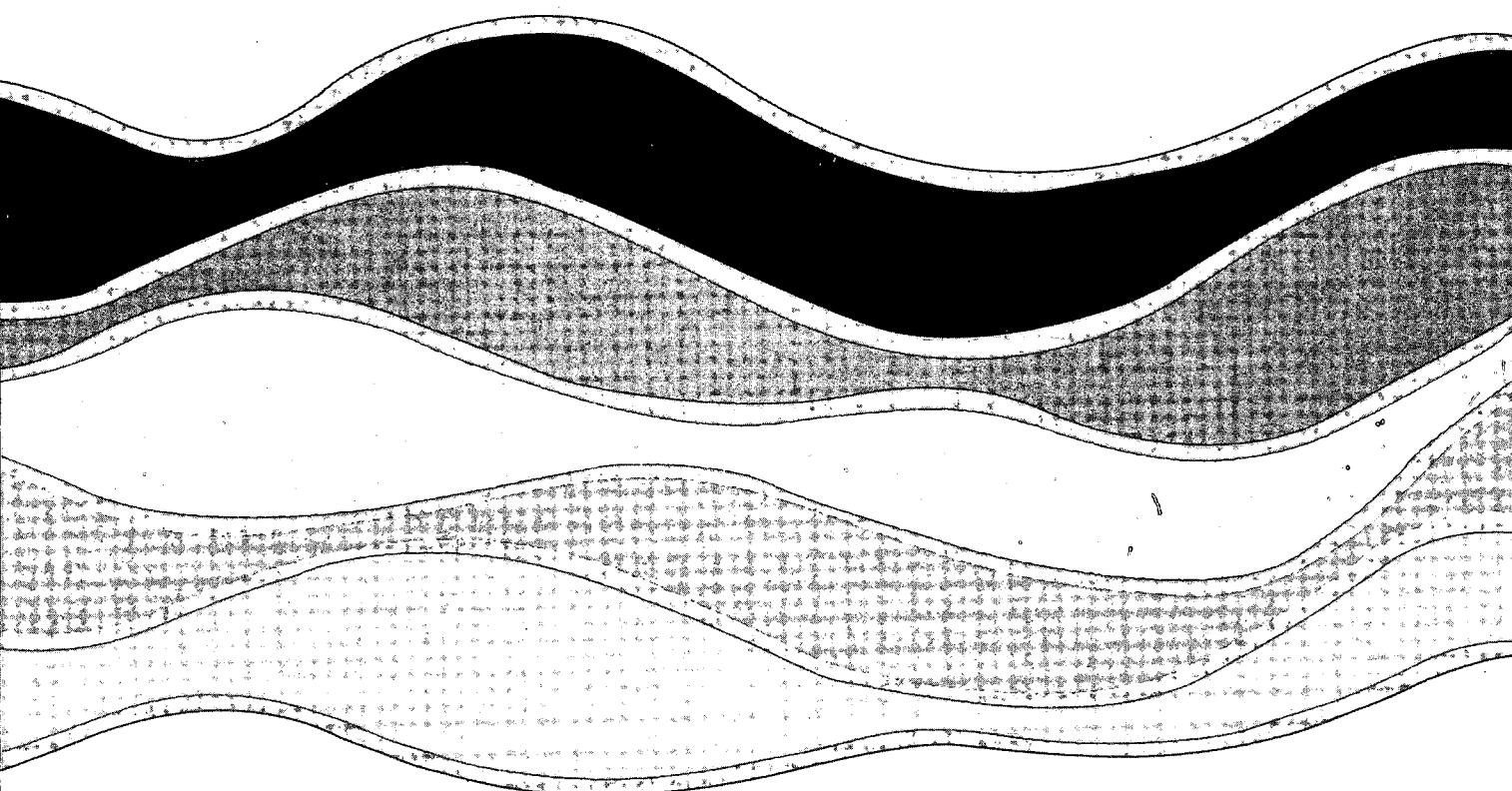


**NATIONAL
WATER
RESEARCH
INSTITUTE**

**INSTITUT
NATIONAL
de RECHERCHE
sur les
EAUX**



**SIMULATION OF DISULFECTON FATE IN THE
RIVER RHINE WITH THE TOXFATE MODEL**

E. HALFON AND R. BRUEGGEMANN

NWRI Contribution No. 90-04

TD
226
N87
No. 90-
04
c. 1

SIMULATION OF DISULFOTON FATE IN THE RIVER RHINE

WITH THE TOXFATE MODEL

by

Efraim Halfon

**Lakes Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, Canada L7R 4A6**

and

**Rainer Brueggemann
Projektgruppe Umweltgefaehrungspotentiale von Chemikalien
Gesellschaft fur Strahlen- und Umweltforschung
Ingolstaedter Landstrasse 1
D-8042 Neuherberg
Germany**

November 1989

MANAGEMENT PERSPECTIVE

Modeling the fate of chemicals in lakes and rivers has been the subject of much research. In this paper we use a fate model, TOXFATE, originally developed with Lake Ontario data to analyze the fate in the River Rhine of a chemical, Disulfoton, spilled by Sandoz in November 1986. Predicted and observed concentrations along the river are compared. This work has allowed the testing of the model TOXFATE, developed at NWRI, with a different data set. simulations can be displayed on paper or on a TV monitor driven by a desktop personal computer.

PERSPECTIVES GESTION

La modélisation de l'avenir des produits chimiques dans les lacs et les cours d'eau a fait l'objet de nombreuses recherches. Dans le présent rapport, nous utilisons le modèle TOXFATE, initialement mis au point avec les données recueillies dans le lac Ontario, pour analyser l'avenir du Disulfoton, produit chimique déversé dans le Rhin par l'usine Sandoz, en novembre 1986. Les concentrations prévues et observées dans le fleuve ont été comparées. Ce travail a permis de tester le modèle TOXFATE, mis au point à l'INRE, avec une série de données différentes. Les simulations peuvent être portées sur papier ou présentées sur un écran de télévision commandé par un ordinateur personnel de table.

ABSTRACT

In 1986 a chemical spill occurred at the Sandoz AG plant in Basel, Switzerland. Several chemicals entered the River Rhine and were transported downstream. In this paper we model the fate of one of the eight chemicals, Disulfoton, found in the German section of the River Rhine with TOXFATE, a TOXic contaminants FATE model. Simulations show that the TOXFATE model can describe the fate of Disulfoton in the River Rhine. The main problem is that the model has to be calibrated by adjusting the shape of the river sections at different localities. Inputs to the model are Disulfoton concentrations at Maxau and five physico-chemical properties, namely molecular weight, water solubility, octanol/water partition coefficient (K_{ow}), soil/adsorption coefficient (K_{oc}), vapour pressure or Henry's Law constant. Simulations are compared with Disulfoton data. TOXFATE predicts concentrations in the water column as well as volatilization and transport rates. Predicted and observed concentrations agree well at most locations. At Lobith, on the Dutch-German border, however, predicted concentrations are double the observed concentrations. Two explanations can be brought forward to explain this discrepancy, but none can be verified with field data. Thus, the model is not modified any further to improve its prediction capability at Lobith.

RÉSUMÉ

En 1986, un déversement accidentel s'est produit à l'usine Sandoz AG, à Basel, en Suisse. Plusieurs substances chimiques ont été déversées dans le Rhin et transportées en aval. Dans ce rapport, nous modélisons l'avenir de l'une des huit substances chimiques, le Disulfoton, relevées dans la partie allemande du Rhin, à l'aide de TOXFATE, un modèle de l'avenir des contaminants toxiques. Les simulations montrent que ce modèle peut décrire l'avenir du Disulfoton dans le Rhin. Il faut toutefois étalonner le modèle pour respecter la forme des tronçons du fleuve à différents endroits, ce qui représente un problème majeur. Les données incluses dans le modèle sont les concentrations de Disulfoton observées à Maxau et cinq propriétés physico-chimiques, soit le poids moléculaire, la solubilité de l'eau, le coefficient de partage octanol/eau (K_{ow}), le coefficient d'adsorption du sol (K_{oc}), et la pression de vapeur ou la constante de la loi d'Henry. Les simulations sont comparées aux données sur le Disulfoton. TOXFATE prévoit les concentrations dans la colonne d'eau de même que les vitesses de volatilsation et de transport. Les concentrations prévues correspondent à celles observées à la plupart des endroits. Toutefois, à Lobith, sur la frontière germano-hollandaise, les concentrations prévues sont le double des concentrations observées. Deux raisons peuvent expliquer cet

INTRODUCTION

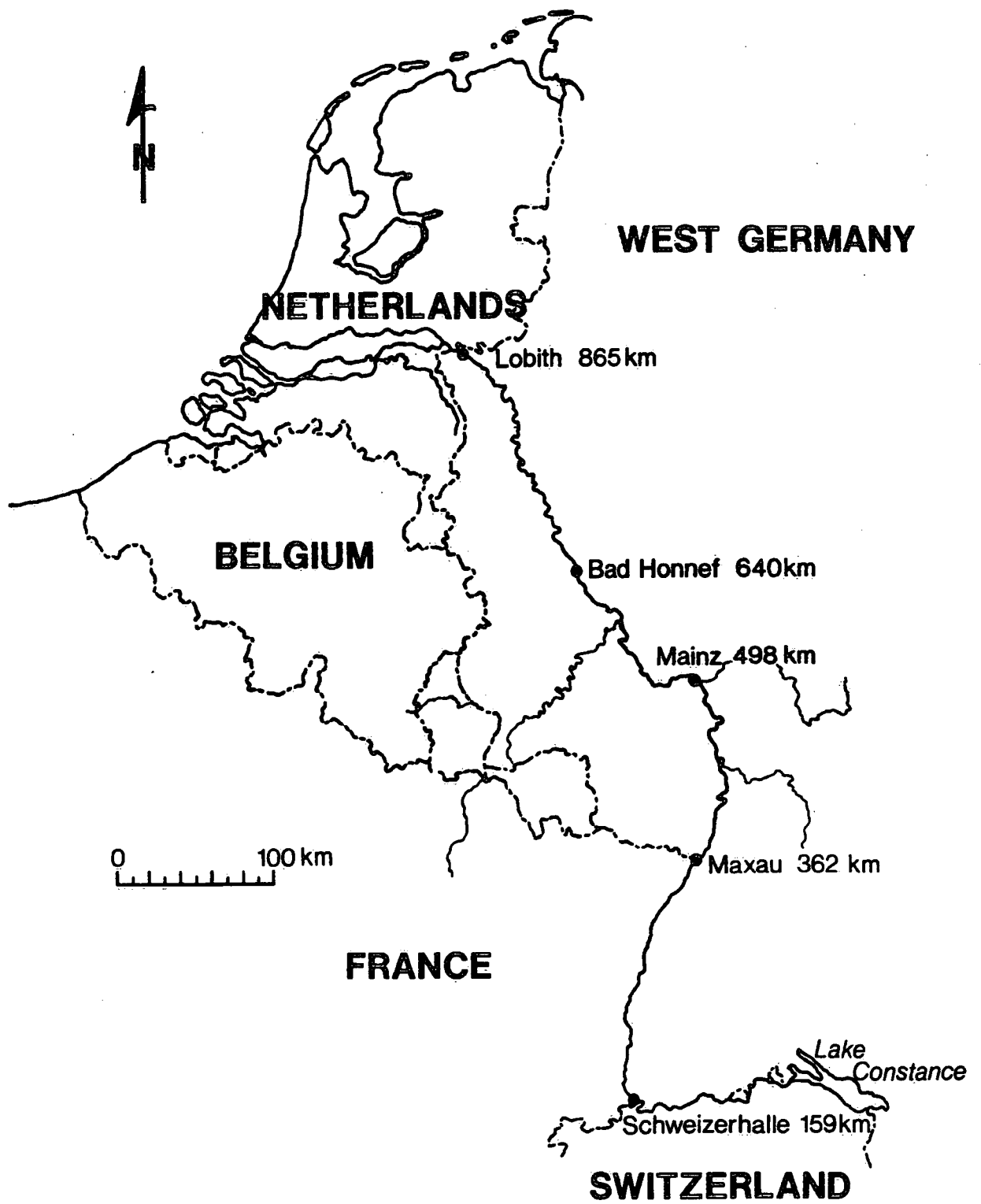
In 1986 a chemical spill occurred at the Sandoz AG plant in Schweizerhalle, an industrial complex near Basel, Switzerland (Bundesminister für Umwelt, 1987; Nachrichten aus Chemie und Technik, 1986). Several chemicals entered the Rhine River and were transported downstream into Germany and the Netherlands. Capel et al. (1988) have described the cause of the spill, the effects of the spill on the river ecosystem and calibrated a hydrodynamic model to describe the fate of several contaminants. Some chemicals that entered the river are Disulfoton, dinitroorthocresol, Propetamphos, Thiometon, Parathion, Etrimphos, Metoxuron and Fenitrothion. All these eight chemicals were found in the German section of the River Rhine. Brueggemann et al. (1987) have performed assessed the hazard of these chemicals to the river and Brueggemann and Matthies (1987) used the EXAMS framework to analyze some contaminants distribution.

In this paper we model the fate of Disulfoton from Maxau to Lobith on the German-Dutch border following the spill in Switzerland on November 1, 1986. The simulation does not describe contaminant concentrations between Schweizerhalle and Maxau, because dams regulate the flow in this set of the Rhine and there are no reliable available data that describe the flow of the river between these two cities in that particular period. The initial conditions of the simulation are therefore the observed concentrations of Disulfoton at Maxau on November 4, 1986. Figure 1 shows the geography of the Rhine.

TOXFATE was developed (Halfon, 1984a; version 1.0) for the specific purpose of modeling the fate of toxic contaminants in large lakes after a preliminary effort of using the EXAMS framework (Lassiter et al., 1979) was only partially successful (Halfon, 1984b). The main purpose of this study is to verify whether TOXFATE could be applied to a river. In its present updated configuration (Halfon and Oliver, 1989; version 2.1), TOXFATE describes and predicts the fate of a toxic contaminant which enter any water body. The model includes degradation processes but biodegradation and photolysis terms are set to zero since these processes are presumed to be very low or negligible for Disulfoton. This assumption is opposite to the assumption of Reichert and Wanner (1987) who claim that biodegradation of Disulfoton is an important removal process. To us, the only processes that seem relevant to the fate of Disulfoton are dilution and in a minor way volatilization of the chemical. Biodegradation is not included since Capel et al. (1988) set it as a zero order process in their model. To us the inclusion of biodegradation as a zero order process feels as a calibration effort rather than as an understanding of the real rates taking place in the Rhine.

THEORETICAL CONSIDERATIONS

TOXFATE simulates the time-varying concentrations of a toxic contaminant in the water column. The equations can be parameterized to represent a variety of contaminants and the model is formalized as a system of ordinary differential equations. The state variables of the lake version of TOXFATE are organic



contaminant concentrations in suspended clay and colloidal matter, suspended silt, suspended sand, water, plankton, and fish, bottom sediments and benthos compartments. In the river version of TOXFATE only contaminant concentrations in water are modeled. Disulfoton is water soluble and with a low K_{ow} . Thus this chemical tends to stay in the water rather than attach itself to suspended solids or sediment to the bottom.

The transport processes of advection in water are handled by a box model and the pollutant is assumed to be immediately and completely mixed within each compartment. Each compartment, or river reach, has a length of 2.5 km. This distance has been chosen for two reasons: a) to maximize the numerical stability of the integration algorithm and b) to match the numerical dispersion in the model with the longitudinal dispersion in the river.

Volatilization

The volatilization rate is modeled using the well known two-film representation of the water surface (Liss, 1973). Equation 1 shows the calculation of the volatilization parameter k_v [h^{-1}]

$$k_v = \frac{1}{K_{liq} + K_{gas}} \frac{A}{V} \quad (1)$$

where, K_{liq} [hour/m] is the reciprocal of the liquid phase mass transfer coefficient, K_{gas} [h/m] is the gas-phase mass transfer coefficient, and A [m^2] and V [m^3] are the areas and volumes of the lake, or lake compartments if the lake is divided into spatial compartments. The parameter K_{liq} is computed as:

$$K_{liq} = \frac{1}{k_{o_2} \sqrt{(32/MW)}} \quad (2)$$

where k_{o_2} is the oxygen (molecular weight 32) exchange constant [m/hour] computed according to measured wind speeds (u) at 10 metres over the water surface (Banks, 1975),

$$k_{o_2} = 1.51 \times 10^{-2} u, \quad \text{for } u \leq 5.5 \text{ m/s} \quad (3)$$

$$k_{o_2} = 1.15 \times 10^{-3} u^2, \quad \text{for } u > 5.5 \text{ m/s}. \quad (4)$$

In this model the effects of intermittent turbulent and advective transport events are not included since, as Burns et al. (1981) noted, Whitman models usually differ very little from more complex (e.g. surface renewal) models (Danckwerts, 1970).

The gas resistance, K_{gas} , is

$$K_{gas} = \frac{1}{\frac{W}{R} \frac{H}{T} \sqrt{(18/MW)}} \quad (5)$$

where W [m/h] = $0.1857 + 11.36 u$ [m/sec] at 10 metres over the water surface (Liss, 1973), 18 is the molecular weight of water, R is the gas constant [m^3 -atm/mole] and T is the water temperature ($^{\circ}K$). If H is not known, it can be computed from vapour pressure V_p (in mm Hg) and the contaminant solubility S (mole/ m^3)

$$H = \frac{V_p}{760 S} \quad (6)$$

The factor 760 in Eq. 6 converts the vapour pressure from mm Hg to atmospheres. Another method to compute volatilization is the

approach of Southworth (1979). Trapp and Brueggemann (1988) have shown that Southworth method is quite reliable too.

DATA

Data for the simulation were obtained from Reichert and Wanner (1987), Capel (1987), Capel et al. (1988) and on-line data base in Germany with the river flows at different locations. The Rhine has an average speed of about one metre per second in most locations. The river (Fig. 1) passes a series of rapids between Mainz and Bad Honnef. After Cologne the river is wide and relatively shallow. The flow at Lobith is about 2,000 cubic metres per second. The hydraulic characteristics of the river thus help in the prompt dilution of chemicals in the water column. The average transient time between Basel and Lobith is about 12 days. The flow at Maxau is about 1,100 cubic metres per second. A number of large rivers, the Neckar, the Main, the Mosel and several others join the Rhine and doubles its flow between Maxau and Lobith. This large influx of water tends to create a numerical instability in the model. Thus a time step of 15 minutes is used in the integration routine. The Henry's Law constant of Disulfoton is quite low, about 1.5×10^{-4} [dimensionless].

CALIBRATION OF THE MODEL

The part of the TOXFATE model that describes the behaviour of the chemical need not be calibrated. Nevertheless, the topography of the Rhine needs to be included in the model. The discharge Q [m^3/s] and the linear velocity v [m/s] of the Rhine and of all

tributaries are well known. The width, W [m] of the river can be deduced from topographic surveys (annual averages). The model describes the river as a series of rectangular prisms connected in series. Each prism has width, W , and depth, d . Thus, the cross section A [m^2] of the prism is $A = d \times W$. The cross section A can be computed as the ratio of the discharge and the linear velocity, $A = Q/v$. Since the real shape of the cross sections is probably trapezoidal, the average depth of the river must be computed as $d = A/W$. However, the width of the river is not constant for each reach as assumed in the model but it changes continuously. Thus, for modeling purposes the depth of the river is not a constant but a parameter and must be calibrated. Reichert and Wanner (1987) and Capel et al. (1988) used a one-dimensional model in the form of partial differential equations. They also had a problem with calibration and had to adjust six parameters to fit their simulations to the data.

In conclusion any river model must be calibrated to match the topography of the real river with the assumed topography in the model. If the model is used in the future for other applications, it must be calibrated again since discharges in the river and in its tributaries are not constant.

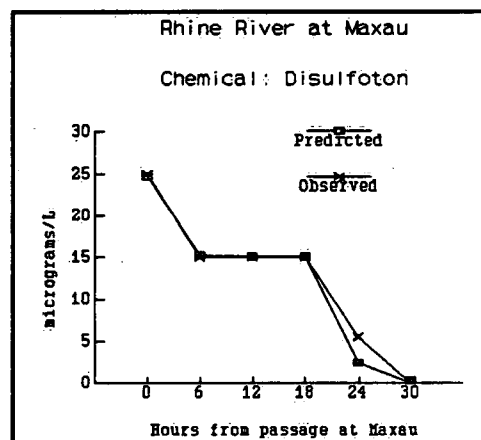


Figure2: Concentrations at 80 km from spill site

RESULTS

Figures 2 to 5 show the predicted and observed concentrations (Capel et al., 1988) of Disulfoton in the Rhine at different locations, namely at Maxau, Mainz, Bad Honnef and Lobith at the Dutch-German border. The predicted concentrations at Maxau (Fig. 2) closely match the observations since these

concentrations were used as initial conditions to the model. Figure 3 shows the predicted and observed concentrations at Mainz. The model simulations are similar to the observations although concentrations at Mainz fall to zero six hours earlier than observed. At Bad Honnef (Fig. 4), predicted and observed concentrations seem to be about three hours out of phase and Disulfoton is predicted to be present in the waters six hours longer than observed. At Lobith (Fig. 5), no phase lags are

observed but

predicted concentrations are higher by a factor of two of observed concentrations.

The Rhine is

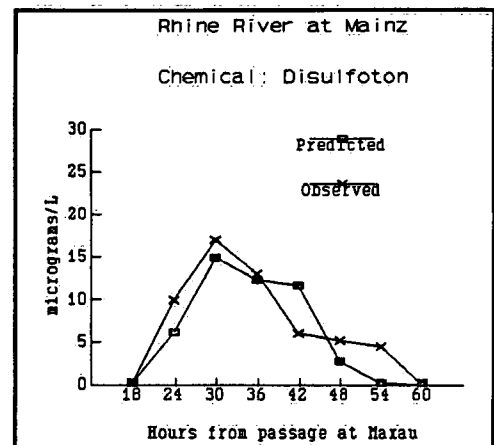


Figure 3: Concentrations at 134 km from spill site

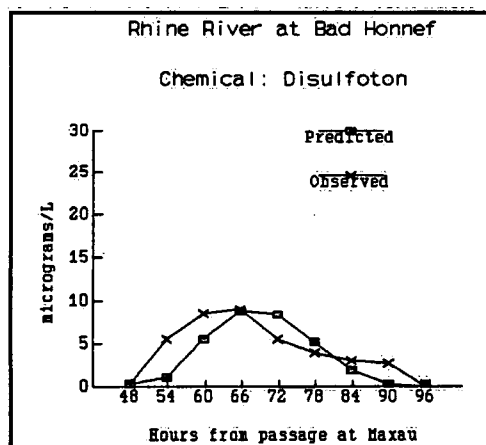


Figure 4: Concentrations at 191 km from spill site

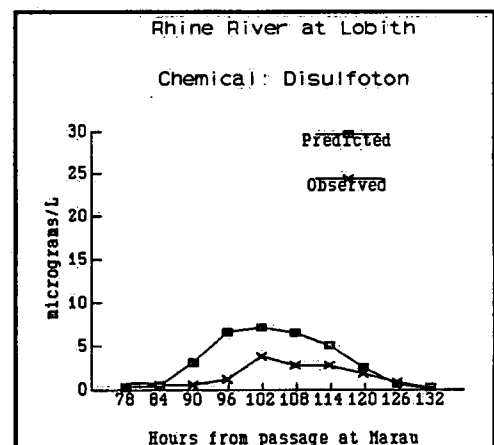


Figure 5: Concentrations at 280 km from spill site

fairly wide and shallow between Bad Honnef and Lobith and therefore two explanations can be given for this discrepancy. One explanation is that given the slow flow of the river and the shallow dead water zones in that region (Trapp and Brueggemann, 1989), Disulfoton may be volatilized. The volatilization flux is not efficient due to the low Henry's Law constant. The second explanation follows Capel et al. (1988) who note that Disulfoton is being biodegraded. The model predictions could be improved by either increasing the volatilization rate due to the shallow dead water zones or by adding a biodegradation parameter. Since at this point in time we do not know the exact reason for this difference, we do not deem it meaningful to change the model structure just to obtain a better fit to the data.

Figure 6 shows the predicted and observed concentrations of Disulfoton in the whole river. The different peaks represent the passage time of the spill relative to the time the spill passed at Maxau.

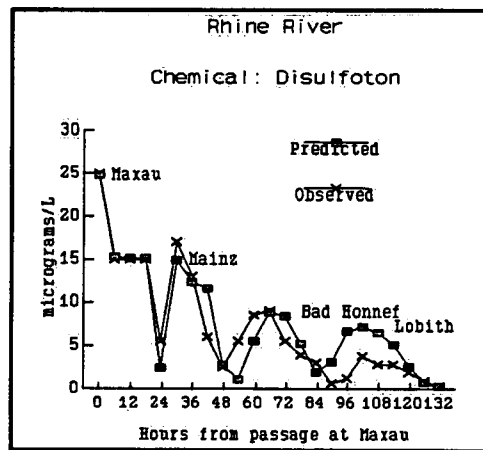


Figure 6: Predicted and observed concentrations along the River Rhine

DISCUSSION

The Rhine crosses three countries, Switzerland, Germany and The Netherlands before entering the Atlantic Ocean at Rotterdam. The river is heavily polluted because of the large number of cities and industries located along its shores. The spill that occurred in Basel in 1986 is particularly interesting because of the magnitude of the spill which perturbed

the river ecosystem for more than 200 kilometres downstream (Bundesminister für Umwelt, 1987).

Disulfoton is water soluble with a relatively low octanol/water partition coefficient ($\log K_{ow} = 3$). This coefficient is quite low compared with, for example, hexachlorobenzene ($\log K_{ow} = 5.1$) and Mirex and PCB's ($\log K_{ow}$ 5 to 8). A simulation model, TOXFATE, has quantified the behaviour of a spill in the Rhine. From a modeling point of view this one time event means that the model can not be validated since all the data available have been used for calibration. Thus the main purpose of this study is to verify whether TOXFATE, originally developed for lake environments, could be applied to a river.

The predicted and observed concentrations in the different components of the ecosystem agree well but this is expected since the model was calibrated. The model of Reichert and Wanner (1987) also fits the data well. The interesting divergence of the two models is not in fitting the data but the mechanisms used to fit the data in addition to the calibration of the hydrodynamic model. Reichert and Wanner (1987) and Capel et al. (1988) noticed that dilution alone could not explain the disappearance of Disulfoton from the water. Thus in their model they included a parameter k [$g_{\text{contaminant}} \cdot m_{\text{water}}^{-3} \cdot s^{-1}$] that quantified the disappearance of Disulfoton. The researchers at EAWAG (EAWAG, 1986) also performed laboratory experiments with river water and concluded the total mass of the chemical diminished as it flowed down the Rhine, indicating the presence of strong environmental removal processes. They identified the main removal process as biodegradation. Since

the parameter k is zero order, the conclusion of Capel et al. (1988) is that biodegradation is constant along the river. In our model, the calibration procedure is different from the one described above because of the different mathematical formulation. In our model water dilution is the only important process in reducing the concentration of Disulfoton as far as Bad Honnef. Past Cologne the river becomes wider and shallower. Therefore, in our formulation, volatilization may become a relevant mechanism of removal only after Cologne in the last stretch of the River before the border with the Netherlands.

This apparent contradiction cannot be resolved at this time. Removal data are missing and cannot be collected again since the spill is a one time event. On one side our model indicates that dilution is important in reducing Disulfoton concentration while volatilization is a removal process only after Cologne. Conversely, Capel et al. (1988) state that biodegradation takes place everywhere from Basel onward and volatilization is not a relevant removal process. This discrepancy, which modeling efforts alone cannot resolve, warrants further research. Which removal processes are the most important for Disulfoton and other chemicals? Volatilization is a physical process that depends on the geography and bathymetry of the river and turbulence at the water surface. Biodegradation is a biological process and can be influenced by other forms of pollution. For example, microorganisms which may be critical for biodegradation could be destroyed by the pollution itself, thus a polluted river might become more and more polluted as pollution increases since this

feedback mechanism, helpful in self cleaning, might be destroyed. In the case of this spill at the Sandoz AG plant, however, there seems to be no bacterial toxic effect as the report of the Deutsche Kommission fuer Reinhaltung des Rheins (1986) has shown.

The main problem of the prediction of toxic contaminants fate, once a model has been satisfactorily validated for a few compounds, is the lack of loading data.

ACKNOWLEDGMENTS

This study was supported by a GSF grant to the first author.

REFERENCES

- Banks, R.B. 1975. Some features of wind action on shallow lakes. J. Environ. Eng. Div., Proc. ASCE 101(EE5): 813-827.
- Brueggemann, R. and Matthies, M. 1987. Simulation des Verhaltens von Chemikalien in Fließgewässern. In: J. Halin (Ed.) Simulationstechnik. Fourth Symposium Simulationstechnik, Zuerich, 9-11 September 1987, Springer Verlag, pp. 50-79.
- Brueggemann, R.; Borchers, C., Rohleder, H. 1987. Anwendung des Modells EXWAT zum Vergleich von Chemikalien in Fließgewässern am Beispiel eines Chemieunfalls. Deutsche Gewässerkundliche Mitteilungen, 31:103-107.
- Bundesminister für Jugend, Familie und Gesundheit Chemikaliengesetz vom 16.09.1980; BGBI: I S. 1718 und Gefährlichkeitsmerkmale-Verordnung vom 18.12.1981 BGBI. I S. 1487-1489.
- Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit; Umweltbrief; Rhein-Bericht, Bericht des Bundesregierung über die Verunreinigung des Rheins durch die Brandkatastrophe bei Sandoz AG/Basel und weitere Chemieunfälle, Nr. 34, 12.02.1987.
- Burns, L., Cline, D.M. and Lassiter, R.R., 1981. Exposure Analysis Modeling System (EXAMS): User manual and system documentation. U.S.EPA, Athens, Georgia, 440 pp.
- Capel, P.D. 1987. Predictions of the Environmental fate of 21 pesticides in the River Rhine based on their physical/chemical and environmental properties. EAWAG Technical Report, Swiss Federal Institute for Water Resources and Water Pollution Control; Dübendorf, Switzerland..
- Capel, P.D., Giger, W., Reichert, P and Wanner, O. 1988. Accidental input of pesticides into the River Rhine. Environ. Sci. Tech., 22:992-997.
- Charlton, M.N. 1983. Downflux of sediment, organic matter, and phosphorus in the Niagara River area of Lake Ontario. J. Great Lakes Res., 9: 201-211.
- Danckwerts, P.V., 1970. Gas-liquid reactions. McGraw-Hill Book Co., New York, 276 pp.
- Deutsche Kommission fuer Reinhaltung des Rheins, 1986 - Deutsche Bericht zum Sandoz-Unfall mit Messprogramm.
- Durham, R.W. and Oliver, B.G. 1983. History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis. J. Great Lakes Res., 9:160-168.

EAWAG 1986, First report on the ecological assessment and recommendations for measures and future investigations after the Sandoz Accident in the River Rhine at Basel (in german); Swiss Federal Institute for Water Resources and Water Pollution Control; Dubendorf, Switzerland, 65 pp.

German commission for water pollution control of the River Rhine, 1986. German Report on the Sandoz Accident with analytical results (in german); International Organization for the protection of the River Rhine against pollution; Koblenz, Federal Republic of Germany. Taetigkeitsbericht, 221 pp.

Halfon, E. 1984a. Modeling the fate of toxic contaminants in the Niagara River and Lake Ontario. Part I and Part II, Environment Canada, NWRI report No. 84- 39.

Halfon, E., 1984b. Error analysis and simulation of mirex behaviour in Lake Ontario, Ecological Modelling, 22:213-252.

Halfon, E. 1987. Modelling the pathways of toxic contaminants in the St. Clair-Detroit River system using the TOXFATE model: the fate of perchloroethylene. Water Poll. Res. J. Canada, 21: 411-421.

Halfon, E. and Oliver, B.G. 1989. Simulation and data analysis of four chlorobenzenes in a large lake system (Lake Ontario) with TOXFATE, a contaminant fate model. In S.E. Jorgensen (Ed.) Simulation of toxic contaminants. Elsevier (in press).

Halfon, E., Simons, T.J. and Schertzer, W.M. 1989. Modeling the spatial distribution of seven halocarbons in Lake St. Clair in June 1984 using the TOXFATE model. J. Great Lakes Res., (in press)

Jensen, A.L., Spigarelli, S.A. and Thommes, M.M., 1982. PCB uptake by five species of fish in Lake Michigan, Green Bay of Lake Michigan and Caiuga Lake, New York. Can. J. Fish. Aquat. Sci., 39:700-709.

Lassiter, R.R., G.L. Baughman, L.A. Burns. 1979. Fate of toxic organic substances in the aquatic environment. In S.E. Jorgensen ed. State of the Art in Ecological Modelling, Intern. Society of Ecological Modelling, Copenhagen, Denmark, pp. 219-246.

Liss, P.S., 1973. Processes of gas exchange across an air-water interface. Deep-Sea Res., 20:221-238.

Nachrichten aus Chemie, Technik und Laboratorium. 1986. Deutsche Chemie denkt ueber Konsequenzen von Basel nach. Chem. Tech. Lab., 34, 1184.

Reichert, P and Wanner, O. 1987. Simulation of a severe case of pollution of the River Rhine. In Proceedings of the 12th Congress of the International association of Hydraulic Research, Lausanne, Switzerland; Water Resources; Littleton, CO, pp:239-244.

Rohleder, H.; Matthies, M.; Benz, J.; Brueggemann, R.; Muenzer, B.; Trenkle, R.; Voigt, K. Umweltmodelle und Rechnergestuetzte Entscheidungshilfen fuer die vergleichende Bewertung und Prioritaetensetzung bei Umweltgefaeherchemikalien, Projektgruppe Umweltgefaehrdungspotentiale von Chemikalien, GSF-Bericht 42/86, Gesellschaft fur Strahlen- und Umweltforschung, Muenchen-Neuherberg (1986).

Simons, T.J. and Murthy, C.R. 1985. Winter Circulation in Lake Ontario. J. Great Lakes Res., 11:423-433.

Southworth, G.R. 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contam. Toxicol., 21:507- 514.

Trapp, S. and Brueggemann, R. 1988. Untersuchung der Ausgasung Leichtfluechtiger Substanzen aus Mitteleuropaischen Fliessgewaessern mit dem Fliessgewaesser modell EXWAT. Deutsche Gewaesserkundliche Mitteilungen, 32: 79-85.

Trapp, S. and Brueggemann, R. 1989. Schadstoffausbreitung im Rhein. II Untersuchungen zu Transport und Ausgasung des Loesungsmittels 1,2-Dichlorethan. Deutsche Gewaesserkundliche Mitteilungen, 33: 82-85.

Environment Canada Library, Burlington



3 9055 1017 0740 3



NATIONAL WATER RESEARCH INSTITUTE
P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

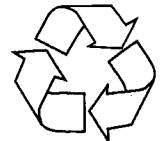


Environment Environnement
Canada Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

Think Recycling!



Pensez à Recycling!