61	2.20	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	3, 1-4-7, 6, 2-5
2,4,5-Trichloronitrobenzene	3.40	1.84	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	3, 7, 1, 4, 5, 6, 2
2,4,6-Trichloronitrobenzene	3.69	2.88	*Oncorhynchus mykiss*	Niimi *et al.* (1989)	5, 2-6, 7, 1, 4, 3
2,4,6-Trichlorophenol	3.75	1.94	*Jordanella floridae*	Smith *et al.* (1990)	3, 4, 1, 7, 2-6, 5
	3.75	2.37[§]	*Oryzias latipes*	Sugiura *et al.* (1984)	5, 3, 4, 1, 7, 2-6
Tricresyl phosphate	5.11	2.22	*Pimephales promelas*	Veith *et al.* (1979)	4, 1, 2, 5, 3-6, 7
	5.11	2.90	*Alburnus alburnus*	Bengtsson *et al.* (1986)	4, 1, 2, 5, 3-6, 7
Trifluralin	5.34	3.50	*Pseudorasbora parva*	Kanazawa (1981)	4, 2, 1, 6, 5, 3, 7
Triphenyl phosphate	4.59	2.60	*Alburnus alburnus*	Bengtsson *et al.* (1986)	4, 1, 2-5, 3, 6, 7

[†]log BCF expressed on a lipid content basis; [§]log BCF estimated from the rate constants k_1 and k_2; *Dichlorodibenzo-*p*-dioxin; [$]Hexa- and hepta-chlorodibenzo-*p*-dioxin; [£]Heptachlorodibenzofuran; **Isomer not specified; [$$]Pentachlorodibenzo-*p*-dioxin; [ff]Pentachlorodibenzofuran; [&]Tetrachlorodibenzo-*p*-dioxin; [&&]Tetrachlorodibenzofuran; °Classification of the models by increasing order of the absolute values of the residuals; x: model presenting a negative residual; x-y: models with identical residuals (absolute value).

Table II *n*-octanol/water partition coefficients (log P), bioconcentration data (log BCF) obtained under static and semi-static conditions and classification of the seven models.

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
Acridine	3.45	3.11	*Poecilia reticulata*	de Voogt *et al.* (1991)	2, 5, 6, 4, 1, 7, 3
Aniline	0.90	0.41	*Brachydanio rerio*	Kalsch *et al.* (1991)	2, 4, 1, 6, 5, 3, 7
Anthracene	4.45	2.95	*Lepomis macrochirus*	Spacie *et al.* (1983)	4, 1, 5, 3, 2, 6, 7
	4.45	3.86	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 7, 6, 2, 3, 1, 4
Atrazine	2.61	0.78	*Brachydanio rerio*	Görge and Nagel (1990)	3, 5, 7, 1, 4, 6, 2
Benzo[*b*]furan	2.86	2.56	*Poecilia reticulata*	de Voogt *et al.* (1991)	2, 6, 5, 4, 1, 7, 3
Benzo[*b*]naphtho(*2,3-d*)thiophene	5.07	4.17	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 7, 6, 3, 2, 1, 4
Benzo[*a*]pyrene	5.97	3.69	*Lepomis macrochirus*	Spacie *et al.* (1983)	6, 4, 2, 1, 7, 5, 3
Benzo[*b*]thiophene	3.26	2.53	*Poecilia reticulata*	de Voogt *et al.* (1991)	2, 5, 6, 4, 1, 7, 3
2,2'-Bithiophene	3.75	3.55	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 2-6, 7, 1, 4, 3
p-sec-Butylphenol	3.08	1.57	*Salmo salar*	McLeese *et al.* (1981)	3-5, 7, 1, 4, 6, 2
t-Butylphenyldiphenyl phosphate	5.12	2.89	*Pimephales promelas*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
	5.12	3.04	*Oncorhynchus mykiss*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
Carbazole	3.84	2.70	*Poecilia reticulata*	de Voogt *et al.* (1991)	6, 2, 5, 7, 1, 4, 3
2-Chloroaniline	1.93	1.18	*Brachydanio rerio*	Kalsch *et al.* (1991)	2, 7, 4, 6, 1, 5, 3
3-Chloroaniline	1.91	1.06	*Brachydanio rerio*	Kalsch *et al.* (1991)	4, 6, 1, 2, 7, 5, 3
4-Chloroaniline	1.88	0.91	*Brachydanio rerio*	Kalsch *et al.* (1991)	1-6, 4, 2, 5, 3, 7
2-Chloronaphthalene	4.14	3.63	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	6, 7, 2, 1-3, 5, 4
2-Chloronitrobenzene	2.52	2.29†	*Poecilia reticulata*	Deneer *et al.* (1987)	3, 5, 7, 1, 4, 6, 2
3-Chloronitrobenzene	2.50	2.42†	*Poecilia reticulata*	Deneer *et al.* (1987)	5, 7, 1, 3, 4, 6, 2
4-Chloronitrobenzene	2.39	2.46†	*Poecilia reticulata*	Deneer *et al.* (1987)	7, 1-4-6, 5, 2, 3
2-Chloro-6-nitrotoluene	3.09	3.09†	*Poecilia reticulata*	Deneer *et al.* (1987)	5, 4-6, 1, 2, 7, 3
4-Chloro-2-nitrotoluene	3.05	3.02†	*Poecilia reticulata*	Deneer *et al.* (1987)	4, 5, 1, 6, 7, 2, 3
2,8-DCDD*	5.60	2.83	*Carassius auratus*	Sijm and Opperhuizen (1988)	5, 4, 2, 1, 6, 3, 7
Dibenzo(1,4)dioxan	4.19	3.85	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 6, 7, 2, 3, 1, 4
Dibenzofuran	4.21	3.54	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 6, 7, 2, 3, 1, 4
Dibenzothiophene	4.49	3.82	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 7, 6, 2, 3, 1, 4
1,2-Dibromobenzene	3.64	2.70	*Pimephales promelas*	Sijm *et al.* (1993)	2, 6, 7, 1-4, 3, 5
	3.64	3.50	*Poecilia reticulata*	Sijm *et al.* (1993)	5, 2, 6, 7, 1-4, 3
1,4-Dibromobenzene	3.79	2.70	*Poecilia reticulata*	Sijm *et al.* (1993)	6, 2, 7, 1, 4, 3, 5
	3.79	3.40	*Pimephales promelas*	Sijm *et al.* (1993)	6, 2, 7-5, 1, 4, 3
2,4-Dichloroaniline	2.91	1.98	*Brachydanio rerio*	Kalsch *et al.* (1991)	2, 6, 4, 1, 7, 3-5
3,4-Dichloroaniline	2.78	1.48	*Brachydanio rerio*	Kalsch *et al.* (1991)	3-5, 7, 1, 4, 6, 2
1,2-Dichlorobenzene	3.43	2.40	*Poecilia reticulata*	Sijm *et al.* (1993)	2, 6, 5, 1-4, 7, 3
	3.43	2.70	*Pimephales promelas*	Sijm *et al.* (1993)	2, 6, 1-4, 5, 7, 3
1,3-Dichlorobenzene	3.53	3.78†	*Poecilia reticulata*	Opperhuizen *et al.* (1988)	2, 6, 1-4, 7, 3-5
1,4-Dichlorobenzene	3.44	1.70	*Poecilia reticulata*	Sijm *et al.* (1993)	5, 3, 7, 1, 4, 6, 2
	3.44	2.40	*Pimephales promelas*	Sijm *et al.* (1993)	2, 6, 4, 1-5, 7, 3
1,4-Dichloronaphthalene	4.66	3.36	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	3, 5, 2, 6, 1, 7, 4
1,8-Dichloronaphthalene	4.19	3.79	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	6, 7, 2, 3, 1-5, 4
2,3-Dichloronaphthalene	4.51	4.04	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	7, 6, 2, 3, 5, 1, 4
2,3-Dichloronitrobenzene	3.05	3.01†	*Poecilia reticulata*	Deneer *et al.* (1987)	4, 1, 5, 6, 7, 2-3
2,4-Dichloronitrobenzene	3.05	3.02†	*Poecilia reticulata*	Deneer *et al.* (1987)	4, 5, 1, 6, 7, 2, 3
2,5-Dichloronitrobenzene	3.03	2.92†	*Poecilia reticulata*	Deneer *et al.* (1987)	7, 1, 4, 5, 3, 6, 2
3,5-Dichloronitrobenzene	3.09	3.01†	*Poecilia reticulata*	Deneer *et al.* (1987)	1, 4, 7-5, 6, 3, 2
2,3-Dimethylnitrobenzene	2.83	2.86†	*Poecilia reticulata*	Deneer *et al.* (1987)	4, 6, 5, 1, 7, 2, 3
3,4-Dimethylnitrobenzene	2.91	2.84†	*Poecilia reticulata*	Deneer *et al.* (1987)	1, 7, 5, 4, 6, 3, 2
1,2-Dinitrobenzene	1.69	1.02†	*Poecilia reticulata*	Deneer *et al.* (1987)	3, 5, 1, 6, 4, 2, 7
1,3-Dinitrobenzene	1.49	1.87†	*Poecilia reticulata*	Deneer *et al.* (1987)	4, 2, 1-6, 5, 3, 7
2,4-Dinitrotoluene	1.98	2.31†	*Poecilia reticulata*	Deneer *et al.* (1987)	7, 2, 4, 6, 1, 5, 3
2,6-Dinitrotoluene	2.10	2.44†	*Poecilia reticulata*	Deneer *et al.* (1987)	2, 7, 4, 6, 1, 5, 3
p-Dodecylphenol	7.91	3.78	*Salmo salar*	McLeese *et al.* (1981)	7, 6, 5, 2, 4, 1, 3
Fluorene	4.18	3.35	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 6, 7, 2, 3, 1, 4
Hexachlorobenzene	5.73	5.62†	*Poecilia reticulata*	Opperhuizen *et al.* (1988)	7, 5, 3, 1, 6, 2, 4
γ-Hexachlorocyclohexane	3.72	2.34	*Brachydanio rerio*	Görge and Nagel (1990)	3-5, 1-4, 7, 2-6
	3.72	2.41	*Salmo salar*	Carlberg *et al.* (1986)	3-5, 1-4, 7, 2-6
	3.72	2.84	*Salmo salar*	Carlberg *et al.* (1986)	2-6, 7, 1-4, 3-5

Table II (continued)

Chemical	*log P*	*log BCF*	*Species*	*Reference*	*Classification°*
2-Nitroaniline	1.85	0.91	*Brachydanio rerio*	Kalsch *et al.* (1991)	6, 1, 4, 2, 7, 5, 3
3-Nitroaniline	1.37	0.92	*Brachydanio rerio*	Kalsch *et al.* (1991)	2, 4, 1-6, 7, 5, 3
4-Nitroaniline	1.39	0.64	*Brachydanio rerio*	Kalsch *et al.* (1991)	4, 1-6, 2, 5, 3, 7
Nitrobenzene	1.85	1.47†	*Poecilia reticulata*	Deneer *et al.* (1987)	3, 5, 1, 6, 4, 2, 7
2-Nitrotoluene	2.30	2.28†	*Poecilia reticulata*	Deneer *et al.* (1987)	5, 1, 6, 7-4, 3, 2
3-Nitrotoluene	2.42	2.21†	*Poecilia reticulata*	Deneer *et al.* (1987)	5, 3, 1, 7, 4-6, 2
4-Nitrotoluene	2.37	2.37†	*Poecilia reticulata*	Deneer *et al.* (1987)	5, 1, 7, 6, 4, 3, 2
p-Nonylphenol	5.76	2.45	*Salmo salar*	McLeese *et al.* (1981)	4, 2, 6, 1, 7, 5, 3
Pentachloroaniline	5.08	3.78	*Poecilia reticulata*	de Wolf *et al.* (1992)	6, 3, 7, 2, 1, 5, 4
Pentachlorobenzene	5.18	3.45	*Carassius auratus*	Sijm and Opperhuizen (1988)	4, 1, 2, 6, 3, 5, 7
	5.18	5.18†	*Poecilia reticulata*	Opperhuizen *et al.* (1988)	3, 5-6, 7, 2, 1, 4
	5.18	4.23	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	7, 3, 5-6, 2, 1, 4
Pyrene	5.18	3.68	*Poecilia reticulata*	de Voogt *et al.* (1991)	1, 2, 4, 6, 3, 7, 5
2,3,7,8-TCDD[&]	6.42	3.90	*Pimephales promelas*	Adams *et al.* (1986)	6, 7, 4, 2, 1, 5, 3
2,3,4,5-Tetrachloroaniline	4.57	3.28	*Poecilia reticulata*	de Wolf *et al.* (1992)	3, 2, 6, 1, 7, 4, 5
2,3,5,6-Tetrachloroaniline	4.46	3.59	*Poecilia reticulata*	de Wolf *et al.* (1992)	5, 7, 6, 2, 3, 1, 4
1,2,3,4-Tetrachlorobenzene	4.64	4.74†	*Poecilia reticulata*	Opperhuizen *et al.* (1988)	6, 7, 3, 2-5, 1, 4
3,3',4,4'-Tetrachlorobiphenyl	6.63	4.59	*Poecilia reticulata*	Opperhuizen and Voors (1987)	7, 4, 2, 1, 6, 5, 3
3,3',4,4'-Tetrachlorodiphenylether	5.78	4.51	*Poecilia reticulata*	Opperhuizen and Voors (1987)	3, 5, 7, 1, 6, 2, 4
Tetrachloroguaiacol	4.45	3.15	*Salmo salar*	Carlberg *et al.* (1986)	2, 3, 5, 1, 6, 4, 7
Thianthrene	4.47	3.56	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 7, 6, 2, 3, 1, 4
2,3,4-Trichloroaniline	3.68	2.61	*Poecilia reticulata*	de Wolf *et al.* (1992)	5, 2, 6, 7, 1, 4, 3
2,4,5-Trichloroaniline	3.69	2.88	*Poecilia reticulata*	de Wolf *et al.* (1992)	5, 2-6, 7, 1, 4, 3
2,4,6-Trichloroaniline	3.69	3.13	*Poecilia reticulata*	de Wolf *et al.* (1992)	5, 2-6, 7, 1, 4, 3
3,4,5-Trichloroaniline	3.32	3.04	*Poecilia reticulata*	de Wolf *et al.* (1992)	2, 5-6, 4, 1, 7, 3
1,3,5-Trichlorobenzene	4.19	4.35†	*Poecilia reticulata*	Opperhuizen *et al.* (1988)	6, 7, 2, 3, 1-5, 4
2,4,5-Trichlorobiphenyl	5.90	4.26	*Poecilia reticulata*	Opperhuizen and Voors (1987)	2, 6, 1-4, 7, 5, 3
2,4,5-Trichlorodiphenylether	5.44	4.18	*Poecilia reticulata*	Opperhuizen and Voors (1987)	7, 3, 5, 6, 1, 2, 4
1,3,7-Trichloronaphthalene	5.35	4.43	*Poecilia reticulata*	Opperhuizen *et al.* (1985)	7, 3, 5, 6, 1, 2, 4
2,4,6-Trichlorophenol	3.75	2.84	*Salmo salar*	Carlberg *et al.* (1986)	2-6, 7, 1, 4, 3, 5
Tri-*m*-cresyl phosphate	5.11	2.78	*Pimephales promelas*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
	5.11	2.89	*Oncorhynchus mykiss*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
Tri-*p*-cresyl phosphate	5.11	2.97	*Pimephales promelas*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
	5.11	3.15	*Oncorhynchus mykiss*	Muir *et al.* (1983)	4, 1, 2, 5, 3-6, 7
Triphenyl phosphate	4.59	2.75	*Pimephales promelas*	Muir *et al.* (1983)	4, 1, 2-5, 3, 6, 7
	4.59	2.76	*Oncorhynchus mykiss*	Muir *et al.* (1983)	4, 1, 2-5, 3, 6, 7
Xanthene	4.23	3.62	*Poecilia reticulata*	de Voogt *et al.* (1991)	5, 6-7, 2, 3, 1, 4

†log BCF expressed on a lipid content basis; [$]log BCF estimated from the rate constants k_1 and k_2; *Dichlorodibenzo-*p*-dioxin; [&]Tetrachlorodibenzo-*p*-dioxin; °Classification of the models by increasing order of the absolute values of the residuals; x: model presenting a negative residual; x-y: models with identical residuals (absolute value).

Table III RMS values for the seven selected models.

	*Eq. (1)**	*Eq. (2)*	*Eq. (3)*	*Eq. (4)*	*Eq. (5)*	*Eq. (6)*	*Eq. (7)*
Flow-through							
log P ≤ 6 (n = 267)	0.58	0.59	0.60	0.58	0.60	0.59	0.64
log P > 6 (n = 75)	1.93	1.78	2.32	1.79	1.83	0.86	1.13
Total (n = 342)	1.04	0.99	1.21	0.98	1.01	0.66	0.77
Static or semi-static							
Total (n = 94)	0.58	0.55	0.67	0.57	0.55	0.51	0.60

* (1) Veith *et al.* (1979); (2) Veith *et al.* (1980); (3) Mackay (1982); (4) Isnard and Lambert (1988); (5) Nendza (1991); (6) Bintein *et al.* (1993); (7) Connell and Hawker (1988).

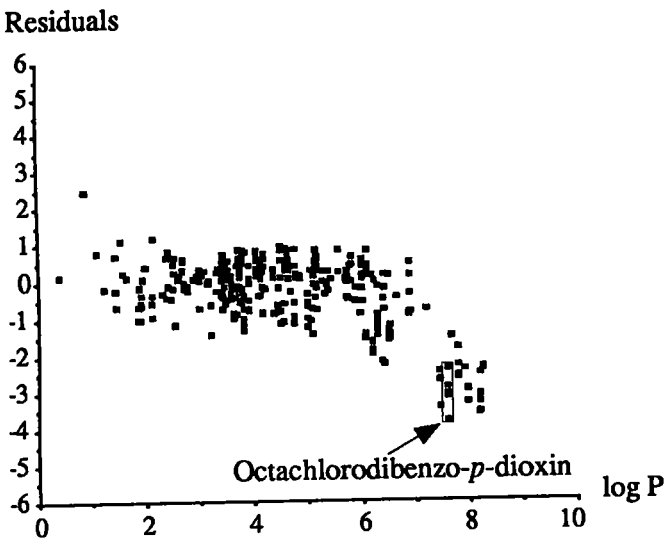

Figure 1 Residuals of Eq. (1) vs log P for BCF data obtained under flow-through conditions.

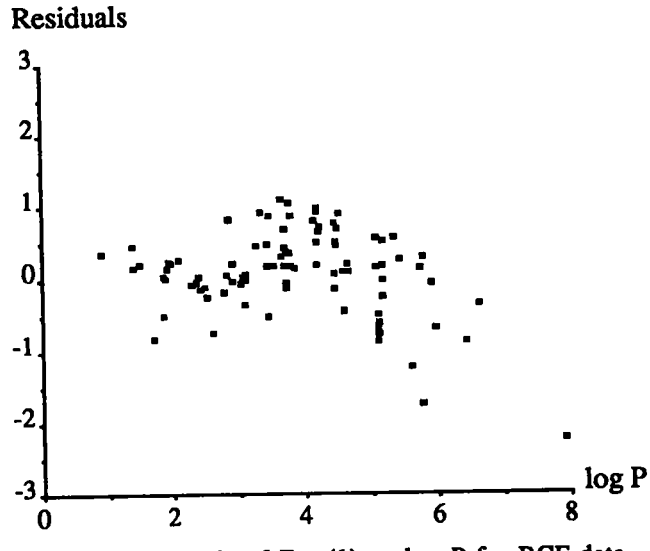

Figure 2 Residuals of Eq. (1) vs log P for BCF data obtained under static and semi-static conditions.

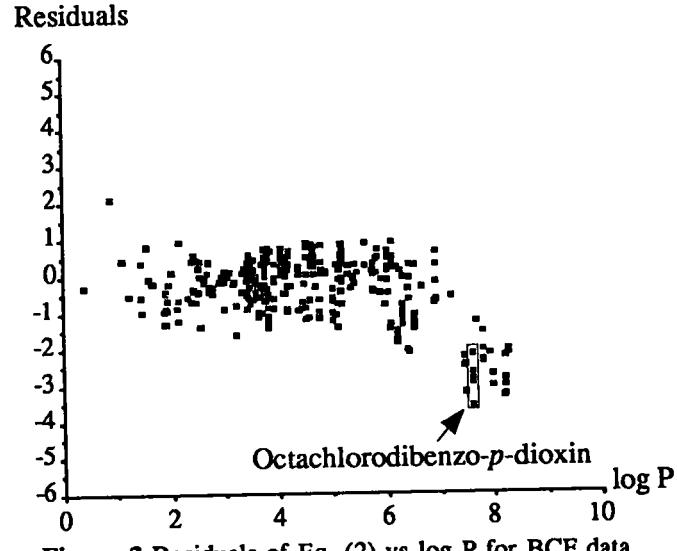

Figure 3 Residuals of Eq. (2) vs log P for BCF data obtained under flow-through conditions.

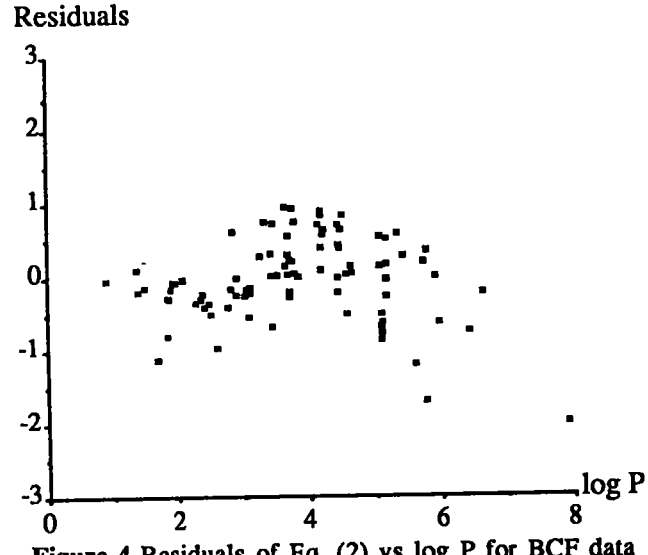

Figure 4 Residuals of Eq. (2) vs log P for BCF data obtained under static and semi-static conditions.

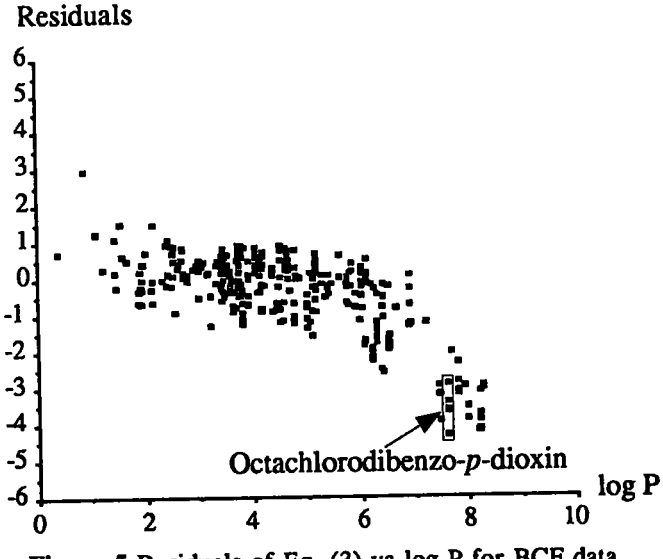

Figure 5 Residuals of Eq. (3) vs log P for BCF data obtained under flow-through conditions.

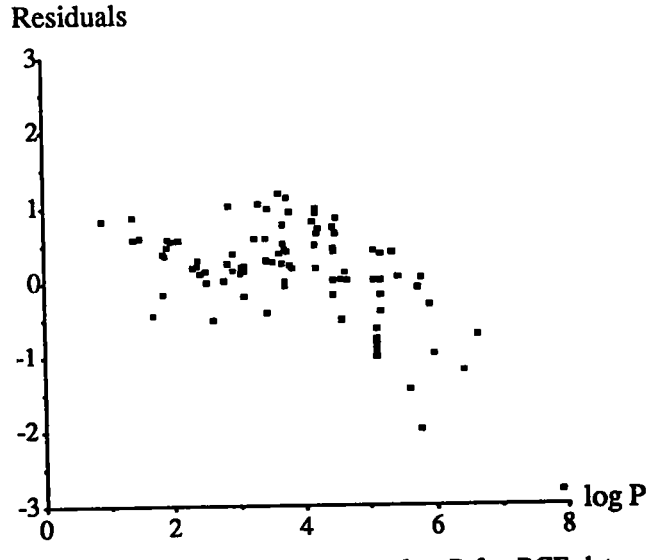

Figure 6 Residuals of Eq. (3) vs log P for BCF data obtained under static and semi-static conditions.

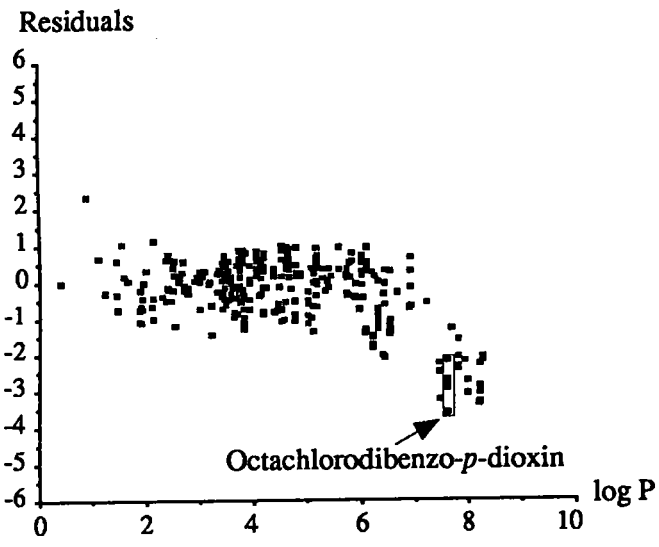

Figure 7 Residuals of Eq. (4) vs log P for BCF data obtained under flow-through conditions.

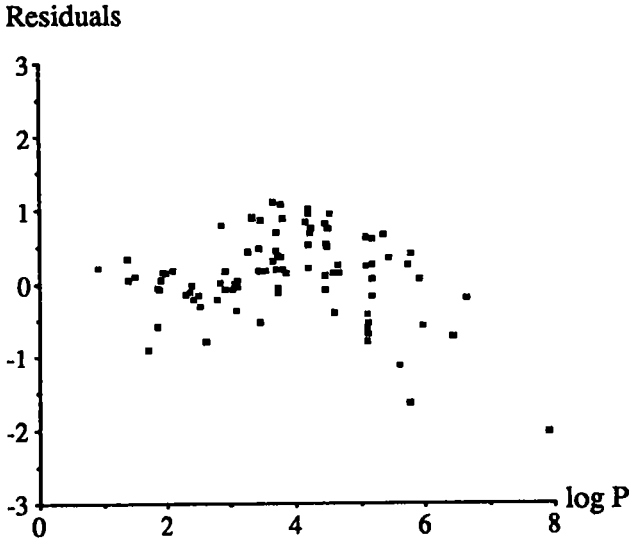

Figure 8 Residuals of Eq. (4) vs log P for BCF data obtained under static and semi-static conditions.

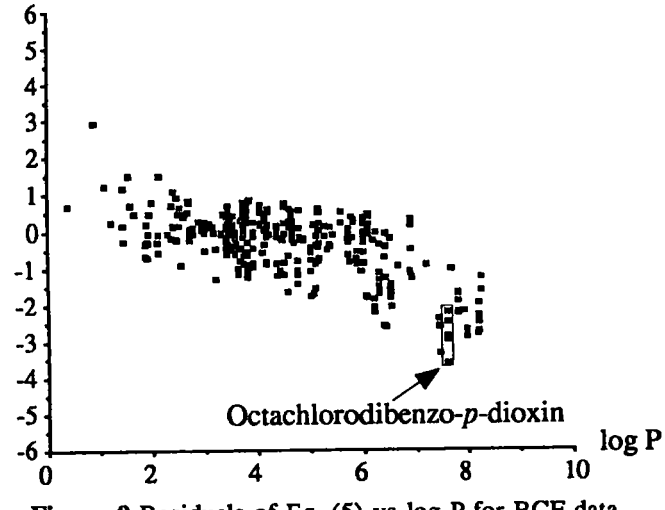

Figure 9 Residuals of Eq. (5) vs log P for BCF data obtained under flow-through conditions.

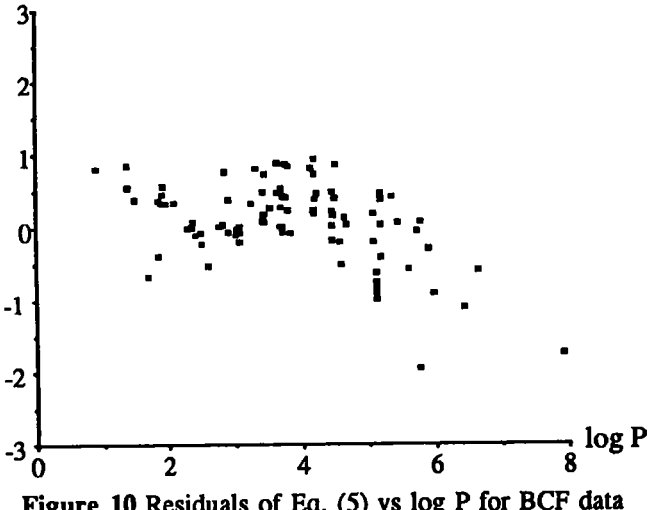

Figure 10 Residuals of Eq. (5) vs log P for BCF data obtained under static and semi-static conditions.

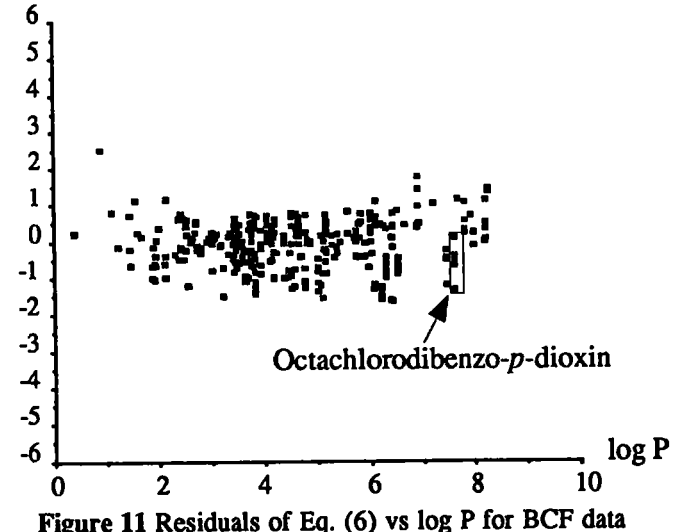

Figure 11 Residuals of Eq. (6) vs log P for BCF data obtained under flow-through conditions.

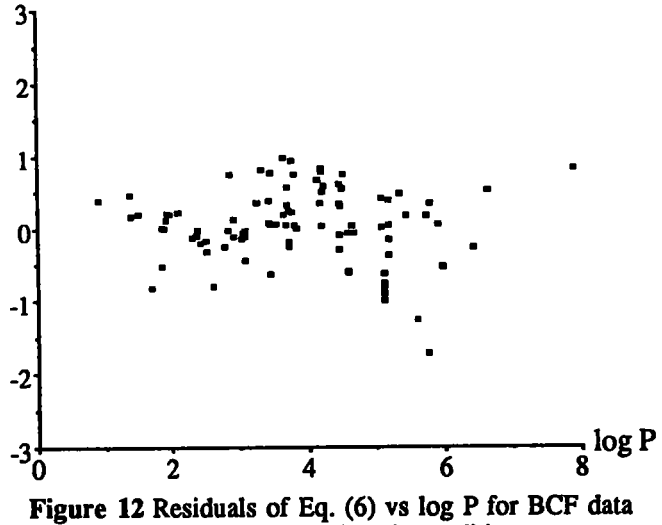

Figure 12 Residuals of Eq. (6) vs log P for BCF data obtained under static and semi-static conditions.

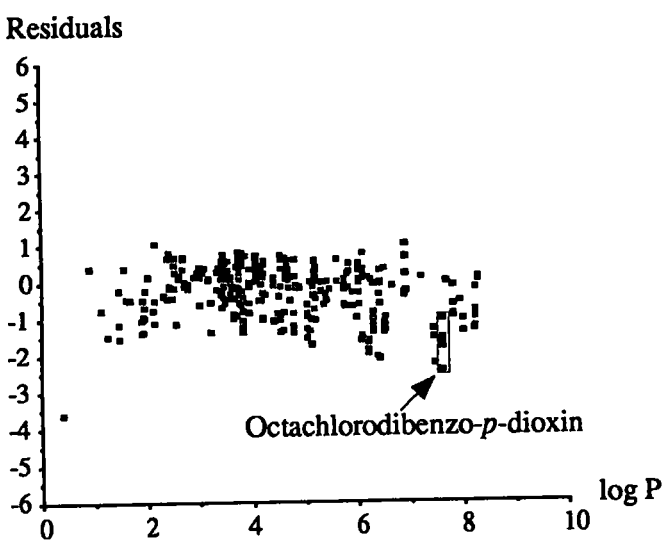

Figure 13 Residuals of Eq. (7) vs log P for BCF data obtained under flow-through conditions.

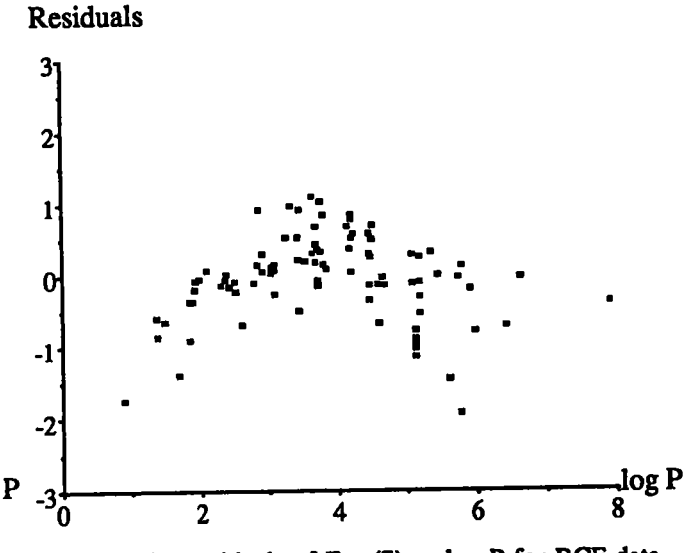

Figure 14 Residuals of Eq. (7) vs log P for BCF data obtained under static and semi-static conditions.

octachlorodibenzo-*p*-dioxin (Figure 11). This underlines the necessity to estimate the performances of a model from different values for a same chemical.

Last, to obtain a general approximation of the predictive performances of the studied models, the RMS (i.e., root mean square error) values (Eq. (8)) for the seven studied models were calculated (Table III).

$$RMS = ((\Sigma (\log BCF_{obs.} - \log BCF_{calc.})^2)/\text{number of observations})^{1/2} \quad (8)$$

The results reported in Table III confirm that for compounds with log P values inferior to 6, the different models yield equivalent results. At the opposite, for molecules presenting log P values superior to 6, the bilinear model of Bintein *et al.* (1993) is largely superior to the other studied models. From our results, it appears that the different models under study do not present the same predictive power and domain of application. This can be problematic if they are incorporated in different computer programs designed to support decision-making in the evaluation of the hazards and risks of chemicals. For highly hydrophobic chemicals, the linear models (i.e., Eqs. (1) to (4)) tend to considerably overestimate the BCF values and Eq. (5) often gives unacceptable predictions. Eq. (7) provides better simulations than Eq. (5) but the statistical validity of this model is questionable. From a risk assessment point of view, highly conservative models could be judged interesting. However, from a modeling point of view, it is obvious that the first requirement for a model is to simulate with accuracy the reality. Therefore, among the seven models, we can consider that Eq. (6) (Bintein *et al.*, 1993) meets at best this objective. Indeed, it presents the best predictive power and the widest domain of application. However, it is important to stress that we do not claim that this model allows to simulate the bioconcentration behavior of all the organic chemicals susceptible to contaminate the aquatic ecosystems. Indeed, we simply assume that on the basis of BCF QSAR models using the *n*-octanol/water partition coefficient, it is the most efficient. It is obvious that all these models do not take into account the transformation of the chemicals in the fish. The lack of this information in the design of the models can explain some of the bad simulations obtained for the seven studied BCF models.

Acknowledgment

The work presented in this paper was supported by different contracts from the French Ministry of the Environment.

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RESUME

L'élaboration d'une équation bilinéaire reliant le coefficient de partage *n*-octanol/eau (log P) à la bioconcentration des molécules organiques chez les poissons a permis de mieux simuler le comportement bioaccumulatif des substances très lipophiles. L'adsorption par les sols et les sédiments des substances ionisées et non-ionisées a pu être modélisée par une équation régressive prenant en compte le log P, le potentiel d'ionisation des molécules, le pourcentage en carbone organique et le pH des substrats. L'intégration de ces deux relations dans CHEMFRANCE a élargi le domaine d'application de ce modèle régional de fugacité niveau III appliqué à la France. Des études menées sur le lindane et l'atrazine ont démontré le haut potentiel de simulation de CHEMFRANCE pour ces pesticides. Enfin, une analyse comparatives des principales relations structure-bioconcentration utilisant le log P comme descripteur moléculaire a été réalisée afin de tester l'intérêt du modèle que nous proposons.

Mots clés: CHEMFRANCE; bioconcentration; adsorption; QSAR; validation; lindane; atrazine.

SUMMARY

The elaboration of a bilinear relationship between the *n*-octanol/water partition coefficient (log P) and the accumulation of chemicals in fish allowed to simulate more accurately the bioconcentration potential of very lipophilic molecules. The soil and sediment adsorption of ionized and non-ionized chemicals has been modeled by a regression equation integrating log P, the ionization potential of compounds, the percentage of organic carbon and the pH of the substrates. The incorporation of these two equations in CHEMFRANCE allowed to increase the domain of application of this regional level III fugacity model applied to France. Studies performed on lindane and atrazine underlined the high simulation potential of this model for these pesticides. Last, a comparative analyse of structure-bioconcentration relationships using log P as molecular descriptor was performed in order to test the usefulness of the model we proposed.

Key words: CHEMFRANCE; bioconcentration; adsorption; QSAR; validation; lindane; atrazine.

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May 28, 1996
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RE: COMPARISON OF BCF MODELS BASED ON LOG P

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PII: S0045-6535(96)00246-9

Chemosphere, Vol. 33, No. 6, pp. 1047–1065, 1996

0045-6535/96 $15.00+0.00

COMPARISON OF BCF MODELS BASED ON LOG P

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(Received in Germany 9 January 1996; accepted 24 May 1996)

ABSTRACT

Seven linear and nonlinear BCF models based on log P have been compared in order to estimate their accuracy, predictive power, and domain of application. This comparison was performed from a data set constituted of 436 experimental BCF values recorded for 227 chemicals. We showed that for chemicals with log P<6, the different models yielded equivalent results. At the opposite, for highly hydrophobic chemicals (log P>6), the bilinear model log BCF = 0.91 log P - 1.975 log (6.8 10^{-7} P + 1) - 0.786 (n = 154; r = 0.95; s = 0.347; F = 463.5) was superior to the other studied models. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Numerous attempts have been made for modeling the accumulation of organic chemicals by fish since the experimental determination of this important biological activity is a time-consuming and costly exercise. The most widely used method consists in correlating laboratory bioconcentration factors (BCFs) determined in fish and *n*-octanol/water partition coefficients (log P). Bioconcentration can be defined as the result of the uptake, distribution, and elimination of a chemical in a fish due to water-borne exposure (Barron, 1990), whereas bioaccumulation includes all routes of exposure, and biomagnification deals with accumulation via food chains. Numerous test guidelines for the experimental determination of BCF in fish are available (e.g., OECD, ASTM). BCF is determined as the concentration of the chemical in whole fish at steady state divided by the concentration of the chemical in water during the exposure period and/or as the ratio between the uptake (k_1) and depuration (k_2) rate constants assuming first order kinetics. The accumulation of an organic compound in a fish basically depends on its hydrophobicity. Therefore, log P is the physicochemical descriptor of choice for modeling bioconcentration. As a result, numerous BCF QSAR equations derived from log P are available in the literature and there is a need for the evaluation of their domain of application. Under these conditions, the aim of this study was to compare different BCF/log P models in order to estimate their accuracy, predictive power, and domain of application.

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